Mexico-Uk Researchers Links Workshop on Biorefinery Identified Important Developments and Research Needs for Sustainable Bioeconomy

“The Mexico Biorefinery Workshop in May 2015 was a unique experience, one of few allowing such an in-depth viewpoint into the development of the biorefinery concept in a country very different from the UK.” “I have a clearer picture of the situation and initiatives on biorefining which are taking place in Mexico (and also in UK). I am now more aware of the complexity of a biorefining plant, and how the tools for process integration and life cycle analysis can assist the design of biorefining process and individual processing units.” “The Workshop brought together established experts and young researchers working within the biorefinery field from the participating countries.” “I found the Workshop to be of tremendous interest which greatly added to my knowledge and broadened my thinking regarding biorefineries. The ideas exchanged and contacts made will absolutely yield a fruitful result” – these are just a few of the feedbacks collected after a very successful Mexico-Uk Researchers Links Workshop: “Biorefinery research - promoting international collaboration for innovative and sustainable solutions” funded by CONACYT. About 60 researchers and practitioners in the field from the two nations gathered at the Instituto Mexicano del Petróleo (IMP), in Mexico City, Mexico, for a week-long Workshop, on 18 May, 2015. The Workshop covered the following topics:

1. Recent advances in biorefinery technologies.
2. Biomass including waste stocks in the two nations and also important ones world-wide.
3. Industrial biorefinery activities.
4. Process Integration and Sustainability Analysis.
5. Discussions on “Biomass availability, characterization and processing” and “Waste processing, circular economy and sustainability”.

The event coincided with 50th Anniversary of the IMP and was marked by the inauguration of The Institution of Biorefinery Engineers, Scientists and Technologists (IBEST), a network of biorefinery researchers and practitioners, for “Advancing cross-disciplinary knowledge and education in Biorefinery Engineering”. A participant said, “Initiatives emerged from group discussions held during the Workshop, such as the creation of Institution of Professionals in Biorefining related topics, show the important role that Biorefinery is foreseen to play in the future, but also the wide scope and variety of disciplines it will require from.” To celebrate the Mexico-UK Bilateral year, 2015, research and networking outcomes will be disseminated through journals, webinars and news on the IBEST website. A dedicated Special Issue (SI) on Biorefinery Value Chain Creation in Elsevier: Chemical Engineering Research & Design guest edited by the organizers for disseminating the selected papers is under preparation. About half the papers in the SI (out of 30) would be from the Workshop.
Recent advances in biorefinery technologies

There was a consensus on the definition of biorefinery, which is different from a bioprocess for energy or biofuel production only. “In the most advanced sense, a biorefinery is a facility with integrated, efficient and flexible conversion of biomass feedstocks, through a combination of physical, chemical, biochemical and thermochemical processes, into multiple products. The concept was developed by analogy to the complex crude oil refineries adopting the process engineering principles applied in their designs, such as feedstock fractionation, multiple value-added productions, process flexibility and integration.” – Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, Wiley’s major advanced textbook, 2014.

“A key take-home message regarding biorefineries of the future iterated the importance of value biochemicals production as a by-product to ensure cost competitiveness with fossil fuels and also value creation by reducing/reusing resources. Some presentations also focused on non-traditional alternative fuels which appeared to be environmentally sound” – says Mr Bhavish Patel, a prospective PhD Graduate at Imperial College, London and the best oral presenter from the UK.

Dr Jorge Arturo Aburto-Anell, Research Manager of Biomass Conversion at IMP, Mexico Coordinator of the Workshop, mentioned a consortium (IPN, INIFAP, enterprises) to develop versatile and adaptable processes to several biomass feedstocks: agave bagasse, cane sugar bagasse, spent malt grain, corn stover, wheat straw, forestry residues and grasses. He gave an overview of the biomass fractionation technologies to produce bioethanol via sugar platform and lignin developed at IMP, in his keynote. Dr Myriam A. Amezqua Allieri of IMP, an Organizer of the Workshop presented an evaluation of the performance of bioethanol from lignocellulosic materials and the sustainability of the process. Beyond the analysis and quantification of environmental impacts of all the stages of the bioethanol's life through life cycle assessment (LCA), she took into consideration the process parameters (path analysis conversion), engine performance (thermodynamic variables) and
energy efficiency. The assessment of environmental impacts would help elude environmental concerns by interpreting the results and generate more informed decisions for the authorities. Also, the assessment would help define the chemical specifications of second generation bioethanol, to reflect the main advantages/disadvantages of using the already existing infrastructure in the transportation sector.

The team at IMP led by Dr Aburto Anell also developed biodegradable biosurfactants for preparation of inverse emulsion, Biodegradable biodemulsifiers for crude oil dehydration and technology for transport of heavy and extra heavy crude oil.

