Microalgal-based biorefineries: towards a potential solution for sustainable bioenergy production.

Anne-Lise Hantson
UMONS – Chemical and Biochemical Process Engineering
anne-lise.hantson@umons.ac.be
Plan

✓ Introduction
✓ Microalgae as raw materials for biorefinery & circular economy
✓ 3G biorefinery
✓ Examples of microalgae integration in 3G and environmental biorefineries
✓ LCA
✓ Improvements
✓ Conclusions
Introduction

Limitation of the fossil resources


Projection of energy-related CO₂ emission

**CO₂ Production and Biomitigation**

![Diagram of CO₂ cycle for fossil fuel and biofuels]

**Fig. 2.** CO₂ cycle for fossil fuel and biofuels.
Microalgae as raw materials in biorefinery concept and circular economy
Circular economy concept
Circular economy

7 Key Principles:

- Ecoconception
- Industrial Ecology
- The functional Economy
- Re-employment
- Repairs
- Ruse
- Recycling

Attempt to reconcile: growth (economic, demographic), resources and environment
Algae: Polyphyletic group of organisms

Biochemical composition

**High plasticity to direct bioproduction to specific fatty acids or other metabolites of interest**

**Triacylglycerides**
(triacylglycerides with mainly $C_{16}$ to $C_{18}$ fatty acids, unsaturated)
Up to 70% of dry weight

**Storage lipids**

**Glyco- et phospholipids**
(up to 40% of fatty acids are polyunsaturated, i.e. eicosapentaaenoic acid (EPA))
Up to 7% EPA of dry weight

**Carbohydrates**
$\alpha$-(1-4)-glucose, $\beta$-(1-3)-glucose, fructane, glycerol
Up to 50% of dry weight

**Proteins**
Proteins with all amino acids
Partly soluble and partly bounded as particulate
Up to 50% of dry weight

**Valuable compounds**
Carotenoids (astaxanthin, fucoxanthin, lutein)
Phytosterols, all vitamins et antioxidants
Antifungal, -viral ou -microbial
From 1 – 5% each of dry weight
Factors Affecting Biochemical Profiles

Factors

- Light (photo-period and intensity)
- Temperature
- Nutrient-status (nitrogen availability)
- Nutrition (media)
- Salinity
- Carbon availability (CO$_2$ or organic carbon)
- Growth phase

Affect the biochemical composition and therefore bioproduct potential of microalgae

A.C. Wilkie et al. 2011
Traditional biorefinery concept

- Biomass
  - Hydrolysis
  - Fractionation
- Biorefinery
  - Separation
  - Gasification
  - Combustion
  - Pyrolysis
  - Fermentation
- Products
  - Bioenergy
  - Chemicals and materials
    - Feed
    - Food

Life Cycle Analysis
Environmental damage and investment cost
Social impacts
SUSTAINABILITY
Value pyramid of biomass in a biorefinery concept

- Health & Lifestyle (farma, chemicals, cosmetics, nutraceuticals...)
- Alimentation (food, feed)
- Chemistry and Materials (Commodity and building chemicals, fertilizers, ...)
- Energy (Heat, Power, Fuels, ..)

Added Value

Yield Volume
Value pyramid of biomass in a microalgal biorefinery concept

- **Phycobiliproteins**: 0.13 – 15 US$/mg
- **Chlorophyll**: $1 \times 10^{-5} - 1 \times 10^{-4}$ US$/mg
- **High Value Proteins**: $6.6 \times 10^{-6}$ US$/mg DW
- **Polyunsaturated Fatty Acids (PUFA’s)**: $2.64 \times 10^{-6}$ US$/mg
- **Carbohydrates for energy**: $1.32 \times 10^{-6}$ US$/mg DW
- **Bulk proteins**: $9.9 \times 10^{-7}$ US$/mg DW
- **Lipids for energy**: $6.6 \times 10^{-7}$ US$/mg DW

Ramirez & Olvera, 2006
Wijfels, Barbosa & Eppink, 2010
Microalgae: 3G biorefinery

First Generation: edible crop
Sugarcane, rice, wheat, patato, sugar beet, etc

Second generation: wastes, lignocellulosic biomass
Sugarcane bagasse, forest residues, grass, cell biomass from fermentation, etc

Third generation: Algae
Botryococcus braunii, Cryptothecodinium, Nitzschi sp., etc

