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Hydrothermal conversion of micro-algae as new biomaterials for pavement

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Algoroute

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 ....)

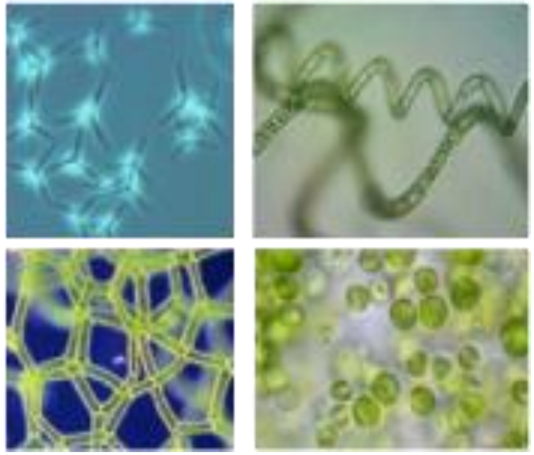
→ Necessity to anticipate alternatives to petroleum bitumen

Petroleum worldwide production, BP Statistical Review, ***2013***
(Website: http://www.manicore.com)

Alternatives : why not microalgae
(Biomass of the future ?)

Phaeodactylum tricornutum

Spirulina platensis



Hydrodictyon sp.

Chlorella vulgaris

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

J. Soc. Bio. **2008**, *202*, 201

Use of microalgae <u>residues</u> after a first high value valorisation

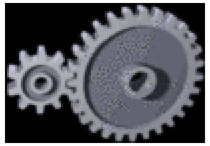
Microalgae residues are provided by Algosource Technologies

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



Objectives
Scientific challenges

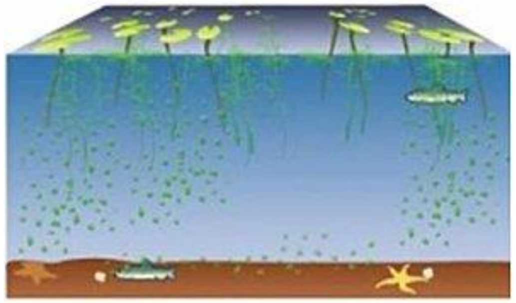
?

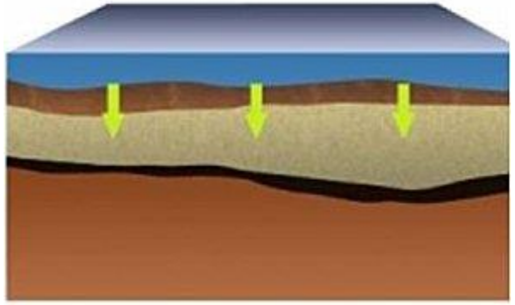


How to get a material with the following properties ?

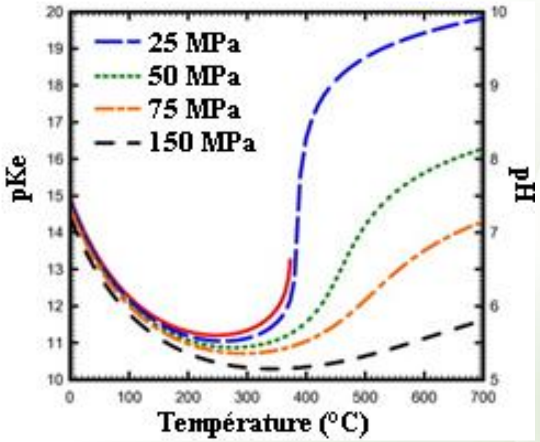
– Hot melt
– Viscoelastic
- Sticky
- Hydrophobic

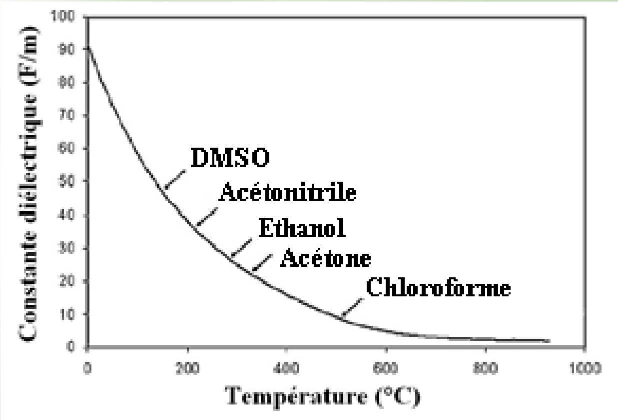
Hydrothermal liquefaction (HTL)