A much debated subject of the utilization of the lignin was covered by Dr. Jose A. Toledo Antoni of IMP in detail and mentioned by Dr Sadhukhan. The lignin depolymerization has shown techno-economic prospects in the context of integrated biorefinery. Dr Jhuma Sadhukhan from the Centre for Environmental Strategy (CES), the University of Surrey, UK Coordinator of the Workshop gave a comprehensive overview of systematically integrated innovative biorefinery configurations and engineering design and sustainability analysis methodologies in her keynote to set out the scene of the Workshop. A very fundamental aspect of biomass valorization was addressed – "In order to produce products of desired properties, coordinated activities of cleavage of bonds are required, which must be assisted by genetic engineering and enzymatic pathway analysis. Each fraction, cellulose, hemicellulose and lignin can be converted into a range of products."1 Compositions of lignocellulosic feedstocks are often unpredictable when they are accumulated within a system boundary, maybe an urban system. Hence, which products can be generated and what are those flexible processes that can uptake the mixture of feedstocks and still achieve the desired product slate pose a huge challenge to solve. Unoptimized schemes would suffer from waste formation of low values that will ultimately be released to the atmosphere after combustion or cogeneration or to land from disposal to landfills or to an aquatic body by leaching. Most routes produce low value lignin residues. The lignin and hemicellulose fractions are increasingly being recognized as a valuable source of value-added productions in the top of the pyramid. There are numerous possibilities, amongst which the niche areas need to be carefully selected based on market drives within a geographical region and policy context. The application principles encompass integrated feedstock management, conversion, use of end products, and reuse in cyclical and synergistic loops. Renewable feedstocks from a range of local activities can be converted into products to fulfill local needs. With co-optimization of agricultural, forestry, residential, industrial and commercial activities and demand management, the impacts on land, soil, water and atmosphere will be reduced. A true sustainable biorefinery design calls for such a challenging solution for "whole systems." However, the complete fusion of an industrial symbiosis framework is a gradual process and requires years to stabilize from one state to another, for example, from a fossil based era to a renewable era.1 A slide from Dr Sadhukhan’s presentation:
Dr Jorge Martínez Herrera of the Instituto Nacional de Investigaciones Forestales, Agrícolas y Pecuarias (INIFAP) discussed a very important issue of the Value chain creation around “piñon mexicano” (Jatropha curcas L.) – Tabasco case study, in his keynote. Jatropha plantations in Mexico, have declined in different states like Michoacán, Morelos, Chiapas and Yucatán, among others, 3,500 ha Chiapas; 3,000 ha Yucatán; 1,000 ha Michoacan and 200 ha Morelos. The low yield was due to lack of financial support for the farmers; there were about 50 of them and the specie needed 2 years planting, removal after plantation and changing crop thereafter. The poor support resulted in poor yield <1 tpha and low income 0.25 USD per kg. There were seven genotypes selected, and their performances were evaluated for six years. There were fluctuations in each year. The fourth, fifth and sixth years’ best returns were monitored, however, inadequate to self-sustain. The chemical analysis of different genotypes shows high oil and protein content, however. It was the overall yield per ha did not make economic sense. Dr Herrera also gave insights into potential competitions with non-fuel products, for which the volume required is low and the market value is high, hence making a more economic sense. Jatropha oil (around 45% by weight of the seed) was found to be too good to burn, for example as, industrial lubricants, biolubricants, dielectric coolants, surfactants, plastics and resins. Both the oil and flour derived from seed kernel can be used as pesticide, fungicide. Also, the residents of the region Totonacapan for many years have used J. curcas seed for the preparation of traditional dishes. The flour is used to make various food products for human and animal consumption. “The kernel meal left over from oil extraction has a protein content of around 65% of the dry matter. Due to its high protein content, high protein digestibility and good amino acid composition, Jatropha kernel meal has considerable potential as a supplemental source in the diets of ruminant and monogastric animals including fish” – quoted from Rakshit Devappa Kodekalra by Dr Herrera. The study also concluded that Jatropha protein film could be appropriate for the use in food packaging.
The keynote by Professor Richard Murphy, Director of CES, University of Surrey, also revealed that energy or biofuel production is not always the best use of biomass. He focused on wheat straw (UK), short rotation coppice (SRC), poplar and willow, bamboo (China & Colombia) and waste papers and cardboard (UK) as the biomass for potential use as bio-based materials, chemicals etc. to help decouple economic activity from GWP. He commented: “Bioplastics & other bio-based materials (e.g. fibres, wood, WPCs) with ‘negative’ carbon footprints and careful life cycle management offer the potential not only to absolutely decouple GHG emissions from economic growth but further offer a “mitigation decoupling” potential”.

Dr Marcos Millan-Agario, Reader at Imperial College, London, explained his research on valorization of heavy fractions predominantly originated from lignin in pyrolysis or separation processes in his keynote. These fractions are high in molecular weight and contain polyaromatic hydrocarbon (PAH) structures, which act as coke precursors affecting process units and catalysts. These species need to be treated as can be harmful to health and the environment if discarded as part of waste streams. Catalytic Steam Cracking can achieve transformation of bio-oil heavy ends into lighter products. There is a trade-off between conversion and selectivity to liquid phase as a consequence of the reaction pathways followed. The gas phase is hydrogen rich, which makes this process attractive as part of a
Preferential reaction on internal aromatic rings can take place leading to higher yields of lower boiling point liquid products. Hydrogenation is an important process to remove oxygen from bio-oils, a pyrolysis product of biomass, and produce thereby drop-in biofuel or chemical.

Dr Lee Durndell’s research at Aston University focuses on design of catalyst with the ability to reduce a plethora of functional groups, including C=C, C≡C, C=O, C≡N, NO₂ and aromatic structures, such versatility, which being beneficial in the scope of reactions achievable, is highly problematic where multiple reactive moieties exist within one substrate and as such control over which sites are converted is far from trivial. Controlled hydrogenation of allylic and benzylic aldehydes and ketones, to unsaturated alcohols, represents a class of reaction that is vital to industrial chemical production, due to high product utilization within flavour and fragrance chemistry and pharmaceuticals. He showed the results of platinum supported mesostructured (SBA-15) silica for the selective hydrogenation of cinnamaldehyde - using batch and continuous flow systems. The effect of temperature, hydrogen pressure, Pt geometric constraints, support architecture and surface hydrophobicity was also discussed with a view to developing a more sustainable route to selective hydrogenation.

Dr Rafael Martínez Palou of IMP gave an overview of ionic liquid applications in biorefineries with demonstrations of two cases: pretreatments of lignocellulosic materials for efficient bioethanol production and ionic liquids as catalyst in biodiesel synthesis.