Forth generation: non-edible
CO₂, Jatropha, Castor, Karanja

Low scale
Antioxidants, medicines, dietary

Large scale
Biopolymer, biofuels, chemicals, food, biofertilizers

Adapted from Romeo-Garcia et al. 2017
Comparaison between the 3 generations of biofuels based on their feedstock: 1G to 3G

<table>
<thead>
<tr>
<th>Generations of Biomass Feedstock</th>
<th>Prosperities</th>
</tr>
</thead>
</table>
| **1st Generation (food crops)**  | 1. Produced mainly from agricultural crops traditionally grown for food and animal purposes  
| Starchy Materials                | 2. Causes food crisis and contributes to higher food prices, carbon stores, and land use |
| Corn                             | Sugar Beet                                                                  |
| Sucrose-Containing Feedstocks    | Sugar Cane                                                                  |

| **2nd Generation (waste and energy crops)** | 1. Produced from non-edible crops grown on non-arable land  
| Lignocellulosic biomass            | 2. Produced from wood waste, agricultural waste, energy crops, organic waste, waste water, and landfill wastes  
| Wood residues                      | 3. Harder to extract the required fuel                                          |
| Straw                             | Energy Crops                                                                |

| **3rd Generation**                | 1. Most microalgae grow through photosynthesis by converting sunlight, CO2, and a few nutrients, including nitrogen and phosphorous, into biomass  
| Algae                             | 2. Algae can be grown using non-arable land and water unsuitable for food production (brackish, sea and wastewater), therefore reducing the strain on already depleted water sources  
|                                  | 3. High yield per acre                                                       |
|                                  | 4. Minimal impact on fresh water resources                                    |
|                                  | 5. Using CO₂ emissions from power plants                                     |
|                                  | 6. The oil productivity of microalgae is greater than that of other energy crops |

Microalgae : 3G biorefinery

Aquatic biomass cultivation, i.e. microalgae

- Sunlight, CO₂, nutrients
- Fertiliser/nutrients

Oil fraction
- Extraction fatty acids & purification
- Transesterification

Cell disruption, product extraction and separation

Protein fraction
- Fermentation

Minerals

Carbohydrate fraction

Oleochemistry

- Chemicals
- Value-added products (e.g. omega fatty acid)
- Biodiesel
- Value-added products & chemicals (e.g. amino-acids)
- Feed
- Biogas/CHP
- Fuels and chemicals (ethanol, butanol and etc.)
- Value-added products (e.g. iodine)

Cultivation options
And microalgae harvesting

Fig. 1. Applications in microalgae biorefinery.
Algal Cultivation Options

- Autotrophic
  - Open Pond
  - Photo Bioreactor
- Heterotrophic
  - Fermenter

Cultivation

Water
- Fresh Water
- Saline Water
- Waste Water

Nutrients
- Synthetic Fertilizer
- Recycled residual Biomass
- Waste Water

Light
- Solar Isolation
- Artificial PAR

CO₂
- Atmosphери CO₂
- Flue Gas
- Soluble Carbonates and Bicarbonates
Microalgae harvesting

**Screening**

**Thickening**:  
- Coagulation/  
- Floculation/  
- Biofloculation  
- Electrical methods

**Separation**:  
- Gravity separation  
- Dissolved air flottation (DAF)

**Dewatering**:  
- Filtration  
- Centrifugation

**Drying**
Comparison of algal harvesting methods (Udumann et al. 2010).

TSS = total suspended solids.

<table>
<thead>
<tr>
<th>Dewatering process</th>
<th>Highest possible yield</th>
<th>Energy usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centrifugation</td>
<td>&gt;22% TSS</td>
<td>Very high - 8 kWh/m$^3$</td>
</tr>
<tr>
<td>Flocculation</td>
<td>&gt;95% removal of algae</td>
<td>Low for slow mixing: varies largely</td>
</tr>
<tr>
<td>Natural filtration</td>
<td>1-6% TSS</td>
<td>Low (vibrating screen) - 0.4 kWh/m$^3$</td>
</tr>
<tr>
<td>Pressure filtration</td>
<td>5-27% TSS</td>
<td>Moderate (chamber filter press) - 0.88 kWh/m$^3$</td>
</tr>
<tr>
<td>Tangential flow filtration</td>
<td>70-89% removal of algae</td>
<td>High - 2.06 kWh/m$^3$</td>
</tr>
<tr>
<td>Gravity sedimentation</td>
<td>0.5-1.5% TSS</td>
<td>Low (lamella separator) - 0.1 kWh/m$^3$</td>
</tr>
<tr>
<td>Dissolved air flotation</td>
<td>1-6% TSS</td>
<td>High - 10-20 kWh/m$^3$</td>
</tr>
<tr>
<td>Dispersed air flotation</td>
<td>90% removal of algae</td>
<td>High</td>
</tr>
<tr>
<td>Electrocoagulation</td>
<td>99.5% TSS</td>
<td>Medium to high - 0.8-1.5 kWh/m$^3$</td>
</tr>
<tr>
<td>Electroflotation</td>
<td>3-5% TSS</td>
<td>Very high</td>
</tr>
<tr>
<td>Electrolytic flocculation</td>
<td>&gt;90% removal of algae</td>
<td>Low to medium - 0.33 kWh/m$^3$</td>
</tr>
</tbody>
</table>