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



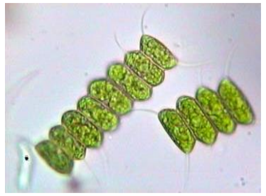


J. Supercrit. Fluids. **2008**, *43*, 490 ; *Corrosion Science* **2012**, *65*, 48
Chem. Eng. J. **2011**, *172*, 1

Characterization of the initial biomass

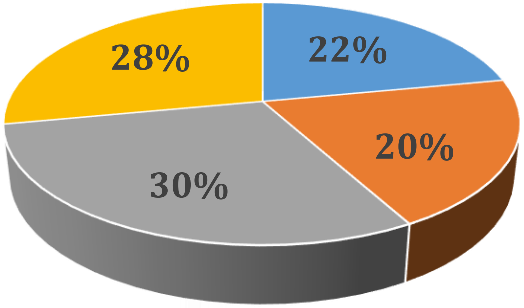
Two residues studied : Scenedesmus and Spirulina sp.

Scenedesmus sp. residues

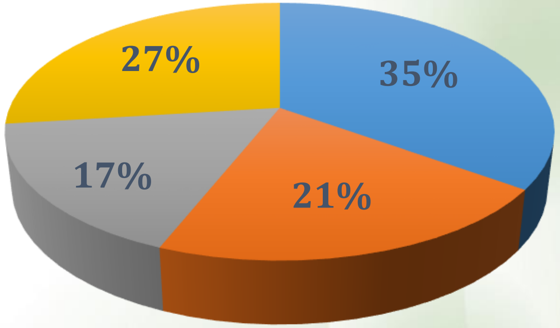


Spiruline sp. residues

Scenedesmsus sp



Spirulina sp.



Lipids Proteins Carbohydrates Others

Lipids : only free fatty acids according to ^{1}H NMR

Hydrophobic fraction from HTL

Batch reactor

HTL parameters:

Temperature : 260 °C, 280 °C and 300 °C

Reaction time : 1 H

Aqueous fraction

Gaz (CO_2)