Algae biorefinery, outlined as follows by Dr Sadhukhan, was further looked at depth by Mr Patel and Professor Prof. Eugenia J. Olguin of the Instituto de Ecología (INeCOL), both being the best oral presenters. “Synergetic opportunities for algae based-biorefineries can exploit interactions with other natural resources and industrial wastes. Natural resources include, for example, wind and solar power which can be used to supply energy for algae production. Algae cultivation by either open pond or artificially illuminated photobioreactors (PBRs) is used as part of the treatment process of residential wastewater. The energy for the paddle wheels in open ponds or the illumination lamps in PBRs is provided by electricity generated by solar panels and wind turbines. The residual biomass after oil extraction is digested to produce biogas. The biogas is used in a combined heat and power (CHP) plant to provide energy for households. Nutrients and water are recycled from the anaerobic digestion plant while CO₂ from biogas combustion in CHP plant is supplied to the algae. One challenge is the regeneration of water in order to be recycled and reused by households and to avoid losses during algae biomass processing. The energy production from the residual algae biomass via anaerobic digestion offers flexibility to cope with the intermittency in energy supply from solar panels and wind turbines. Thus, part of the electricity generated by CHP plant can be used as backup for periods of
low sunlight irradiance and low wind speed. Another possibility is the algae cultivation as part of the architecture of buildings to produce various energy carriers. Flat panel PBRs form the façade produce algae biomass from solar irradiation thus making the buildings "green". Furthermore, the wastewater generated in the building can be treated by the algae growing in the façade PBRs. The algae biomass produced is converted into biogas by anaerobic digestion. Biogas can be used as fuel to provide energy to the building or can be upgraded to high purity methane for the gas grid. In addition, solar thermal energy is also captured within the liquid culture medium. The associated heat can be recovered and stored geothermally, underneath the building, or by the use of heat pumps. The recovered heat is then used for thermal comfort inside the building and to supply hot water.

Patel investigated hydrothermal liquefaction (HTL) of wet algae in a continuous plug flow quartz lined reactor using cyclohexane as a co-solvent to enhance extraction. Temperature range between 300-380°C and residence time of < 4 min was investigated. LCA was carried out for fast HTL to investigate the environmental profile of algal biomass to potential refinery drop-in biocrude production process. They also investigated in situ production of biodiesel and biocrude by simultaneous supercritical transesterification and HTL of algae paste in a batch reactor. Professor Olguín (INeCOL) discussed algae biorefinery producing biodiesel and chemicals as a way to treat stillage streams and wastewaters.

Dr Jose Bermúdez, Research Fellow at Imperial College, London presented a novel method for the microwave-assisted drying of microalgae for its subsequent use in processes of extraction of valuable compounds (such as lutein) or bio-oils. Two different kinds of microalgae, Scenedesmus almeriensis and Nannochloropsis gaditana, were selected for the study. A conventional furnace and modified commercial microwave oven were used.

Figure 17.12  Integration of algae cultivation with other natural, industrial and residential elements of the ecosystem.

Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez. © 2014 John Wiley & Sons, Ltd. Published 2014 by John Wiley & Sons, Ltd.
Companion Website: http://www.wiley.com/go/sadhukhan/biorefineries
Mexico has a great potential to produce energy from organic waste according to the results obtained in different experiments, besides the largest proportion of citrus. The construction of the first anaerobic digestion (AD) pilot plant to treat organic solid waste is one step to create a culture of zero waste at the Universidad Nacional Autónoma de México (UNAM). Dr Alfonso Durán Moreno further concluded that the alkali pretreatment increased the methane generation in the agave bagasse and the green waste. The highest methane production was using the KOH reagent with 48% more methane than NaOH alkali. Adding a Se⁴ metallic ion as a micronutrient could improve the anaerobic digestion process. The disintegrated anaerobic granule released the methanogenic archaea and, as a result, can increase the methane production of 24% more than using anaerobic granule without disintegration. The dry anaerobic digestion process has 20% more methane generation than the wet process.

“...In Mexico, AD has been used primarily for animal waste treatment; in 2011, it was reported that 721 of such units had been constructed. However, in practice, digesters are abandoned after a few years in use due either to operational problems or inadequate performance. To minimize these risks, the following elements should be taken into consideration: 1) feedstock composition is a critical component, which determines the type, quantity and quality of product, thus needs to be considered during design; 2) co-digestion of different types of waste is an option to achieve an adequate balance of nutrients and improve performance and yield; 3) mixing needs to be considered during design to reduce operation and maintenance problems; 4) materials of construction need to be suitable for corrosive environments and exposure to sunlight; 5) for a cost-effective system, in addition...
to energy production and use of the electricity produced, the AD facility must generate other marketable products such as sale of biosolids (as fertilizer, soil amendment or fiber), and possibly the sale of greenhouse gas credits. As organic materials and wastes become more valuable and are being treated as resources, traditional AD as a single technology may not be longer adequate. An alternative is to see this technology as a component of biorefineries, where through the integration of other technologies (i.e. aerobic composting, thermal processing, and nutrient recovery facilities) biomass is converted into renewable energy, added-value chemicals (fertilizers), and other products. Furthermore, as an integrated process, biorefineries have the potential to assist in overall pollution minimization while creating a range of environmental and economic benefits.” – reported Dr Maritza A Macias-Corral of the Centro de Investigación en Materiales Avanzados (CIMAV). In another study by Dr Linda Victoria González Gutiérrez of the Centro de Investigación y Desarrollo Tecnológico en Electroquímica (CIDETEQ), agro-wastes were selected as raw materials for anaerobic digestion for biogas production. The wastes included were swine manure, dairy manure, fruit and vegetable waste, corn straw, milk whey, and sewage sludge.

Bioelectrochemical systems have come out prominently to convert stillage streams from biofuel production plants, food and dairy industries and wastewaters into value added products. Dr Iain Michie and coworkers at the Sustainable Environment Research Centre at the University of Wales developed a novel bioelectrochemical bioreactor system to biologically metabolize glycerol to produce platform chemicals provides an opportunity for sustainable chemical production that would otherwise be manufactured from petrochemical sources, particularly when considered as part of a biodiesel production process. Using a synthetic biotechnology approach S. oneidensis will be genetically engineered with genes that facilitate the uptake of glycerol (glycerol kinase (glpK)), convert glycerol to 3-hydroxypropionaldehyde (3-HPA) (dhaB) in association with glycerol dehydratase reactivase (gdrAB) and then convert 3-HPA to 3-hydroxy propionate (3-HP). The genes are to be sourced from microorganisms such as Klebsiella pneumoniae and Azospirillum brasiliense, using E.coli DH5 alpha for plasmid cloning/maintenance and S. oneidensis MR1 strain for protein expression.

