Biorefineries, Sustainability Considerations, & Innovation

Workshop on Renewable Chemical Raw Materials

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IV ENCONTRO DA ESCOLA BRASILEIRA DE QUÍMICA VERDE
Topics

• Biorefineries
• Green Chemistry and Green Engineering leading to Sustainable Technologies
• How do we know renewable chemicals and materials are green and sustainable?
• Examples of tools and pathways to get there
• Sustainability and big picture
• Renewable chemicals, materials, and biorefineries
• Exciting science, technology, systems need to be integrated with the specific biomass context
The Possible Role of Biorefineries in a Bio-Economy – Activities of IEA Bioenergy Task 42 “Biorefining”
Gerfried Jungmeier
4th Central European Biomass Conference, January 15 – 18, 2014, Graz AUSTRIA

This is a Biorefinery

Biomass Resources
- oil
- starch
- sugar
- lignocellulose
- ....

Bioenergy
- liquid/gaseous transport biofuels
- electricity
- heat
- solid fuels

Bioproducts
- bulk chemicals
- fine chemicals
- animal feed
- food
- pulp&paper
- materials
- fertilizer
- gases
- ....

Based on different conversion processes
- Bio-chemical
- Thermo-chemical
- Physical-chemical
- Others

“Biorefinery is the sustainable processing of biomass into a spectrum of marketable products”
Biorefinery: concepts, facilities, processes, clusters of industries
Sustainable: maximising economics & social aspects, minimising environmental impacts, fossil fuel replacement, closed cycles
Processing: upstream processing, transformation, fractionation, thermo-chemical and biochemical conversion, extraction, separation, downstream processing
Biomass: wood & agricultural crops, residues, forest residues, aquatic biomass
Spectrum: multiple energetic and non-energetic products
 Marketable: Present and forecasted (volume and prices)
Products: both intermediates and final products (i.e. food, feed, materials, chemicals, fuels, power, heat)
Current Market Size

Fossil based Chemicals: 330 million tonnes

Main molecules:
- methanol, ethylene, propylene, butadiene,
- benzene, toluene and xylene

Biobased Chemicals & Materials 50 million tonnes

Main molecules:
- Non-food starch, cellulose fibres/derivatives,
- tall oils, fatty acids and fermentation products

Product Commercialization

Key criteria

Market assessment
- Market fundamentals (local, regional, global)
- Feedstock availability and price
- Product profitability
- Competitive nature of market
- Need for partnerships
- Downstream development opportunities

Technology assessment
- Commercial experience
- Necessary capital investment
- Process complexity
- Access to technology
- Environmental considerations

Drop-in versus New Functionality

<table>
<thead>
<tr>
<th>Bio-based chemicals</th>
<th>Reference petrochemicals</th>
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<tbody>
<tr>
<td>Ethyl lactate</td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td>Ethylene</td>
<td>Ethylene</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>Adipic acid</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>n-Butanol</td>
</tr>
<tr>
<td>PTT</td>
<td>PTT &amp; Nylon 6</td>
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<tr>
<td>PHA</td>
<td>HDPE</td>
</tr>
<tr>
<td>PLA</td>
<td>PET and PS</td>
</tr>
<tr>
<td>FDCA</td>
<td>Terephthalic acid</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>Maleic anhydride</td>
</tr>
</tbody>
</table>

Dana Kralisch,* Denise Ott* and Dörthe Gericke*
## Green Chemistry Principles

1. Waste prevention instead of remediation  
2. Atom efficiency  
3. Less hazardous/toxic chemicals  
4. Safer products by design  
5. Innocuous solvents and auxiliaries  
6. Energy efficient by design  
7. Preferably renewable raw materials  
8. Shorter syntheses (avoid derivatization)  
9. Catalytic rather than stoichiometric reagents  
10. Design products for degradation  
11. Analytical methodologies for pollution prevention  
12. Inherently safer processes

## Green Engineering Principles

- **P** – Prevent wastes  
- **R** – Renewable materials  
- **O** – Omit derivatization steps  
- **D** – Degradable chemical products  
- **U** – Use of safe synthetic methods  
- **C** – Catalytic reagents  
- **T** – Temperature, Pressure ambient  
- **I** – In-Process monitoring  
- **V** – Very few auxiliary substrates  
- **E** – E-factor, maximize feed in product  
- **L** – Low toxicity of chemical products  
- **Y** – Yes, it is safe

A survey of solvent selection guides

Denis Prat,*a John Haylerb and Andy Wells*c

Table 4  Ranking comparison

<table>
<thead>
<tr>
<th>Family</th>
<th>Solvent</th>
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<td>AZ</td>
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</table>

Table 5  Overall ranking of solvents

- **Recommended**
  - Water, EtOH, i-PrOH, n-BuOH, EtOAc, i-PrOAc, n-BuOAc, anisole, sulfolane.
  - MeOH, t-BuOH, benzyl alcohol, ethylene glycol, acetone, MEK, MIBK, cyclohexanone, MeOAc, AcOH, Ac₂O.

