Hydrothermal liquefaction of microalgae to produce a bio-binder: feedstock type influence

Ilef BORGHOL
Clémence QUEFFELEC, Emmanuel CHAILLEUX, Bruno BUJOLI, Jack LEGRAND, Delphine DROUIN, Christophe LOMBARD

Paper N°: 95
Searching for petroleum-based bitumen alternatives, why?

- Bitumen: comes from petroleum refinery
- Petroleum: fossil fuel, nonrenewable, influenced by geopolitical and socio-economic concerns
- World bitumen annual production estimated: 122.5 MT/year in 2019
  - Pavement construction (90%)
  - Roofing membrane manufacture

Anticipate new alternatives to petroleum bitumen
Search for efficient routes to produce bitumen substitutes from renewable biomass sources
Micralgae residues are provided by Algosource Technologies (Assérac, Loire-Atlantique, France)

- growing in open raceway
- water soluble proteins were extracted for another valorization

**Feedstock supply**

- Rapid growth
- Biodiversity > 200000
- High photosynthetic yield
- No competition with more noble uses

**Alternatives Why not microalgae?**

*Phytochem. 1976, 18, 51*

*Ultrason. Sonochem. 2013, 20, 95*

*J. Soc. Bio. 2008, 202, 201*
Two residues studied: initial composition

- Scenedesmus sp. residues
- Spirulina sp. residues

<table>
<thead>
<tr>
<th></th>
<th>Scenedesmus sp</th>
<th>Spirulina sp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lipids</td>
<td>28%</td>
<td>27%</td>
</tr>
<tr>
<td>Proteins</td>
<td>22%</td>
<td>35%</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>

Microalgae residues studied
Hydrothermal liquefaction (HTL): Green transformation process

- Mimic the conditions under which petroleum naturally occurred (high pressure and temperature)
- Clean process: no organic solvent
- Wet biomass: no drying step

How to get a material similar to petroleum bitumen?

Binder:
- Hot melt
- Viscoelastic
- Sticky
- Hydrophobic
Two microalgae residues types tested: *Scenedesmus* sp. and *Spirulina* sp.

Aqueous fraction $\rightarrow$ Gaz (CO$_2$) $\rightarrow$ Hydrophobic fraction = Green binder

HTL parameters:
- Temperature: 260 °C
- Load factor: 0.6

ACS Sustain. Chem. Eng. 2015, 583-590
Green Chem, 2018, 2337-2344
### 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 ±0,5</td>
</tr>
</tbody>
</table>

- Aromatic compounds, mainly based on phenol and indole derivatives
- Highly aliphatic compounds, including (a) long chain alkenes likely resulting from the decarboxylation of fatty acids (b) free fatty acids and their amide derivatives

*ACS Sustain. Chem. Eng. 2015, 583-590*  
*Green Chem, 2018, 2337-2344*
What influence have the feedstock type on bio-binders rheological properties

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

*ACS Sustain. Chem. Eng. 2015, 583-590*
*Green Chem, 2018, 2337-2344*
What influence have the feedstock type on bio-binders rheological properties

**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 as a standard petroleum bitumen (35/50)

ACS Sustain. Chem. Eng. 2015, 583-590
Green Chem, 2018, 2337-2344
What influence have the feedstock type on bio-binders rheological properties

**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 as a standard petroleum bitumen (35/50)

---

*ACS Sustain. Chem. Eng. 2015, 583-590*
*Green Chem, 2018, 2337-2344*
What influence have the feedstock type on bio-binders rheological properties

**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 as a standard petroleum bitumen (35/50)

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

---

ACS Sustain. Chem. Eng. 2015, 583-590
Green Chem, 2018, 2337-2344
What influence have the feedstock type on bio-binders rheological properties

**Scenedesmus sp. bio-binder:** the most rigid of all binders

**Spirulina sp. bio-binder:** less sensitive to temperature than Scenedesmus sp. and standard bitumen especially in the high temperature domain

**Isochronous curves at 1 Hz**

- **Scenedesmus sp. bio-binder**
- **Standard bitumen**
- **Spirulina sp. bio-binder**
- **Elastomer rich binder**


Green Chem, *2018*, 2337-2344
From microalgae residues to bio-binder: A challenge

- HTL temperature influence on Spirulina sp. bio-binder stiffness

**Isochronous curves at 1 Hz**

- **HTL temperature increase** → **bio-binder stiffness decrease**

**Possibility of change the bio-binder stiffness by adjusting the HTL temperature**

→ Using bio-binders in substitution of different conventional bitumen grades

Green Chem, 2018, 2337-2344
Conclusions and outlooks: A promising bio-binder production process

- **Results**
  - Chemical characterization: hydrophobic fraction which consisted of an oily fatty acid-based fraction mixed with organic and inorganic solid residues.
  - Rheological behavior is influenced by the feedstock type:
    - *Scenedesmus* sp. bio-binder ≈ petroleum-based bitumen
      → Might be used as a direct alternative
    - *Spirulina* sp. bio-binder ≈ Binder loaded with a high percentage of elastomers
      → Might be used as a bitumen modifier
  - Possibility of change the bio-binder stiffness by adjusting the HTL temperature

- **Outlooks**
  - Understand more deeply HTL (especially reactions mechanism)
  - Determine the influence of catalyst on the bio-binder rheological properties
  - Study on scaling influence: from laboratory batch to continuous HTL pilot
Acknowledgments

Christophe LOMBARD
Pr Jack LEGRAND
Delphine DROUIN

Bruno Bujoli
Clémence QUEFFELEC

Emmanuel CHAILLEUX
Thank you for your attention