Dr Kok Siew Ng, Research Fellow at CES, University of Surrey, co-author of Wiley’s major textbook “Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis” and Mentor of the Workshop and Dr Sadhuikhan work on a NERC funded project for resource recovery from wastewater with Bioelectrochemical system (BES). Their research considers integration of bioelectrochemical system with industrial systems that produce wastewater, including pulp and paper, mining, steel and biorefinery industries. Furthermore, CO₂ can be reused in the bioelectrochemical system to generate fuels and chemicals. Life cycle sustainability assessment is an important part of this project and will be conducted to justify the economic, environmental and social impacts and performances for different scenarios. Combining engineering and life cycle approaches is the main goal of this project and will involve multidisciplinary collaboration with industrial partners and academic institutions.

Dr Bibiana Cercado of CIDETEQ gave an interesting overview of waste remediation by electricity generation in microbial fuel cells (MFCs) and bioelectrode synthesis for the MFCs. She has made a fundamental contribution in the field of new carbon based anodes as well as using them in MFCs. The facilities available at CIDETEQ are noteworthy.
Dr Asaff Torres of the Centro de Investigación en Alimentación y Desarrollo A.C. (CIAD) shared his tremendous experience in added productions from tortilla industry’s organically rich wastewaters, usually called “nejayote”. It was estimated that, just in Mexico, around 16-20 million m³ per year of this pollutant are generated leaving companies exposed to penalties for water contamination, since its complex nature difficult efficient treatments by conventional methods. However, nejayote contain valuable products or chemical intermediates that can transform a pollution concern in a business opportunity through a biorefinery approach \(^7\)-\(^{10}\).

Mr Diego Merced Jimenez, a prospective PhD Graduate at UNAM, one of the best poster prize winners at the Workshop showed how to add value to mango skin and seed. The skin is composed by soluble and insoluble fiber, which can be treated and purified for livestock feed or human consumption. The seed contains lipids that can be extracted by extrusion or chemical extraction using solvents. The extracted lipids called essential oil can be used to produce creams, soaps or biodiesel. Also, other renewable energies, such as hydro, solar and wind energy, can be used in the various processes.

Glycerol was much discussed as a potential substrate as well. “If I consider glycerol as potential carbon sources that a bacteria could use to produce secondary metabolites better known as biosurfactants that could be used for the degradation of potential oil spills, I could find the way to improve my knowledge/skills in how to engage the process of producing and degrade carbon products using the biorefinery concept; and apply them into my daily basis during my postdoctoral research. Once I establish the parameters that I need to get for the optimum process for the highest biosurfactant production, I will be able to interact with people in the same field and exchange it through conferences or internships in different laboratories, finding new raw materials, and further applications. Being in this Workshop allowed me to share and acquired knowledge on biosystems and how to use them to get the best sustainable benefits, is one of the things that I’m grateful for, as well as feel the feedback from other researchers about the things that I could improve.” – Stated Dr Mayri Diaz de Rienzo, Research Fellow at The University of Manchester, winner of the best poster from the UK.

Polyhydroxybutyrate (PHB) is the best studied biodegradable bioplastic and Cupriavidus necator one the most common wild strain that synthesizes PHB from substrates different from sugars. Glycerol has been exploited as an inexpensive biological feedstock acting as sole carbon source for PHB production in the study by Ms Cristina Pérez Rivero, a prospective PhD Graduate at The University of Manchester. Her winning of the 2nd best poster prize is the testament of her contribution in both experimental and computational fields to justify such process developments.
Testing various food-industry wastes for electricity production in microbial fuel cell

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Fermented apple juice; Wine lees; Yogurt wastes

Table 2

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Fig. 3: Current density vs. time in sludge-MFC and compost-leachate-MFC with sodium acetate 2 mM (E = 1000 Ω, A = 10 cm²). The curves start just after the addition of acetate.

Garden compost inoculum leads to microbial bioanodes with potential-independent characteristics

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Mr Daniel García-López and coworkers at INeCOL undertook assessment of aquatic plant *Pistia stratiotes* as substrate for biohydrogen production and made to one of the two best poster presenters from Mexico. “During the first stage, ruminal fluid was used as inoculum for hydrolysis and acid fermentation. At a second stage, the effluent was used to culture *Rhodobacter sphaeroides*. The highest hydrogen production, 678.29 ± 70.64 mL H₂ L⁻¹, was obtained with conditions of high light intensity (130 Wm⁻²), high effluent concentration (100% v/v) and low ammonium concentration (1.94 mM). The COD removed was 31%. According to these results, *P. stratiotes* biomass is a promising substrate source for biohydrogen production process with environmental benefits of waste treatment.”

— he described.

Biomass including waste stocks in the two nations and also important ones world-wide

Dr Arturo Sánchez Carmona Cinvestav, Unidad Guadalajara (Gdl) discussed the short through medium to long term biorefinery strategies of Nerixis based on available crop residues, in his keynote.

Dr Mairi Black’s presentation gave an excellent overview of the biomass availability in the UK: wheat, barley, oats, oilseed rape and cereal straw; approved crops: miscanthus, willow, poplar, hazel, silver birch, sycamore, sweet chestnut and lime as well as:

- Crop diversity
- “Large enough” amounts
- Dispersed along vast territory
- Difficult topography
- Global prices (equipment, resources, logistics)

### Top Chemicals for production in Biorefineries

<table>
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<th>Building block</th>
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<th>NREL</th>
<th>BREW</th>
<th>Building block</th>
<th>C No.</th>
<th>NREL</th>
<th>BREW</th>
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<td>Xylonic acid</td>
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<td>Glucaric and Gluconic acid</td>
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<td>Caprolactam</td>
<td>C6</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>Theonine</td>
<td>C4</td>
<td>✗</td>
<td>✗</td>
<td>Lysine</td>
<td>C6</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>C4</td>
<td>✗</td>
<td>✗</td>
<td>Fat and oil derivatives</td>
<td>&gt;C6</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>C4</td>
<td>✗</td>
<td>✗</td>
<td>Polyhydroxyalkanoates (PHA)</td>
<td>&gt;C6</td>
<td>✗</td>
<td>✗</td>
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</table>