Hydrophobic fraction

= biobinder

Solid

Oil

260°C optimal condition for rheology

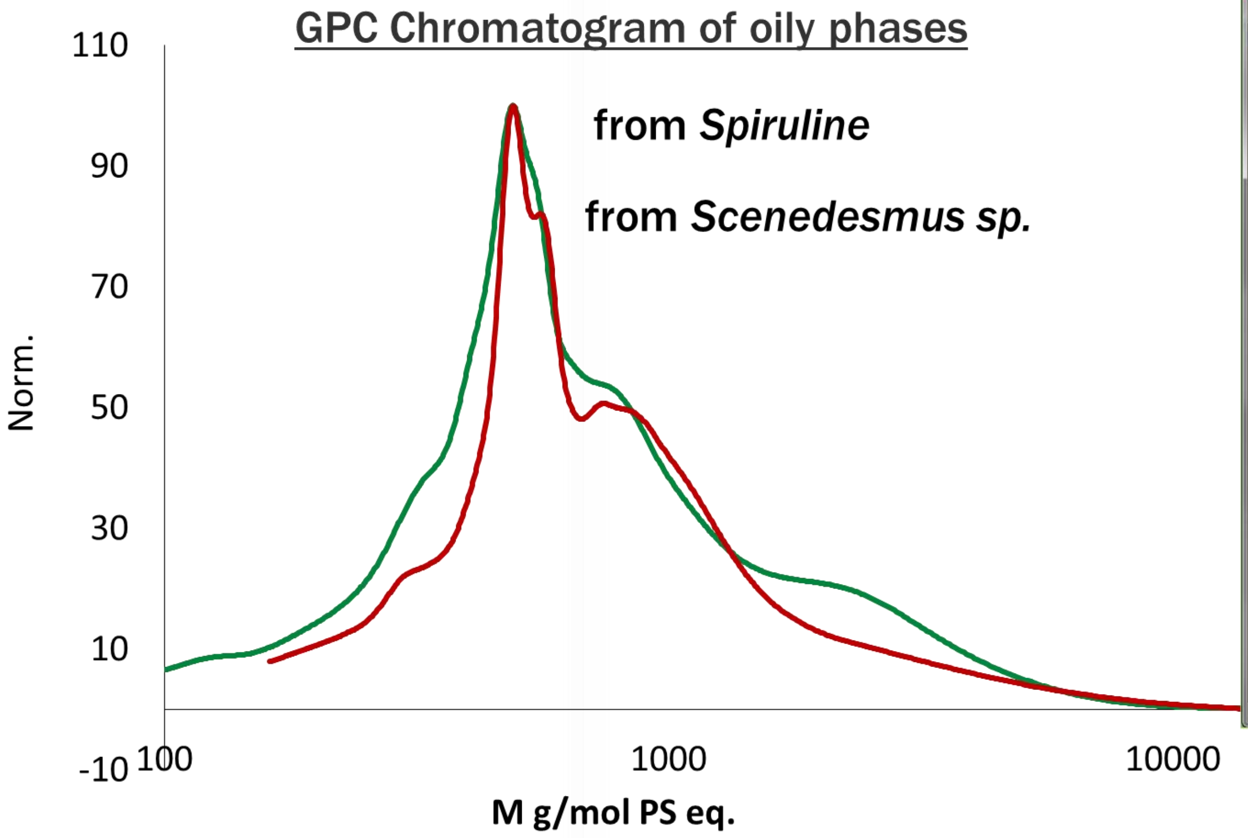
260 °C

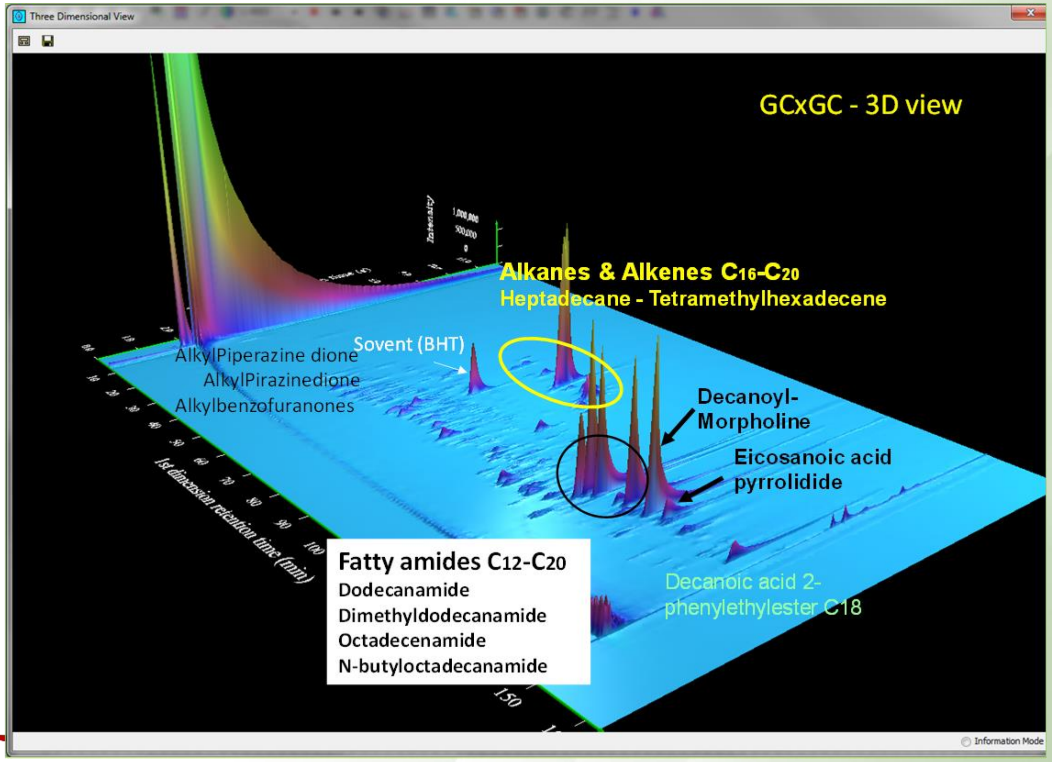
Microalgae residues	Hydrophobic fraction (%)	Aqueous fraction (%)
Scenedesmus sp.	**50 ±0,5**	**21 ±1,5**
Spirulina sp.	**48 ±1**	**32 ±0**

