Hydrothermal conversion of micro-algae as new biomaterials for pavement

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HYDROTHERMAL CONVERSION OF MICRO-ALGAE AS NEW BIOMATERIALS FOR PAVEMENT

Clémence Queffélec, Emmanuel Chailleux

Ilef Borghol, Bruno Bujoli, Dorothée Laurenti, Nolven Guilhaume, Christophe Geantet and Christophe Lombard
Problematic : how to find substitutes to petroleum-based products?

- Bitumen : heavy fraction from petroleum refinery
- World bitumen annual production estimated : 122,5 MT / year in 2019
  - Pavement construction (90%)
  - Roofing
- Production depends on oil companies economical strategies (cracking of heavy fraction) and regulation (reduction of sulfur content in marine fuel ....)

→ Necessity to anticipate alternatives to petroleum bitumen
Alternatives: why not microalgae (Biomass of the future?)

- Rapid growth
- Biodiversity >200000
- Lipid rich: up to 50%
- High photosynthetic yield
- No competition with other crops

Use of microalgae residues after a first high value valorisation

Microalgae residues are provided by Algosource Technologies

- growing in open raceway
- water soluble molecules were extracted for another valorization
Objectives
Scientific challenges

How to get a material with the following properties?

- Hot melt
- Sticky
- Viscoelastic
- Hydrophobic
Hydrothermal liquefaction (HTL)

- Wet biomass
- Water in subcritical state: $T < 374 \, ^\circ C$
- Under pressure $\rightarrow$ liquid water
- Ion product of water increase
  $\rightarrow$ Chemical reactions are facilitated
- Dielectric constant of water decrease
  $\rightarrow$ Water becomes a solvent for organic compounds

Chem. Eng. J. 2011, 172, 1
Characterization of the initial biomass

Two residues studied: Scenedesmus and Spirulina sp.

Scenedesmus sp. residues

<table>
<thead>
<tr>
<th>Component</th>
<th>Scenedesmus sp.</th>
<th>Spirulina sp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lipids</td>
<td>28%</td>
<td>35%</td>
</tr>
<tr>
<td>Proteins</td>
<td>22%</td>
<td></td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>30%</td>
<td>17%</td>
</tr>
<tr>
<td>Others</td>
<td>20%</td>
<td>21%</td>
</tr>
</tbody>
</table>

Lipids: only free fatty acids according to $^1$H NMR
Hydrophobic fraction from HTL

Batch reactor

Aqueous fraction

Gaz (CO₂)

Hydrophobic fraction = biobinder

HTL parameters:
Temperature: 260 °C, 280 °C and 300 °C
Reaction time: 1 H

Solid

Oil
### Microalgae residues

<table>
<thead>
<tr>
<th>Microalgae residues</th>
<th>Hydrophobic fraction (%)</th>
<th>Aqueous fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Scenedesmus sp.</em></td>
<td>50 ±0,5</td>
<td>21 ±1,5</td>
</tr>
<tr>
<td><em>Spirulina sp.</em></td>
<td>48 ±1</td>
<td>32 ±0</td>
</tr>
</tbody>
</table>

**260°C optimal condition for rheology**

- **oil**: GCxGC MS, $^1$H NMR, FTIR, EA etc
- **solid**: GCxGC MS, $^1$H NMR, FTIR, EA etc
Chemical characterization of the oil

GPC Chromatogram of oily phases
from *Spirulina*
from *Scenedesmus* sp.

- *ACS Sust. Chem. Eng.* 2015, 3, 583-590
Chemical characterization of the solid

From Scenedesmus sp.

FT-IR

\[13\text{C CP-MAS NMR}\]
Chemical characterization of the solid

FT-IR and $^{13}$C MAS NMR: high molecular weight aliphatic polymer « Algaenans »


ACS Sust. Chem. Eng. 2015, 3, 583-590

Chemical characterization of the solid

- Oxidative cleavage by RuO$_4$
- Analysis of the oxidized products by GC-MS after esterification

Esters of fatty acids
Diesters of fatty acids
Structure of the biobinder

Colloidal model of petroleum bitumen proposed by Nellensteyn

Asphaltenes = solid particles

Maltenes = liquid matrix

Rheologically Structured oil

= Oily matrix
+ Solid residue
Rheological characterization

Dynamic shear rheometer

$|G^*|$: ratio between sinusoid amplitudes $\rightarrow$ stiffness of the material

$\phi$: phase lag between sinusoids $\rightarrow$ ability of the material to relax stress
From microalgae residues to bio-binder: characterization (rheology)

**Standard bitumen (35/50):** A viscoelastic behavior: elastic solid at low temperatures and a viscous Newtonian liquid at high temperatures.

- **High temperatures, low frequency domain:**
- **Low temperatures, high frequency domain:**
From microalgae residues to bio-binder: characterization (rheology)

**Standard bitumen (35/50):** A viscoelastic behavior: elastic solid at low temperatures and a viscous Newtonian liquid at high temperatures

**Scenedesmus sp. bio-binder:** A viscoelastic behavior similar to a standard petroleum bitumen (35/50)
From microalgae residues to bio-binder: characterization (rheology)

**Standard bitumen (35/50)**: A viscoelastic behavior: elastic solid at low temperatures and a viscous Newtonian liquid at high temperatures

**Scenedesmus sp. bio-binder**: A viscoelastic behavior similar to a standard petroleum bitumen (35/50)

**Spirulina sp. bio-binder**: Rheological behavior similar to elastomer used as additives in petroleum bitumen
Conclusions and outlooks

- The rheology behavior of the water insoluble fractions from both micro-algae is compatible with pavement application: low viscosity at high temperature to coat aggregates, high stiffness at room temperature to ensure aggregate cohesion.
- Consistency of biomaterials can be optimized by adjusting HTL processing parameter.
- Difficulty to identify high mass molecules or molecular structures \( \rightarrow \) analysis by FTICR.

- Need to understand more deeply reactions during HTL.
- Morphology of the solid residues?
- Use of catalysts to tune the physical properties of the biobinder.
- Industrial potential evaluation \( \rightarrow \) production using a continuous process pilot.
Towards continuous hydrothermal liquefaction (HTL)

- 1 to 2 L/h maximum
- Up to 350 °C
Acknowledgments

Fundings
Thank you for your attention