Mr Daniel García-López and coworkers at INeCOL undertook assessment of aquatic plant *Pistia stratiotes* as substrate for biohydrogen production and made to one of the two best poster presenters from Mexico. “During the first stage, ruminal fluid was used as inoculum for hydrolysis and acid fermentation. At a second stage, the effluent was used to culture *Rhodobacter sphaeroides*. The highest hydrogen production, 678.29 ± 70.64 mL H₂ L⁻¹, was obtained with conditions of high light intensity (130 Wm⁻²), high effluent concentration (100% v/v) and low ammonium concentration (1.94 mM). The COD removed was 31%. According to these results, *P. stratiotes* biomass is a promising substrate source for biohydrogen production process with environmental benefits of waste treatment.” — he described.
as globally and the drivers: policy, sustainability, cost, technology and scale. Such information along with the characteristics of globally important biomass has been collated by her in Access-based BIOTARG database, with IP existing with Surrey and Bio-Sep Ltd. Mr. Orlando Ayala Lagunas, FIRCO remarked on biomass availability in Mexico. The most promising crop for producing ethanol is sugar cane, while that for biodiesel is castor, however, the latter has a greater commercial value already. For biodiesel, the viable feedstocks are waste oils, animal fat and castor oil. Dr Alfonso Durán Moreno of UNAM gave important statistics of organic waste composition in Mexico, which can be compared with UK’s statistics from DEFRA[11]. Further, the impacts of lifestyles on the waste generation and recycling in both the countries can be analyzed and lessons can be learnt. Dr. Kenneth O’Callaghan, of the Department for Environment, Food & Rural Affairs (DEFRA), UK, gave an important overview of the potential of bioeconomy, particularly focused on biogenic wastes in his keynote.

[Image of organic waste composition]

**Industrial biorefinery activities**

Industrial presentations from Mexico mainly focused on biofuel production: biodiesel by Mr. Daniel Gómez Iñiguez, SOLBEN, Mexico, bioethanol by Ing. Benito Gabriel López Martínez, BIOMEX and jet fuel by Ing. Tania Buenrostro of BIOTurbosina. The feedstocks for drop-in jet fuel ASTM D7566 for BIOTurbosina are Jatropha, Higuerrilla, Microalgae, Camelina, used cooking oil, palm, animal fat and massive amounts of available solid waste. The Sorghum Based Bioethanol Plant at Tamaulipas Norte is expected to produce 122 million liters of ethanol per year, worth $98 million dollar per year. Distillers Dried Grains and Solubles (DDGS) as animal food amount to 87,500 tons. It will create 1000 jobs for construction and 2500 for operation. The annual economic margin is expected to be $110 million dollar, mostly in rural areas. Ing. Benito Gabriel López Martínez also showed the following important statistics. The domestic demand of bioethanol for the year 2010 was 260 million liters for non-fuel uses. In that year, Mexico produced 120 million liters of ethanol. The deficit of bioethanol was imported at a higher international price (Import Duty). There are 10 facilities in the country to produce alcohols, mainly in sugar mills that use cane molasses and sometimes sugar. The Biofuels’ Promotion and Development Law in Mexico was issued on 1 Feb, 2008. This settled legal basis for biofuels production, storage, transport and market and created the Intersecretarial Commission for biofuels development, involving: SAGARPA, SENER, SEMARNAT, SE and SHCP. This also protected corn from the use for biofuel production and helped the growers. On April 6, 2015, PEMEX signed six contracts with four companies to add 6% bioethanol into gasoline in the States of Veracruz, Tamaulipas and San Luis Potosi. Their contract with local suppliers is for 10 years to supply bioethanol by >77% of the estimated demand. The suppliers are guaranteed for domestic feedstocks and the growers are integrated to the project. The time for bioethanol plants’ construction and expansion fluctuates between 12 months to 36 months. A typical 1 t sorghum processing plant gives 400 L bioethanol, 288 kg DDGS and 275 kg CO₂ – currently either released to the atmosphere or used in industrial plants, in particular the coca cola company, for example, in the USA. BIOMEX owns a share of 150 million Pesos, 35% of the bioethanol plant. The greenhouse gas emission reduction potential has been estimated to be by 40%.
Ing. Bernardo Gonzalez of BD Tomsa Destil discussed the company’s product portfolio: spirits, industrial alcohols, superfine (high purity) alcohols, bioethanol, biodiesel and biokerosene from feedstocks such as urban residues, citrus wastes and algae, process technologies: enzymatic hydrolysis, proprietary yeast development, distillation optimization, fermentation optimization for enhanced bioethanol yield as well as business strategy and drivers, which were primarily economics focused. Dr Sergio Blanco-Rosete gave a talk on a topic “from the Notebook to the Cash” and the IPs of Cargill. Wheat is processed into glucose, gluten, fiber and ethanol. Solid state fermentation is at the core of the process. Distillation and rectification gave bioethanol, while stillage stream from distillation had many other options, which were covered in greater details in other presentations. Mr José Pablo López Gómez of The University of Manchester demonstrated the effectiveness of the Solid State Bioprocessing for the treatment of agro-industrial solid residues for Cargill. In his research, the technology using the edible fungus *R. oryzae* was applied for both preserving and enhancing the nutritional value of animal feed.