oil **solid**

GCxGC MS, ^{1}H NMR, FTIR, EA etc

Chemical characterization of the oil



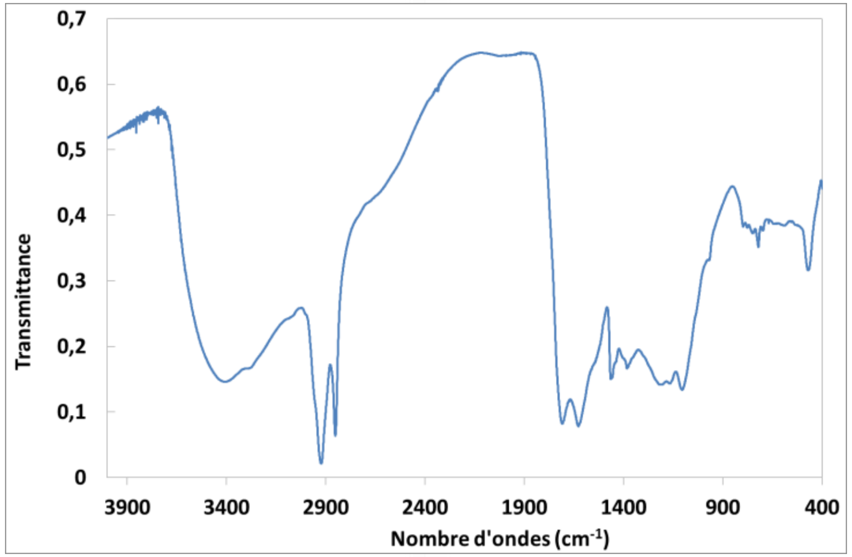


Patent FR 13 59293, **2013**; PCT Int. Appl. **2015**, WO 2015044891 (A1)
ACS Sust. Chem. Eng. **2015**, *3*, 583-590
Green Chem. **2018**, *16*, 1036-1042.

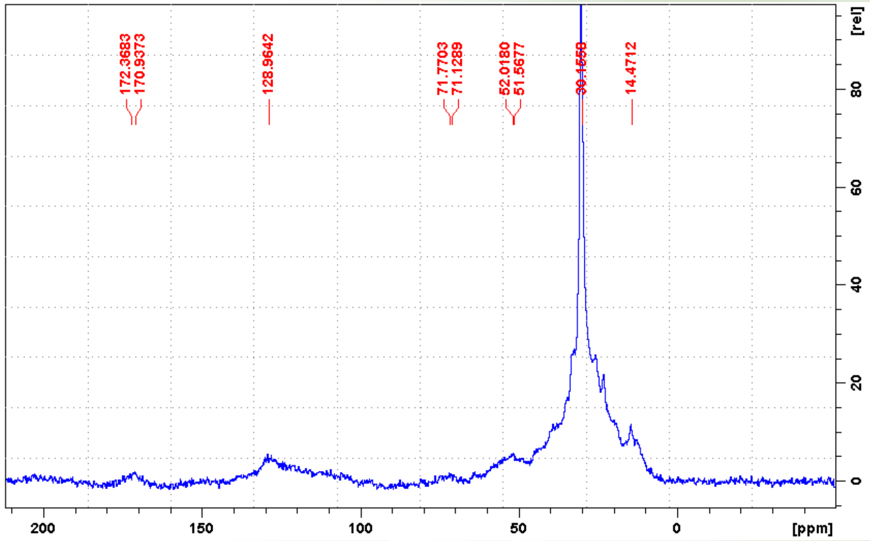
Chemical characterization of the solid

From Scenedesmus sp.