- **Recommended or problematic?**
  - Me-THF, heptane, Me-cyclohexane, toluene, xylenes, chlorobenzene, acetonitrile, DMPU, DMSO.

- **Problematic**
  - MTBE, THF, cyclohexane, DCM, formic acid, pyridine.

- **Problematic or hazardous?**
  - Diisopropyl ether, 1,4-dioxane, DME, pentane, hexane, DMF, DMAc, NMP, methoxy-ethanol, TEA.

- **Hazardous**
  - Diethyl ether, benzene, chloroform, CCl₄, DCE, nitromethane.

Cite this: DOI: 10.1039/c4gc01149j
Organic Solvent Nanofiltration (OSN)

1. Using greener solvents for casting, coating, crosslinking, & interfacial reactions
2. Using low toxicity chemicals that also minimize potential for explosions or fires
3. Using renewable or raw materials for membrane formation
4. Minimizing energy preparing casting solutions and crosslinking at r.t.
5. Designing degradable membrane products that do not persist in the environment

Fig. 10 Processes comparison concerning (A) energy consumption with solvent disposal or solvent recovery as well as (B) batch operation times and solid waste generated.
The evolution of life cycle assessment in pharmaceutical and chemical applications – a perspective

Concepción Jiménez-González\textsuperscript{*a} and Michael R. Overcash\textsuperscript{b}

Green Chemistry, 2014, \textbf{16}, 3392
Lifecycle Assessments

- From specific products
- All the way to
- Systems using products

Emerging approaches, challenges and opportunities in life cycle assessment
Stefanie Hellweg and Llorenç Milà i Canals
*Science* 344, 1109 (2014);
DOI: 10.1126/science.1248361
Emerging approaches, challenges and opportunities in life cycle assessment
Stefanie Hellweg and Llorenç Milà i Canals
Science 344, 1109 (2014); DOI: 10.1126/science.1248361
Lifecycle Assessments – Four phases example

1. Goal and scope definition
   - Resource extraction
   - Production
   - Use
   - Disposal

2. Inventory analysis
   - Technical inputs and outputs of all processes
   - Emissions (to air, water, and soil)
   - Resource use (land, water, fossils, metals)

3. Life-cycle impact assessment
   - Climate change
   - Ozone depletion
   - Photochemical ozone creation
   - Human toxicity
   - Ecotoxicity
   - Eutrophication
   - Acidification
   - Land stress
   - Water stress
   - Resource depletion

4. Interpretation

Freight transportation

Emerging approaches, challenges and opportunities in life cycle assessment
Stefanie Hellweg and Llorenç Milà i Canals
Science 344, 1109 (2014);
DOI: 10.1126/science.1248361
Fig. 4 Comparison of human health cancer impacts by E85 and gasoline, broken down into different contributors. 2001, 2005, and 2010 reflect different corn production and ethanol conversion technologies used in different years, respectively. Error bars for ...

Yi Yang

Life cycle freshwater ecotoxicity, human health cancer, and noncancer impacts of corn ethanol and gasoline in the U.S.

Journal of Cleaner Production, Volume 53, 2013, 149 - 157

http://dx.doi.org/10.1016/j.jclepro.2013.04.009
U.S. Corn ethanol freshwater toxicity impact compared to gasoline

Fig. 3  Comparison of freshwater ecotoxicity impact by gasoline and E85, with key pesticides and their contributions identified. 2001, 2005, and 2010 reflect different corn production and ethanol conversion technologies used in different years, respectively...

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Emerging approaches, challenges and opportunities in life cycle assessment

Stefanie Hellweg\textsuperscript{1*} and Llorenç Milà i Canals\textsuperscript{2}

**A. Impacts (three categories) of electricity provided to the grid**

- **Ecosystem impact from water consumption**
- **Climate change**
- **Acidification**
Expanding GREENSCOPE beyond the gate: a green chemistry and life cycle perspective

Gerardo J. Ruiz-Mercado · Michael A. Gonzalez · Raymond L. Smith

DOI 10.1007/s10098-012-0533-y

Fig. 1 Data flow for GREENSCOPE indicators, describing the internal data flow (mass and energy flows, equipment, and operating conditions) from the studied process and external data from different sources (e.g., classification lists, toxicological properties, equipment costs).
Expanding GREENSCOPE beyond the gate: a green chemistry and life cycle perspective

Gerardo J. Ruiz-Mercado · Michael A. Gonzalez · Raymond L. Smith

DOI 10.1007/s10098-012-0533-y
<table>
<thead>
<tr>
<th>Large – Economies of Scale</th>
<th>Medium to Small</th>
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<tr>
<td>Conventional wisdom for chemical processes based on lower capital/operating cost per unit of product</td>
<td>Biomass gasification</td>
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<tr>
<td>Common for liquid and gaseous fuels/chemicals</td>
<td>Some corn dry mills, biodiesel plants</td>
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<tr>
<td>Solids – more difficult; coal (friable) adapted to large scales; coprocessing biomass (small/large) and coal for power</td>
<td>Pulping processes</td>
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<tr>
<td>Corn biorefineries using wet milling process</td>
<td>Biomass pyrolysis to liquids (diesel engines, fragrance chemicals, char)</td>
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<tr>
<td>Coprocessing of biomass and X-TL for liquid fuels</td>
<td></td>
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</tbody>
</table>

Small – Economies of Volume

- Modular systems
- Hurdle to develop enough projects using small scales to reach economies of volume
- Pursued by Gas-to-Liquids developers
- Pursued by biomass pyrolysis to liquids (eg, heating oil replacement, liquid fuels?, etc.)
The Context: Agriculture, Forestry and Other Land Use
GHG emissions growth between 2000 and 2010 has been larger than in the previous three decades.