Professor Malcolm Baily of Link2Energy Ltd. presented four fascinating biorefinery innovations: Pea Pods Biorefinery, Wet Perishable Food Waste, Poultry Litter and Marine Biorefinery, in his keynote. Professor Baily described the process of pea pods biorefinery as: “In the UK, around 300,000 tpa pea pods are produced. Following solvent extraction, useful compounds were obtained including: Sugars
with potential in bio-ethanol production; High value compounds such as beta-Sitosterol which has been proven to be beneficial in reducing blood cholesterol. Microwave pyrolysis was found to be an exothermic process, which has potential to improve energy balance and economics of thermo-chemical processing. Chars obtained have high caloric value. Bio-oils contain phenolic compounds which are suitable as anti-oxidants or platform molecules. Pea pods show antioxidant activity and contain phyto-chemicals including iso-flavonoids and phenolics. They have also been used in cosmetic formulations and shown to have beneficial effects on facial skin. Pea starches have successfully been used to make bioplastics.”

Process Integration and Sustainability Analysis

There was a consensus that hard core Process Integration must drive product and process developments within sustainability constraints. “The presentations by senior academics (and industry) were very interesting as they showed the importance of how scientific developments resulted commercialization of bio technologies as well as highlighting current trends. I found those related to process integration and process engineering most interesting.” – Commented Mr Patel.

Dr Elias Martinez-Hernandez, Research Fellow at the University of Oxford, co-author of Wiley’s major textbook “Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis”¹ and Mentor of the Workshop, who also master-minded the Workshop, gave an insightful presentation: The Biorefinery Sustainability Puzzle. His keynote was on a multilevel and systematic approach for biorefinery sustainability by expanding the boundaries beyond those traditionally addressed by the methods for assessing sustainability such as LCA¹²-¹³, with a special focus on the techno-ecological interactions. The systematic view starts from the biorefinery process inter- and intra- integration, and expands to the integration with the broader value chain and then with the ecosystems and the society¹⁴. Dr Sadhukhan covered the methodology of integrated biorefinery flowsheet and system design for sustainability. She said, “Our work involves selection of techno-economically feasible integrated configurations using an effective Value Analysis methodology, fundamental reaction modelling, e.g. elementary reaction kinetics, Gibbs, equilibrium and stoichiometric reactors as appropriate, comprehensive heat and mass integration applying the pinch analysis techniques and Life Cycle Sustainability Assessment of whole value chains including integrated biorefinery and renewable energy systems and of cradle-to-grave life cycle stages, using biomass compositional analysis as the fundamental basis of all modelling tools.” Professor Grant Campbell of the University of Huddersfield made the difference between bioprocess and biorefinery very clear. A bioprocess is aimed at generation of a biofuel as the main product. The stillage streams can be utilized into some other coproducts in a bioprocess. Production of more than one product from primarily a bioprocess does not make it a biorefinery. For example, bioethanol can be produced from fermentation of biomass and DDGS can be extracted. A biorefinery as to resemble with crude oil refinery must involve extensive extraction of value added products from every fraction of biomass by cost-optimal and integrated unit operations. Biorefinery concept brings unique opportunities for in-process material and heat integration using powerful and systematic techniques such as pinch analysis¹⁵, explained by Professor Campbell, who showed the example of arabinoxylans extraction in integrated bioethanol plant¹⁶-¹⁸ in his keynote. His current research looks at applying the biorefinery concept to sugarcane bagasse.
Dr. Kok Siew Ng emphasized the importance of Process Integration in biorefinery development in his keynote. He gave a historical overview of the industrial evolution to date and how Process Integration played an important role in shaping up the economics. His work focused on polygeneration (trireforming, dry reforming, methanol synthesis and Sabatier’s reactions), carbon capture and coprocessing and bio-oil biorefinery (methanol and Fischer-Tropsch liquid synthesis and combined heat and power generation) case studies using process simulation, heat integration and techno-economic analyses. The processes will come into play, should the refiners find economic incentives (at much higher carbon taxation) to apply engineering know-how in the field.

Process Synthesis
- Analogous to the process of putting pieces of puzzles together.
- Not straightforward
- Understanding the objectives, brainstorming and screening, requires experience and heuristics.
- How to start from a blank sheet of paper?
- How to identify all possible configurations?

Methodology
- Process Modelling: Process configuration & operating condition selection
- Aspen Plus simulation
- Validation of model against literature results
--- Heat Integration: Data extraction and classification of heat integration tasks
- Composite curve analysis
- COP and network design
- Heat and power balance

Dr. Beatriz Fidalgo-Fernandez, Lecturer at Cranfield University, 2nd best oral presenter from the UK, discussed the development of process flow diagram of bio-oil hydropyrolysis and hydrogen production via aqueous reforming using Aspen Plus simulation, followed by pinch analysis based heat exchanger network design and economic analysis.

Dr. Elizabeth Mar Juárez of IMP also discussed biochemical and thermochemical based process technoeconomics from process integration perspective. Furthermore, Dr. Enelio Torres-García of IMP stated: “If we wish to achieve coherent and results well-supported, to establish the basis of design of any process, we must develop some methodology that allows us to identify the type of broken links, nature of involved reactions and the most probable compounds produced in each stage. One method to test and identify the type of bond broken under heating, it is to estimate the activation energy E(α) as a function of temperature (T) or the
transformation degree \((\alpha)\), known as model-free method. So, strictly speaking, any thermal transformation of biomass, i.e., combustion, pyrolysis or gasification, necessarily has to go-through a kinetic and thermochemical approach, which represents a great challenge."

"Due to the high production cost of ethanol from lignocellulosic biomass, it is anticipated that lignocellulosic conversion will focus on biorefining to numerous fractions for the chemical production industry. Lignocellulosic biomass consists mainly of three key polymers, lignin, cellulose and hemicellulose which can be further converted to a number of feedstock and end user chemicals. To this end, value chain optimization analysis may be used to determine the most profitable scenario." – presented by Dr Madeleine Bussemaker, Lecturer at the University of Surrey, 3rd best oral presenter from the UK demonstrated two biorefinery Value Chain Models for the conversion of the lignocellulosic biomass, namely softwood, firstly into ethanol and secondly into a multi-product stream.