FT-IR



^{13}C CP-MAS NMR



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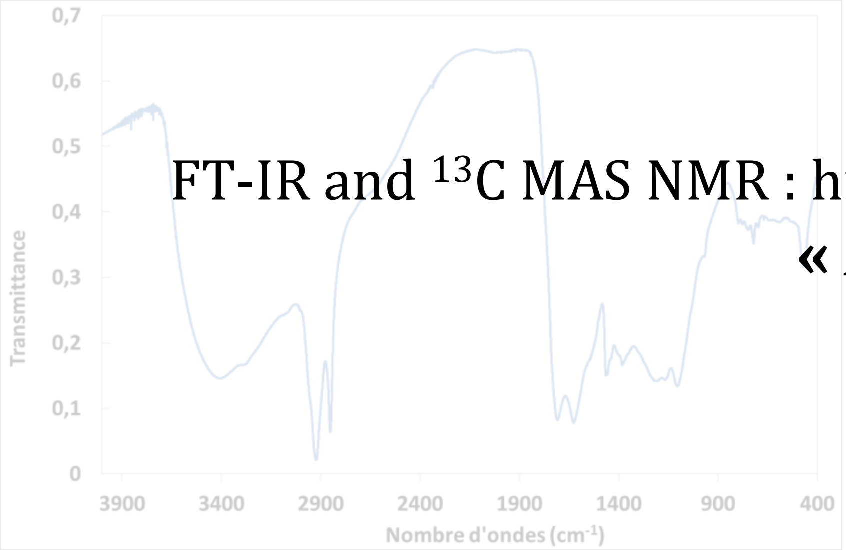
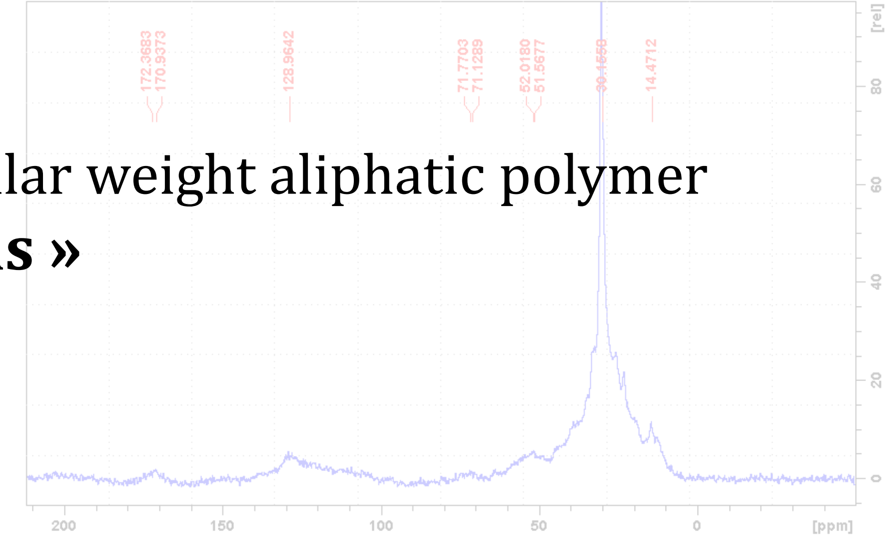
Chemical characterization of the solid

FT-IR



^{13}C CP-MAS NMR



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

« Algaenans »

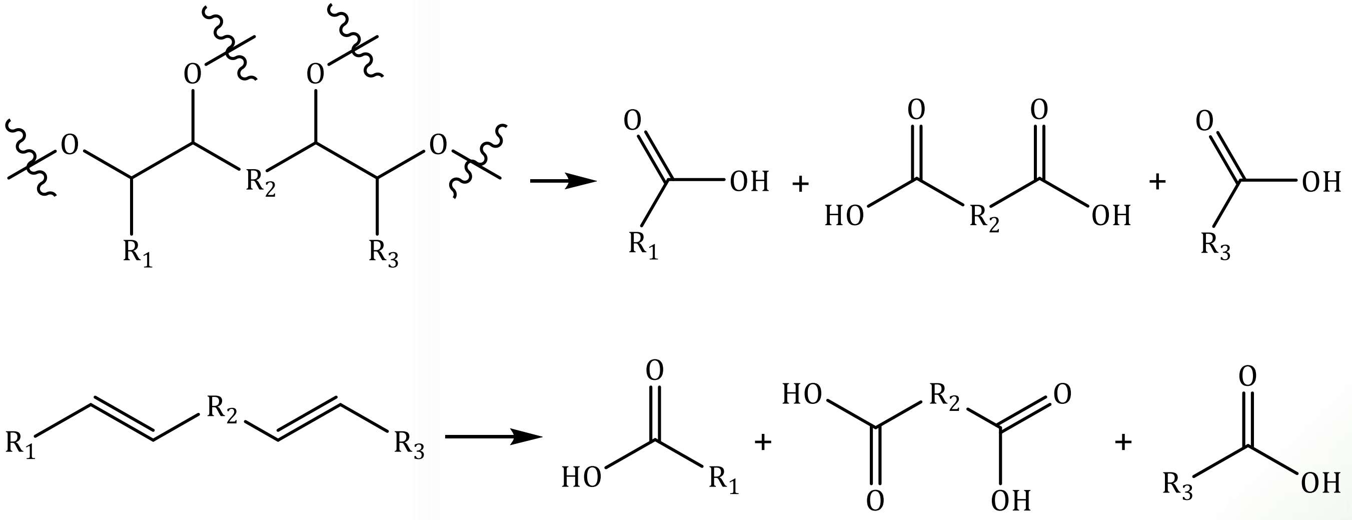
Patent FR 13 59293, **2013**; PCT Int. Appl. **2015**, WO 2015044891 (A1)
ACS Sust. Chem. Eng. **2015**, *3*, 583-590
Green Chem. **2018**, *16*, 1036-1042.

