Biofuels from Biomass – the CO₂ – Algae – BioRefinery case

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INTRODUCTION

Grand Challenges of our time:

- INCREASING POPULATION
  in need of SUSTAINABLE DEVELOPMENT

- DEPLETION OF FOSSIL RESOURCES & SECURITY OF SUPPLY (distribution issue)

- CLIMATE & ENVIRONMENTAL CONCERNS

Most important:
- ENERGY
- SCARCE ELEMENTS
- CO₂ RECYCLING
Earlier in this 'EnergyDays'-series:

(October 4th, 2012: Efficient transportation and energy storage)

“Nothing beats the comfort of fossil fuels” (Hermans)
“wish storage material: something like gasoline” (Haye)
“We are not running out on oil and gas…but are we willing to pay the price?” (Smeulders)
“CO₂ reduction potential through: Biofuels as surrogates for liquid fuels” (Stolten)
...
“There are more fossil fuels than the atmosphere can accommodate” (Kramer, oct. 2011)
“Biomass will become important (transport fuels, feedstock). To what extent depends on the development of other solutions (direct conversion of sunlight to fuels, … ?) (Hellinga, oct. 2011)

• There is clearly an incentive for carbon-neutral (liquid) fuels
• Biofuels are seen as potential candidate solution

Even now... with the recent discovery of shale gas... we should realize:

'It wasn’t a lack of stones, that ended the Stone-Age'
The potential of biofuels
(Fuels derived from sustainable biomass)

- Biofuels will not completely fulfill all our energy needs nowadays: < 10%. **Expected: 10-25%**

- Biofuels for transportation, heating, cooking, energy storage

- Biomass potential (vs. energy needs: **150 kWh/d/person** (McKay, Lysen)):
  *(potential strongly related to available (arable) land)*

  - **NL:** 1200 m²/person → 17 kWh/day per person (1% solar efficiency)
  - **UK:** 3000 ,, 24 kWh/day/person (McKay)
  - **USA:** 13000 ,, 187 ,, (1% solar efficiency)

World oil consumption:
87 M barrel/day (2010)

(Kramer, oct.2011)
Is there sufficient Biomass?

...that depends on population density and need for energy/materials

World energy consumption: $\Rightarrow 550 \text{ EJ/yr}$
Currently, oil consumption is 87 M bbl/day $\Rightarrow 200 \text{ EJ/yr}$ ; $4,0 \times 10^3 \text{ Mt/y}$

10% is used for materials/chemicals: $20 \text{ EJ/yr}$ ; $400 \text{ Mt/y}$

Biomass production in perspective:
World grain production 2,300 million t/y $= 40 \text{ EJ/y}$ (avg. 3-5 t/ha yr; NL: 8)

suppose we replace grain by algae:
algae: potentially 40-60 t/ha yr. (5-7% solar efficiency) $\Rightarrow 400 \text{ EJ/yr}$

$= 400 \times 10^6 \text{ ha}$

(= 30% arable land. Note: marginal land can also be used!)

EU: after fulfilling needs for food production, around 30 Mha arable land is available for energy/biomass production.

Hence, Biomass can provide a very significant contribution!
BIOMASS, ELECTRICITY AND ‘DIE ENERGIE WENDE’

Electricity mix NL (2007)

<table>
<thead>
<tr>
<th>Source</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>24.5 %</td>
</tr>
<tr>
<td>Natural gas</td>
<td>49.6 %</td>
</tr>
<tr>
<td>Nuclear</td>
<td>8.4 %</td>
</tr>
<tr>
<td>Biomass</td>
<td>5.4 %</td>
</tr>
<tr>
<td>Wind</td>
<td>3.9 %</td>
</tr>
<tr>
<td>Hydro</td>
<td>5.2 %</td>
</tr>
<tr>
<td>Rest</td>
<td>3.0 %</td>
</tr>
</tbody>
</table>

CO₂: 0.50 kg/kWh (av.) [2007]  
0.46 kg/kWh (av.) [2010]

Role of biomass in electricity production is most likely limited!  
(storage, co-firing in base-load facilities etc.) => focus on fuels & chemicals
Why use Biomass?