High energy consumption
Same technologies developed for the 1G and/or 2G biorefineries
Fig. 2. Algal biomass conversion processes for biofuels production.
Mainstream Biorefinery with Microalgal Biomass Cascad Principle

Sequential steps for optimal biomass use
→ Energy recovery stage at the end of the lifecycle

Production

Pre-treatment / Harvesting/Dewatering

Highvalue compounds

Carbohydrates/ lipides/ proteins

Crude extract/ fractions

Fermentations / Enzymatic reaction/ Chemical transformation

Energy

Coproducts valorization

Valuables compounds and molecules

Fractions of biomass and utilization cascades
Microalgae for waste treatment and valorization: Environmental Biorefineries

Problem ↔ Process ↔ Products

Benefitting Industries
- Animal feeds
- Algal biofuels
- Fertilizer/Biochar
- Biorefining
- Nutraceuticals
- Carotenoids

Algae Cultivation
- GHG emission abatement
- Water recycling
- Nutrient remediation
- Bioremediation (metals)

CO₂, NOₓ, Waste gases
N, P, Metals
Waste water

Outcomes

Waste gases

Coal-fired Power Stations
Underground coal mines
Metal refineries
Waste water remediation
CO$_2$ biomitigation in a power plant using chemical looping combustion and microalgae cultivation for biofuel production

Mungui-Lopez et al. 2018
Nutrient rich Wastewater as feedstock

Fig. 2. Possible use of microalgae at the Wastewater Treatment Plant – 1. Anaerobic digestion, 2. Biorefinery.

Table 5
Biomass and lipid productivities and nutrient removal from wastewaters for different microalgae species.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Specie</th>
<th>N (mg/L)</th>
<th>P (mg/L)</th>
<th>Biomass (mg/L-d)</th>
<th>Lipid (mg/L-d)</th>
<th>Nutrient Removal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw wastewater</td>
<td><em>Desmodesmus</em> sp. mixed with cyanobacteria</td>
<td>42.13</td>
<td>35.4</td>
<td>13</td>
<td>1.7</td>
<td>84% N 61% P removal</td>
<td>[89]</td>
</tr>
<tr>
<td>Treated wastewater</td>
<td><em>Scenedesmus</em> sp.</td>
<td>28.85</td>
<td>3.51</td>
<td>267</td>
<td>15.19</td>
<td>90% N &amp; P removal</td>
<td>[90]</td>
</tr>
<tr>
<td>Municipal centrate</td>
<td><em>Hindakia</em> sp.</td>
<td>134</td>
<td>212</td>
<td>275</td>
<td>77.8</td>
<td>–</td>
<td>[91]</td>
</tr>
<tr>
<td>Municipal centrate (50%)</td>
<td><em>Muriellopsis</em> sp.</td>
<td>150</td>
<td>18</td>
<td>113</td>
<td>–</td>
<td>90% N &amp; P removal</td>
<td>[92]</td>
</tr>
<tr>
<td>Municipal centrate (50%)</td>
<td><em>Navicula</em> sp.</td>
<td>338</td>
<td>25</td>
<td>400</td>
<td>–</td>
<td>90% P removal</td>
<td>[93]</td>
</tr>
<tr>
<td>Landfill leachate (10%) and municipal wastewater</td>
<td><em>Microalgae-bacteria</em> consortium</td>
<td>221.6</td>
<td>3.19</td>
<td>131.7</td>
<td>24.1</td>
<td>95% ammonia-N removal</td>
<td>[94]</td>
</tr>
</tbody>
</table>
Fig. 3. Microalgae biorefinery concepts: A - two-step biorefinery for biodiesel, bioethanol and biogas production, B - two-step biorefinery with recirculation for enhanced process stability, C - three-step biorefinery with acidogenic fermentation for enhanced microalgae production.
Microalgal biorefinery integrating recovery and recycling of gaseous and liquid industrial effluents + by-products