Chemical characterization of the solid

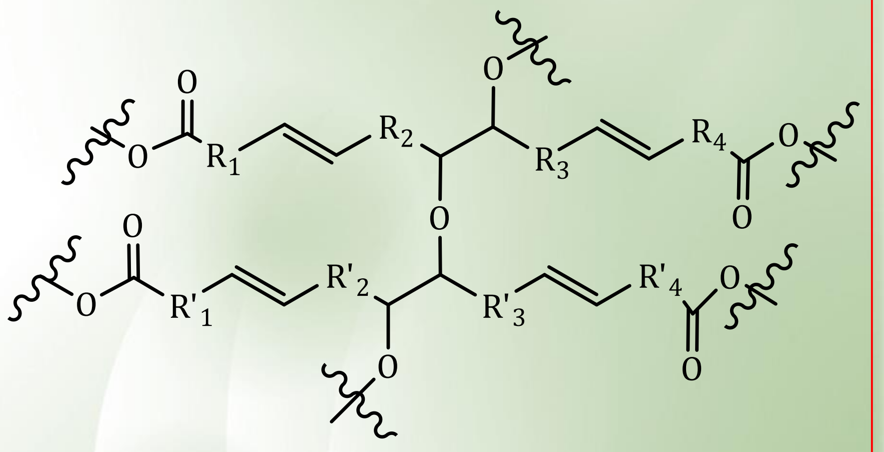
- Oxidative cleavage by RuO_4
- Analysis of the oxidized products by GC-MS after esterification

Esters of fatty acids

Diesters of fatty acids



Possible structure of algaenans



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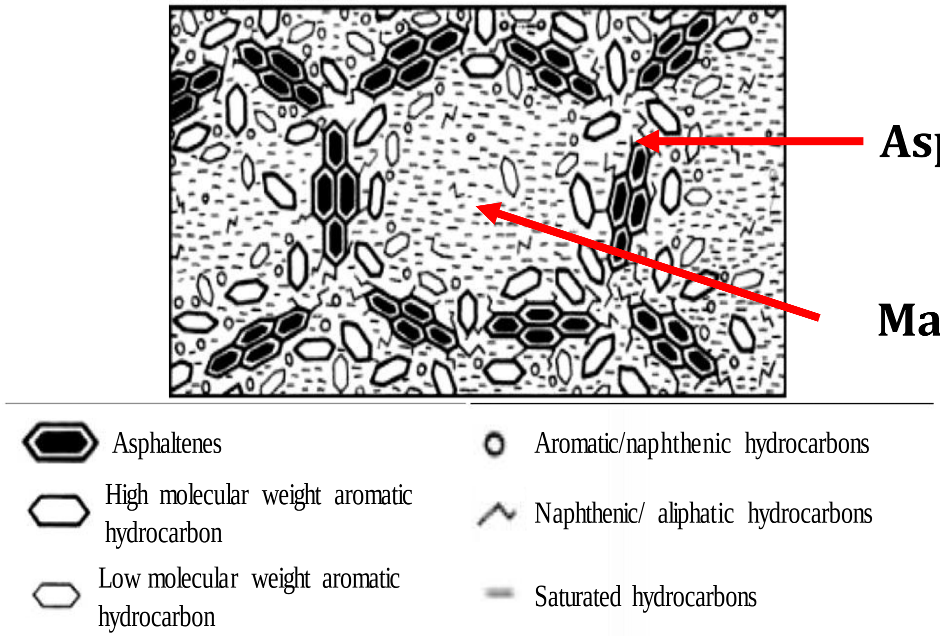
Green Chem. **2018**, *16*, 1036-1042.