Based on Figure 1.3
### GHG Emissions and Sinks Inventory

#### U.S. data

- **UNFCCC reporting -- by IPCC Sector**
- **INVENTORY OF U.S. GREENHOUSE GAS**

#### Table ES-2: Recent Trends in U.S. Greenhouse Gas Emissions and Sinks (Tg or million metric tons CO₂ Eq.)

<table>
<thead>
<tr>
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<td>CO₂</td>
<td>5,108.7</td>
<td>6,112.2</td>
<td>5,936.9</td>
<td>5,506.1</td>
<td>5,722.3</td>
<td>5,592.2</td>
<td>5,383.2</td>
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<tr>
<td>Land Use, Land-Use Change, and Forestry (Sink)</td>
<td>(831.1)</td>
<td>(1,030.7)</td>
<td>(981.0)</td>
<td>(961.6)</td>
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<td>(979.3)</td>
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<td>CH₄</td>
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<td>585.7</td>
<td>606.0</td>
<td>596.5</td>
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<td>567.3</td>
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<td>N₂O</td>
<td>398.6</td>
<td>415.8</td>
<td>423.3</td>
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<td>409.3</td>
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<td>HFCs</td>
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<td>136.0</td>
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<td>PFCs</td>
<td>20.6</td>
<td>5.6</td>
<td>5.1</td>
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<td>3.8</td>
<td>6.0</td>
<td>5.4</td>
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<td>SF₆</td>
<td>32.6</td>
<td>14.7</td>
<td>10.7</td>
<td>9.6</td>
<td>9.8</td>
<td>10.8</td>
<td>8.4</td>
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<tr>
<td>Total</td>
<td>6,233.2</td>
<td>7,253.8</td>
<td>7,118.1</td>
<td>6,662.9</td>
<td>6,874.7</td>
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<td>6,525.6</td>
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<tr>
<td>Net Emissions (Sources and Sinks)</td>
<td>5,402.1</td>
<td>6,223.1</td>
<td>6,137.1</td>
<td>5,701.2</td>
<td>5,906.7</td>
<td>5,772.7</td>
<td>5,546.3</td>
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</table>

Accounted in Land use, land-use change, and forestry are the emissions from (otherwise double counted)

#### Wood Biomass and Ethanol Consumption

|              | 219.4 | 229.8 | 254.7 | 250.5 | 265.1 | 268.1 | 266.8 |
About half of cumulative anthropogenic CO₂ emissions between 1750 and 2010 have occurred in the last 40 years.
One view to examine the impact of materials flows and consumption on GHG and contributions to global environmental problems – UNEP  International Panel for Sustainable Resource Management, 2010
Innovation in Catalysis -- examples

• See 2014 Green Chemistry issues
Green Chemistry, 2014, 16, page - PAPERS

One pot

p. 617

p. 695

p. 653

p. 761
Considerations presented

With the view to increase

- Systems thinking
- Dialogue on how to select sustainable, resource efficient and productive routes for each promising biomass context
- Country/Regional/Global perspectives
Acknowledgments

- Sponsors of the IV ENCONTRO DA ESCOLA BRASILEIRA DE QUÍMICA VERDE for the invitation!
- The U.S. Department of Energy, Bioenergy Technologies Office Sustainability Program
- IPCC co-authors in SRREN and AR5 for very productive discussions
- IEA Bioenergy Agreement – Tasks 38, 39, 40, 42, 43, and inter-task work
- USDA, USEPA, and colleagues from NREL and ORNL, ANL, PNNL, and INL
- US Brazil MOU to Advance Biofuel Technologies
- SCOPE: Bioenergy and Sustainability – Bridging the Gaps (FAPESP/UNESCO)
Sugars and Cellulosic Products Biorefinery

Figura 1.3: Biorrefinaria lignocelulósica: produtos da celulose
Fonte: Pereira Jr. et al., 2008.
Sucrose Products Tree

Examples
AGÊNCIA BRASILEIRA DE DESENVOLVIMENTO INDUSTRIAL.

Comite Gestor com:
ABIQUIM,
ABIPLAST,
Outras associações relevantes
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<th>Estágio do ciclo de inovação</th>
<th>Uso comercial</th>
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<th>Desenvolvimento</th>
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<td>2012</td>
<td>2017</td>
<td>2022</td>
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<td>Nanocompósitos poliméricos in situ</td>
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<td>2012</td>
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<td>Nanocompósitos poliméricos formulados</td>
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<td>2012</td>
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