Biomass:

• ...is stored solar energy
• ...is available (as residue) in food production, forestry, processing, waste
  *(the resource is there...let's use it!)*
• ... is the most versatile- and only renewable energy source with C-content
• ... is potentially CO₂ neutral
Biofuels – Development & Challenges

Rapid developments in last 10-15 yr.

**First Generation**
- Edible oils (palm-, rapeseed), ethanol from sugar cane, (“biodiesel” using agricultural land; food-fuel debate)
- Limited yield: Energy output/Energy input

**Second Generation**
- Lignocellulosic biomass, crop- and forestry residues, waste, …

**Third Generation**
- Algae (and other energy crops)
- Algae Biorefinery concepts

**Fourth Generation**
- Artificial photosynthesis with renewable energy
- Atmospheric CO₂ utilization
  - (CO₂ + H₂O + e⁻ => …. (MeOH, DME, CH₄, …)

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The Challenge and the Potential is in the complexity and richness of the material.
Lignocellulosic biomass

*biopolymers*

**Cellulose**
Polymer of mostly glucose units (up to 8000) chains are linked by hydrogen bonds. If crystalline, insoluble in most solvents 40 to 50 wt% of the cell wall matrix.

**Hemi-Cellulose**
Polymer of C\textsubscript{6} and C\textsubscript{5} units (xylose, arabinose) up to 200 units amorphous, with acetyl groups easy to hydrolyze 25 to 35 wt% of the cell wall matrix.

**Lignin**
3-dimensional aromatic structure of phenyl propane units 20 to 30 % of the wood matrix.
**Biomass to Fuel components**

**Oils / Lipids**: (tri-)glycerides $C_4 - C_{22}$

- Hydrocarbons (current fuels)
- FA Methyl-esters (biodiesel)

**Glucose**

**Proteins**

**Lignin** (monomers)

(some) target compounds
Process routes from Biomass to fuels

Lignocelluloses: Wood, Agricultural waste, Forestry residue

Sugars-rich Biomass: Cane, Corn, Beet, (macro-) Algae

Lipids-rich Biomass: Palm, Jatropha, Rape, (micro-) Algae

Gasification

Liquefaction & upgrading

Sugar extraction / production

Sugar conversion

(LCo)-refining

Lipid extraction

Transesterification

Hydrogenation

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BIOMASS CHALLENGES

- Complex raw material
  - Chemical comp.
  - Structure

- Disperse production
  - Time, place
  - Storage

- Transport

- Quality control

- Pretreatment

- Economy of scale

- Social impacts

- Overall sustainability

- Complex material
- Disperse production in time & place
  - Collection logistics
  - Storage issues
  - Central vs. local processing?

- Variation in quality and quantity
- Low energy density
- Often drying / pretreatment required

Impact:
- Value chain different
- Economy of scale?
- New business models needed?
Biomass Conversion Technologies

To make biomass suitable for (more economic!) large scale processing, the inhomogeneity of the material must be reduced:

- Milling/mixing
- Fractionation (chemical-)
- Liquefaction
- Gasification

For storage, transport and stability, a high energy density is required (liquids!)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>‘Wet’ Biomass</th>
<th>‘Dry’ Biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>Carbonisation</td>
<td>Carbonisation Torrefaction</td>
</tr>
<tr>
<td>Liquid</td>
<td>Hydrothermal</td>
<td>Pyrolysis Solvolysis</td>
</tr>
<tr>
<td>Gas</td>
<td>SCWG</td>
<td>Gasification Combustion Back to $CO_2, H_2O$</td>
</tr>
</tbody>
</table>
Fast Pyrolysis

Densification
Easier transport
Easier processing (blending, mixing, gasification etc.)

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Biomass and pyrolysis oil logistics

Refinery

Pyrolysis plant

Py-oil

Upgrading?