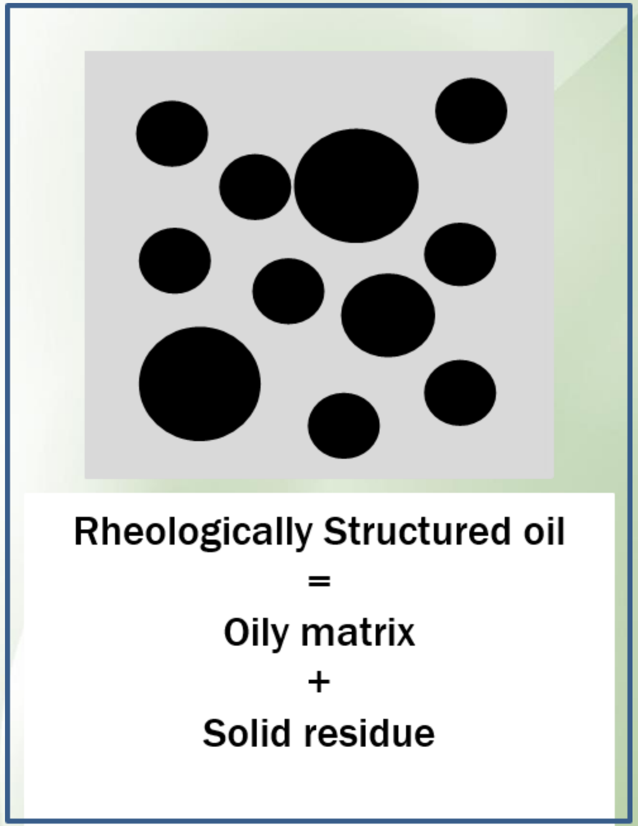
Structure of the biobinder

Colloidal model of <u>petroleum bitumen</u> proposed by Nellensteyn → Colloidal system in biobinder????