Integrated environmental biorefinery

Circular economy concept

Facility design; Species selection; Energy (heat or cooling); Light; Nutrients (wastewater); CO₂ (flue gas)

Microalgal growth

Nutrient recycling

Water recycling

CO₂ recycling

Chemicals; Energy

Harvest and drying

Extraction

High-value products

Post-extracts

Solvents; Energy

Extraction and Esterification

Residues

Anaerobic digestion

Biodiesel

Leftover

Fertilizer

Biogas

Post-extracts

Biostimulants, Biofertilisants, Biopesticides, Mat. premières pour autres productions

Adapted from Zhu 2015
Life cycle assessment

Different LCA approaches for algal biofuels

Exemple of biofuel production pathway and residual processing options for LCA
NER and EROI of microalgal biodiesel

NER = \( \frac{\text{Total energy output}}{\text{Total energy input}} \)

EROI = \( \frac{\text{Total energy output}}{\text{Total fossil energy input}} \)

With « total energy output » = biofuel only or (biofuel + co-products)

LCA for microalgal biodiesel production for different scenarios

LCA comparison for the 3 biofuel generations in terms of CO₂ emissions
LCA comparison for the 3 biofuels generation in terms of NER and ERIO

**a) Well to Gate (WtG) perimeter**

- Biomass, Microalgae, 3rd generation (3) - NER - Algae biomass
- Oil, Microalgae, 3rd generation (5) - NER - Oil
- Biodiesel, Terrestrial crops, 1st generation (5) - NER - Biodiesel
- Biodiesel, Microalgae, 3rd generation (7) - EROI - Biodiesel
- Ethanol, Terrestrial crops, 1st generation (6) - NER - Ethanol
- Ethanol, Terrestrial crops, 2nd generation (1) - EROI - Ethanol
- Biomass, Microalgae, 3rd generation (1) - EROI - Algae biomass
- Oil, Terrestrial crops, 1st generation (2) - EROI - Oil
- Oil, Microalgae, 3rd generation (1) - EROI - Oil
- Biodiesel, Terrestrial crops, 1st generation (1) - EROI - Biodiesel
- Biodiesel, Microalgae, 3rd generation (4) - EROI - Biodiesel
- Fossil Diesel (1) - NER - Fossil Diesel
- Ethanol, Macroalgae, 3rd generation (1) - EROI - Ethanol

**b) Well to Tank (WtT) perimeter**

- Biodiesel, Terrestrial crops, 1st generation (3) - NER - Biodiesel
- Biodiesel, Microalgae, 3rd generation (5) - NER - Biodiesel
- Fossil Diesel (2) - NER - Fossil Diesel
- Ethanol, Terrestrial crops, 1st generation (8) - NER - Ethanol
- Ethanol, Terrestrial crops, 2nd generation (5) - NER - Ethanol
- Biodiesel, Terrestrial crops, 1st generation (2) - EROI - Biodiesel
- Fossil Diesel (1) - ERIO - Biodiesel
- Ethanol, Terrestrial crops, 1st generation (1) - ERIO - Ethanol
- Fossil Gasoline (1) - ERIO - Ethanol

**c) Well to Wheel (WtW) perimeter**

- Biodiesel, Microalgae, 3rd generation (5) - NER - Biodiesel
- Fossil Diesel (2) - NER - Fossil Diesel
- Ethanol, Macroalgae, 3rd generation (1) - NER - Ethanol
- Fossil Gasoline (1) - NER - Ethanol
- Biodiesel, Terrestrial crops, 1st generation (1) - NER - Biodiesel
- Biodiesel, Microalgae, 3rd generation (10) - NER - Biodiesel
- Fossil Diesel (4) - EROI - Biodiesel
- Ethanol, Terrestrial crops, 1st generation (4) - EROI - Ethanol
- Ethanol, Terrestrial crops, 2nd generation (3) - EROI - Ethanol
- Ethanol, Terrestrial crops, 2nd generation (3) - EROI - Ethanol
Efforts required for economic viability and sustainability of 3G biorefinery and biofuel production
Exemples of inducers to increase the content of interesting biochemical compounds