Py-oil

Py-oil

Py-oil

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**Biomass transportation/logistics and Economy of Scale**

**Average transport distance** = 0.382 * S

**Example of a Biorefinery Collective (BRC)**
- consisting of a group of PCs
- feeding a central ATR/FT Facility

Published in: James L. Manganaro; Adeniyi Lawal; *Energy Fuels* **2012**, *26*, 2442-2453.
DOI: 10.1021/ef3001967
Copyright © 2012 American Chemical Society
Fast Pyrolysis

- Increased energy density (transport)
- Liquids easier to process / upgrade
- No solids in oil
- Ashes/minerals in biochar: local recycling
- Char combustion supplies heat for pyrolysis
  - Complex mixture (> 200 comp.)
  - Stability (time)
  - Water content and acidity

1000 kg wood
(10 % moisture)

T = 500°C
P = 1 atm

175 kg gas
650 kg oil
175 kg char

175 kg Gas
650 kg Olie
175 kg Kool

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Pyrolysis status

- Optimization oil yield
  - Temperature, res.time
  - Faster heating
  - Smaller particles (but: cost of milling)

- Oil composition
  - Water content
  - O-content
  - Stability
  - analysis

- Pyrolysis Fundamentals
  - Chemistry
  - Effect of structure

- Process development
  - Pretreatment
  - Fractional Condensation

((Westerhof et al., Energy&Fuels, 2012))
## Pyrolysis oil characteristics

<table>
<thead>
<tr>
<th>Feature</th>
<th>Pyrolysis oil (pine)</th>
<th>Heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. density</td>
<td>21</td>
<td>39 GJ/m³</td>
</tr>
<tr>
<td>Density</td>
<td>1220</td>
<td>963 kg/m³</td>
</tr>
<tr>
<td>Viscosity</td>
<td>13</td>
<td>351 mm²/s (50⁰C)</td>
</tr>
<tr>
<td>Acidity (pH)</td>
<td>2-3</td>
<td>7</td>
</tr>
<tr>
<td>Water content</td>
<td>20</td>
<td>0.1 wt%</td>
</tr>
<tr>
<td>Elemental composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>52</td>
<td>86 wt%</td>
</tr>
<tr>
<td>H</td>
<td>7</td>
<td>10 wt%</td>
</tr>
<tr>
<td>O</td>
<td>40</td>
<td>0.5 wt%</td>
</tr>
<tr>
<td>N</td>
<td>0.1</td>
<td>0.6 wt%</td>
</tr>
<tr>
<td>S</td>
<td>&lt; 0.1</td>
<td>2 wt%</td>
</tr>
</tbody>
</table>
Biomass and (bio-) fuels

Van Krevelen diagram

Pyrolysis oil is not directly suitable as transportation fuel
- O-content
- Stability
- Acidity

Strategy:
- a) UPGRADING
- b) CO-FEEDING
- c) Combination
  (mild upgrading + co-feeding)
Co-refining of pyrolysis oil

Ligno-cellulosic Biomass (waste)

Pyrolysis oil
~40-50 wt.% oxygen
~20-30 wt.% water

Pyrolysis
400-550 °C
Oil yield: 60-70 wt.%
Energy yield: ~60-70 %

Upgrading
Hydrodeoxygenation
Reduce Oxygen & Water content
Improve miscibility fossil fuel
Reduce acidity...

Refinery
Co-refining

Link to existing infrastructure, existing products and markets

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Upgrading of pyrolysis oil

Effect of ‘upgrading’ by hydrogenation

* reduction of O-content
* shorter chain-lengths
* viscosity lowered
* stability increased

Lower O-content, better miscibility but, requires more hydrogen (costs!)

EXAMPLE

77 g H₂/kg oil
1.5 mol H₂/mol O removed

(pine wood basis)

Upgrading of pyrolysis oil

M.v.Schagen (UT., 2012)

U. Twente (2012)

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Trends:

* Fractionation by stepwise condensation
* Minerals removal to increase yield of sugars

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Biorefineries are emerging…
Pyrolysis in Practice

Empty fruit bunches (oil palm)

Dynamotive (Canada), 200 t/day

BTG (NL), 2 ton/hr

Fluid bed – 1 kg/hr
(UT. -TCCB / SPT)

Agri-Therm (2-5 t/day)
BTG Empyro facility, Hengelo (NL) 5 t/h