Dr Miao Guo of Imperial College, London presented a range of environmental and social indicators tailored to developed/developing regions and an evaluation framework using life cycle approach to take into account the impacts of biorefinery network. The developed model was applied in an illustrative study to explore strategic design of a sample biorefinery system (biofuel / bioenergy / biocomposite as an example), which best supported an economically viable and low-GHG bio-product system and demonstrated insights such modelling framework could provide for penetration of biorefinery systems.

Dr Carlos Alberto García Bustamante of UNAM explained the carbon footprint analysis of sugar production in four sugar mills in Mexico employing LCA ranging between 0.45-0.63 kg CO\(_2\)e/kg sugar. Agricultural stage in four cases contributes the most to the carbon emissions, mainly due to the use of nitrogen fertilizers. Similarly, an exploration of more efficient cogeneration that allows the export of electricity achieved reduction in carbon footprint, so this option should be explored in more detail.

Dr. Julio C. Sacramento-Rivero of the Universidad Autónoma de Yucatán, the winner of the best oral presentation from Mexico showed an Indicator based sustainability assessment of biorefinery systems. Dr Rocio Diaz Chavez of Imperial College, London, wrote in the abstract of her important speech, “There is no single best methodology for conducting a sustainability appraisal or assessment. Rather, this requires the use of a wide range of analytical tools which derive from Environmental Impact Assessment, policy analysis and plan evaluation practice, among others.”

<table>
<thead>
<tr>
<th>Biorefinery driver</th>
<th>Indicator</th>
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<tbody>
<tr>
<td>The biorefinery’s feedstock is truly renewable</td>
<td>BVP: Biotechnological Valorization Potential</td>
</tr>
<tr>
<td></td>
<td>RMC: Raw-materials Consumption</td>
</tr>
<tr>
<td>The biorefinery is a better option than the fossil alternative (displacement potential)</td>
<td>WR: Freshwater-use Reduction</td>
</tr>
<tr>
<td></td>
<td>RFE: Reduction of Fossil Energy</td>
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<tr>
<td></td>
<td>RCR: Raw-materials Cost Ratio</td>
</tr>
<tr>
<td>The biorefinery is economically feasible</td>
<td>FRF: Fraction of Revenue for Feedstock</td>
</tr>
<tr>
<td></td>
<td>GM: Gross Margin</td>
</tr>
<tr>
<td>The biorefinery helps achieving fossil energy and emission reduction targets</td>
<td>NRES: Non-renewable Energy Share</td>
</tr>
<tr>
<td></td>
<td>RBE: Reduction of Baseline Emissions</td>
</tr>
<tr>
<td>The biorefinery promotes biodiversity preservation</td>
<td>SLU: Sustainable Land Use</td>
</tr>
<tr>
<td>The biorefinery promotes Social Development</td>
<td>EE: Employment Extent</td>
</tr>
<tr>
<td></td>
<td>CDI: Community Development Investment</td>
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Discussions on “Biomass availability, characterization and processing” and “Waste processing, circular economy and sustainability”

Two afternoon workshops were conducted on the second and fourth days of the Researchers Links Workshop to identify the specific research needs and the challenges faced. These are discussed as follows.

Planning and format: Dr Elias Martinez Hernandez

Chairs: Dr Mairi Black, Dr Kenneth O’Callaghan, Dr Myriam A Amezcua Allieri

Mentors: Professor Grant Campbell, Dr Rocio A Diaz-Chavez, Dr Kok Siew Ng, Professor Richard Murphy, Dr Jorge Arturo Aburto-Anell, Dr Arturo Sánchez Carmona, Professor Eugenia J Olguín, Dr Jhuma Sadhukhan, Dr Marcos Millan-Agorio, Dr Julio César

Idea generators: all the participants.

1. Process development and integration: The workshops strongly recognized the difference between bioprocess and biorefinery. A bioprocess is aimed at generation of a biofuel as the main product. The stillage streams can be utilized into some other coproducts in a bioprocess. Production of more than one product from primarily a bioprocess does not make it a biorefinery. For example, bioethanol can be produced from fermentation of biomass and co-products can be extracted. A biorefinery as to resemble with crude oil refinery must involve extensive extraction of value added products from every fraction of biomass by cost-optimal and integrated processing. Optimization here is meant to systematically opt out sub-optimal options from a superstructure by mathematical programming. An alternative to the approach is rigorous process simulation of options in the superstructure. The superstructure must incorporate all possible platform options, in-process material and energy recovery and usage options and all possible interactions between unit operations. Comprehensive mathematical models are then to be built and mass and energy balances have to be undertaken. The sizing of the equipment thus determined by mass and energy balances can be incorporated into cost, return-on-investment and economic margin formulations. The maximization of the overall economic margin can find the economically optimal biorefinery configuration. Biorefinery concept brings unique opportunities for in-process material and heat integration using powerful and systematic techniques such as pinch analysis. Further, at individual unit operations level, dynamic simulation allows optimization for flexible processing. Bioprocess development does not explicitly deal with process retrofit. Process retrofit allows cost-optimal expansion, hence, synthesis and design phase must be undertaken very carefully to incorporate the possibility of process optimization and retrofit to increase in-process recovery, reduce cost and achieve highest economic margin. This means techno-economic assessments of more than one configuration to systematically decide the overall optimal configuration. Research and education in biorefinery integration is essential to train future engineers in essential tools to deal with complexity from the synthesis level.

2. Characterization of waste was identified as a key topic –

- classification of waste
- chemical composition
- physical properties
3. Feedstock production and supply – It is essential to have spatially explicit biomass resource inventories, such that the Google Map can capture the information. This is essential to develop Integrated Engineering and Waste Management System (IEWMS). As the gaps between rich and poor are to be closed, resource distributions need to be more transparent, but the mobility of resources has to be achieved within a sustainability framework. Community benefits and engagement are important and have to be wide-spread. On technical side, separation technology models (MBT: mechanical biological technology, plant) of heterogeneous waste stocks at a fundamental mechanistic level are extremely important, for wider exploitation and integration.