Fig. 4. Simplified illustration of microalgal species with their relative content of TAGs, LC-PUFAs and carotenoids upon exposure to different inducers applied alone or in combination. In the upper panel TAG-inducing stressor such as nutrient depletion, high temperature, high light and high salinity are shown, whereas stressors such as low temperature, low light and nutrient replete conditions usually lead to elevated LC-PUFA contents as represented in the lower panel.
## Conclusions

<table>
<thead>
<tr>
<th>Plus</th>
<th>Minus</th>
</tr>
</thead>
<tbody>
<tr>
<td>• High surface productivity</td>
<td>• Use of stress conditions to induce the storage of energy-rich compounds</td>
</tr>
<tr>
<td>• Flexible Composition of biomass</td>
<td>• Expensive harvesting and drying processes</td>
</tr>
<tr>
<td>• Limited competition on food production</td>
<td>• Little genetic improvement</td>
</tr>
<tr>
<td>• Urban and industrial effluents and waste recycling (N, P, ... wastewater) or cement plant/power station (CO$_2$))</td>
<td></td>
</tr>
</tbody>
</table>

### Microalgae

| Maximum productivity (T.ha$^{-1}$.year$^{-1}$) | 150-180 | 30 | 60 |
| Observed productivity (T.ha$^{-1}$.year$^{-1}$ (PBR/Field)) | 50-70 | 10-15 | 10-30 |
## Strengths and difficulties of the microalgal sector in large scale production

<table>
<thead>
<tr>
<th>Sectors</th>
<th>Applications, potential</th>
<th>Strengths</th>
<th>Difficulties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environment</td>
<td>• CO₂ remediation • Effluent treatment (ponds/raceway)</td>
<td>• N, P, CO₂ consumption • Existing pond/raceway</td>
<td>• Effluents polluted with toxic compounds</td>
</tr>
<tr>
<td>Energy</td>
<td>• Biodiesel • Bio-crude oil • Biogas</td>
<td>• High lipids contents (7 to 30 higher than rapeseed) • No competition with food • Co-products valorisation</td>
<td>• Large scale production • Industrial technology • Large area needed</td>
</tr>
<tr>
<td>Fish Farming</td>
<td>• Quality food (proteins, omega 3)</td>
<td>• First level of the aquatic food chain • Nutritional quality</td>
<td>• Need of « non polluted » substrates for the culture • Single species culture required</td>
</tr>
<tr>
<td>Feed</td>
<td>• Livestock • Pet</td>
<td>• Co-products valorisation • Protein intake • Reduced dependence on soy</td>
<td>• Large scale production • Industrial technology</td>
</tr>
<tr>
<td>Green chemistry Bio-material</td>
<td>• Bio-polymers • Lipo-chemistry</td>
<td>• New raw materials for bioplastics and agrosurfactants</td>
<td>• Large scale production • Industrial technology</td>
</tr>
</tbody>
</table>
## Strengths and difficulties of the microalgal sector in high value added markets

<table>
<thead>
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<th>Strengths</th>
<th>Difficulties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cosmetics</td>
<td>• Active compounds, dyes/colorants, antioxidants</td>
<td>• Innovative natural compounds, high diversity of species and molecules, rich in antioxidants, good marketing image</td>
<td>• Few cultivated species at large scale, low dry matter content in the culture medium, evolution of the regulations</td>
</tr>
<tr>
<td>Food supplements</td>
<td>• Omega 3</td>
<td>• Important nutritional quality (omega 3, vitamins, proteins), existing markets</td>
<td>• Long and complex regulations, high production costs, almost incompatible CO$_2$ remediation, Market control</td>
</tr>
<tr>
<td>Nutraceutical</td>
<td>• Carotenoids</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Proteins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Human health</td>
<td>• Control Diagnosis</td>
<td>• Very high added value, replaces the use of radioactive products</td>
<td>• Niche market, impossible CO$_2$ remediation, Long regulations</td>
</tr>
<tr>
<td>Human Food</td>
<td>• Food, Colorants, Ingredients</td>
<td>• Nutritional qualities, Natural colorants, Fight undernitrition</td>
<td>• Long and complex regulations, Consumer acceptability</td>
</tr>
</tbody>
</table>
Conclusions

Environmental Microalgal Biorefinery

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Real Opportunity for integrated biosourced products and biofuels developments
Thank for your attention