Advanced biofuels and added value products from residual quasi-homogeneous biomass: from ethanol to *drop-in* fuels

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Biorefinery

• Comes from « bio » et « refinery »
  – Refine biological material
• Despite what we might think:
  – Biomass HAS a market
• It is diversified and complex
• Despite these facts – it stills represents an opportunity:
  – Carbon content, locally available and still as important : IT IS RENEWABLE
A lesson from the master

- Oil industry:
  - Use petroleum and refines it
- The first steps of a refinery
  - COMMODITIES (fuels)
  - For which there will always be a market
  - Commodities covers for the OPEX
- Where is the margin of profit?
  - Added value chemicals
Convert this reality

- Implementing something as a biorefinery:
  - First objective should be commodities
  - It will ensure economical viability
  - Will also cover for the OPEX of the biorefinery

- Where should be the profit?
  - Added value molécules (and it’s not easy!)

- Biomass:
  - As oil: an opportunity
  - Source of renewable and « green » compounds
Biomass

- All biomasses are rich in C [45 - 50 wt%]
- Few biomasses have an homogeneous composition
- Homogeneity will influence «conversion strategies»
- Biomass can be divided in three categories:
  - Homogeneous
  - Quasi-homogeneous
  - Non-homogeneous
Abundance

- **>200 k AMT/year**
  - Dedicated area
  - Large forest/agricultural activities
  - Contracts should go by: Governments, Large corporations

- **25-200 k AMT/year**
  - Residual Biomass
  - Available in more locations
  - Contracts should go by: Region and/or municipalities, Private

- **< 25-200 k TMA/year**
  - Urban biomass (MSW)
  - Available in all cities
  - Abundance depends on population, 100k population ≈ 28 k AMT/y
**Composition VS conversion**

**Predictable composition**
- Cellulose
- Hemicelluloses
- Lignin
- Extracts
- Proteins

**Unpredictable composition**
- Plastics (non-recyclable)
- Wood
- Paper (non-recyclable)
- Fabrics
- Etc

**Fractionation**

**Gasification**
FIRSST process

1. **Extraction**
   - Original Biomass
   - Extracted Biomass
   - Extracts
   - Fibres + Lignin
   - Hemicelluloses
   - Lignin

2. **FIRSST, Step 1**
   - Ethanol
   - Pharmaceuticals
   - Cosmetics
   - P-fuels (biodiesel)
   - Green chemicals
   - L-fuels (Drop-in *)

3. **FIRSST, Step 2**
   - Pulp and paper
   - Ethanol
Extractives

• Extraction is performed before the FIRSST process

• Important:
  – Added value products
  – Limit the inhibitors in the aqueous mixture

• Process – Emulsification-assisted extraction

• Application: Pharma/Cosmetics/Food/Gasification
P-fuels/biodiesel

- C\textsubscript{5} sugars are hard to ferment
- Under acid catalyst – furfural
- Highly efficient 3 step process
  - Furfural
  - Furfurylic alcohol
  - Ethyl levulinate
L-fuels/jetfuel

FIRSST
Lignin

Depolymerization

Purification

Reduction

Gasification
Non-enzymatic hydrolysis

Biomass (100 MU) → FIRSST → Cellulose (43MU)

12 MU - Extractives
20 MU - Hemicelluloses
20 MU - Lignin
05 MU - Proteins

Decrystalisation
Hydrolysis
Hydrogel
Ion rich solution
Reactives
Purification

Glucose solution (4-12%wt) 35-40MU

Distillation
Fermentation
A biorefinery scenario

• Exemple : 1 tonne of agricultural residues (In this case triticale)
  – 221 l of EtOH (+46 l invested in p-fuels)
  – 110 l of p-fuels (biodiesel)
  – 110 l of l-fuels (bio jetfuel)
  – 25 kg of green molecules

• Energetic demand
  – 13 GJ/tonne
Synergetic approach

Quasi-homogeneous biomass
1 tonne (dry basis) + 1 tonne moisture

FIRSST

Residues
(216 kg dry basis)

Gasification

Steam/O₂

Syngas

Water: 210 kg
Solid residues (<8% unconverted C)

CO₂: 644 kg

CO₂ removal

CHP

0.84 MWh(t) + 0.7 MWh (e)

Biofuels

Water: 1017 kg
CO₂: 282 kg
Solid residues (rich in N and K): 8 kg

Green chemicals: 20 kg

EtOH: 220 l
Biodiesel: 120 l
Jetfuel: 130 l

High pressure SG (215 Nm³) for hydrogenation for p-fuels and l-fuels

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## Energy balance

<table>
<thead>
<tr>
<th>Biomass</th>
<th>GJ</th>
<th>MWh</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 AMT</strong> residual lignocellulosic biomass</td>
<td>18</td>
<td>5.0</td>
</tr>
<tr>
<td><strong>0.7 AMT</strong> non-homogeneous biomass</td>
<td>14</td>
<td>3.9</td>
</tr>
<tr>
<td><strong>Total:</strong> <strong>1.7 AMT</strong></td>
<td>32</td>
<td>8.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Products (agricultural residues as an example)</th>
<th>GJ</th>
<th>MWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol (216 l – 167 kg)</td>
<td>5.1</td>
<td>1.41</td>
</tr>
<tr>
<td>P-fuels: Ethyl Levulinate (124 l – 126 kg)</td>
<td>3.3</td>
<td>0.92</td>
</tr>
<tr>
<td>L-fuels: Propylcyclohexane (100l – 88 kg)</td>
<td>3.5</td>
<td>0.97</td>
</tr>
<tr>
<td>Residual syngas</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Lignin derived chemicals (31 kg)</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td><strong>Total Output</strong></td>
<td>3.80</td>
<td></td>
</tr>
</tbody>
</table>

TOTAL EFFICIENCY 42% and up to 45%
Negative » Carbon footprint

- The Chair’s approach
  - Complete utilisation of carbon
    - Including CO₂
- From this the biorefineries:
  - Will only produce biofuels and green molecules
- Three approaches are considered:
  - Thermochemical
  - Chemical
  - Biological
Chemical approach

Products from the second generation biofuel industries

Residues or co-product from 1st and 2nd generation biofuels industries

Green compound: -3rd generation fuel -Monomer -Green compound
Biological approach

- Used industrial water
- Fractionation
- Gasification

Materials and processes involved in the biological approach.
Acknowledgments

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