4. Feedstock characterization and pretreatment – We need a consensus in feedstock specification for classification (hence technology selection) and lab methods / protocols that are cheap for feedstock characterization. More networking activities are therefore needed to come to a consensus and learn from each other. Characteristics of feedstocks must link to pre and downstream processing to give predictive power. Biomass logistics (availability, seasonality, characteristics and independent factors influencing these) are extremely important. Ontology or knowledge-based models are necessary to suggest pre-processing and flowsheet design and hence techno-economics.

5. Data – accessibility to data and data sharing were identified as areas where further research is required. Availability of data at the local level including current management of biowaste; agreement of data format; regulations and incentivization for waste management and social innovation within local clusters must be supported by further research funding.

6. Processing technologies and products – Scale up is an important issue. Is this biomass availability (seasonality, quantity and heating value) or process engineering knowledge that is restricting the scale up – what is the real bottleneck? Closing the loop means lesser waste generation and abiotic resource depletion and more efficient recovery of resources from waste. The gaps between technical, engineering and policy researches have to be closed. Process and product versatility and flexibility by more hard core process integration are important for sustainability of these industries. Process intensification and business models for distributed systems also featured prominently in the discussion.

7. Use of waste (markets and mechanisms for delivery of waste ‘products’ to market) – Markets within local clusters were highlighted. But there is an urgent need for integrated assessment, for e.g. how one local cluster is interacting with another local cluster and their interdependency, risks, and to what extent circular economy opportunities exist considering the nature of the waste – processing operations – product options.

8. Local cluster vs global consensus – The large variation in local cluster scenarios was identified as being both useful for individual application but also problematic in allowing assessment to be made across the broader picture. CRITICAL STEPS to value chains should be better understood to make sense of local data/clusters.

9. Sustainability – trilemma has to be assessed and resolved as far as possible in all of the above issues.

A summary of the areas and topics is highlighted as follows.

Process Integration must drive the development of biorefineries for elegant, complex and optimal designs and efficient operations within sustainability constraints. Life Cycle Sustainability must be assessed to approve a design.
<table>
<thead>
<tr>
<th>AREA</th>
<th>TOPICS</th>
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</table>
| A. Feedstock production and supply | 1. Spatially explicit biomass resource inventory in GIS  
2. Qualitative and distributional issues  
3. Community benefits and engagement  
4. Separation of useful components from heterogeneous feedstocks and mixed feedstocks (e.g. organic fractions of Municipal Solid Waste (MSW))  
5. Innovation and transitions in biomass feedstock production including cultural aspects |
| B Feedstock characterisation and pre-treatment | 1. Classification criteria for feedstocks  
2. Database of biomass characterisation linking to pre-processing and downstream  
3. Logistics is important  
4. Ontology, Knowledge based framework to suggest pre-treatment  
5. Simplify characterisation to reduce cost, establish protocols to measure characteristics |
| C Processing technologies and products | 1. Scale up  
2. Closed loops for waste elimination  
3. Process/product versatility to make it competitive  
4. Business models for distributed systems  
5. Process intensification |
| D Process development and integration | 1. Unique opportunities with a non-environmental driver  
2. Compositional information of in-process materials for integration  
3. Dynamic simulation for a flexible processing  
4. Retrofit- the Cinderella of biorefinery research  
5. Education in biorefinery integration |

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<th>AREA</th>
<th>TOPICS</th>
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| Sustainability | Feedstock sustainable assessment (not only residual rates but including environmental and logistics, )  
Market analysis (sustainable point of view to review which products can be replaced, where they are needed, etc)  
Strategic view (SEA) on how pre-treatment plants, possible biorefineries, current facilities are in place and how to integrate them  
Policy analysis on how the whole bioenergy systems (including biorefineries) with some scenarios for 2020 and 2030 (?)  
Standards used and benefits/barriers in Mexico for this sector  
Data collection and monitoring on current systems (e.g. industry) bank (?) for integrated sustainability assessment using different tools (e.g. EIA, SIA, LCAs, SEA, ecosystems services) |

**Networking**

Socializing has been an important part of the Workshop and in an informal setting everyone could come out of own shell and make friends. Dinning together was an important feature, including two most remarkable evenings out on Wednesday, followed from the Museo Nacional de Antropología excursion and on Thursday in an informal setting.

“I found the Workshop very valuable principally because of its small and intimate nature, which allowed excellent networking and relationship development between the attendees, and because of the inclusion of the participative exercises which made the interactions particularly tangible and valuable.

I personally found the opportunity to connect with former colleagues and collaborators from the UK and to meet new ones, in a context where we were away from the UK and in a conducive and stimulating environment, very valuable; being away together, and being with Mexican colleagues
facing similar issues from a different perspective, has strengthened the coherence of the UK biorefinery community and stimulated new ideas."

"I definitively believe that these types of events are the perfect venue for bringing together experts with diverse background. It is particularly important in topics such as biorefining, in which a multidisciplinary approach is needed in order to achieve significant advance on the state of the art.

I must say that attending the Workshop has been an enriching experience for my professional development but also from a personal point of view. I had the opportunity of meeting very knowledgeable and nice people, and to get to know better Mexico City, which I love more and more!

I would not doubt be attending to any other similar event in the future and recommending these experiences to any of my colleagues."

"This direct contact made it easier to understand the new technologies and to exchange ideas about how can they be improved and to find possible solutions for their main drawbacks. Moreover, the activities of the Workshop, and more concretely the round tables, were very fruitful. In my opinion, this kind of activities can help me to face everyday difficulties at work from a different perspective.

In addition, the attendance to the Workshop has given me the opportunity to interact with them in a more personal way, what can help to set the basis for future collaborations."

"I would like to thank the organisers for taking the initiative to facilitate this Workshop and inviting experts from the UK as well as Mexico. The smooth running and passion exuded by them regarding the subject is a testament to their commitments to push forward this important research area to tackle climate change and yield societal benefit."

– These spoke for all!
Organizing Committee (from left): Drs Elias Martinez-Hernandez, Myriam A. Amezcua Allieri, Kok Siew Ng, Jhuma Sadhukhan and Jorge Arturo Aburto Anell

References


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