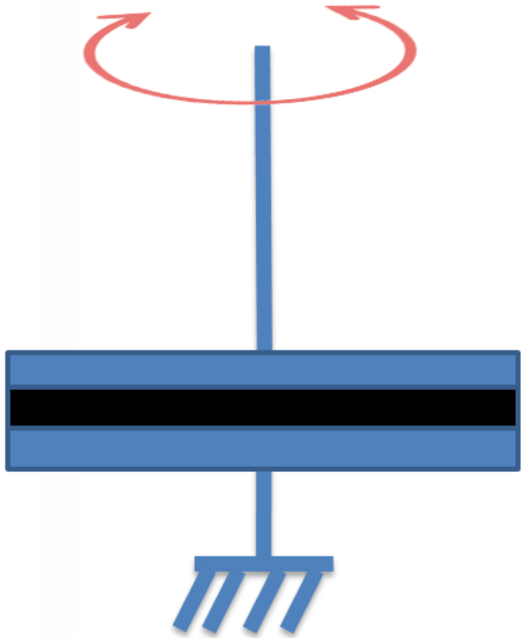
Asphaltenes = solid particles

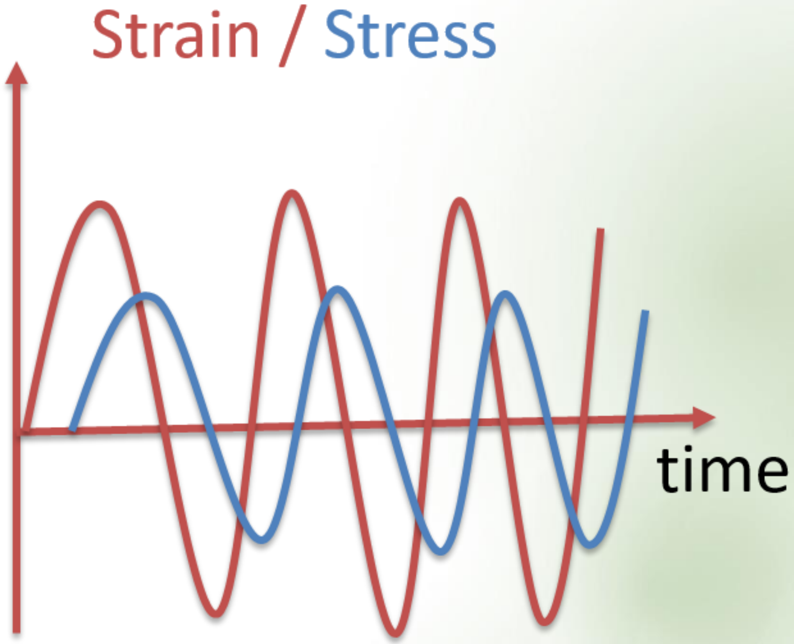
Maltenes = liquid matrix



Rheological characterization

Dynamic shear rheometer

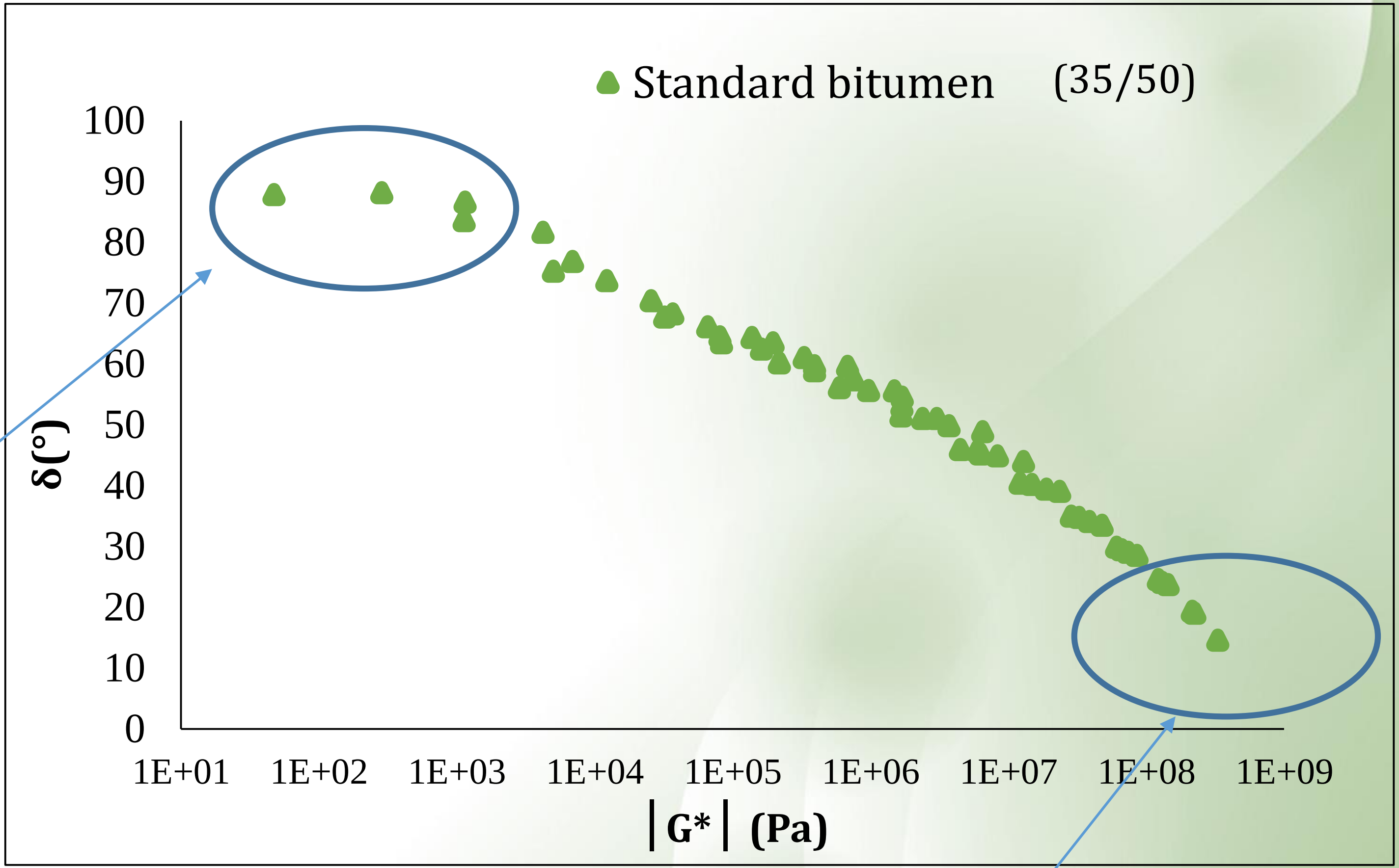




$|G^*|$: ratio between sinusoid amplitudes → stiffness of the material
φ : phase lag between sinusoids → ability of the material to relax stress

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*



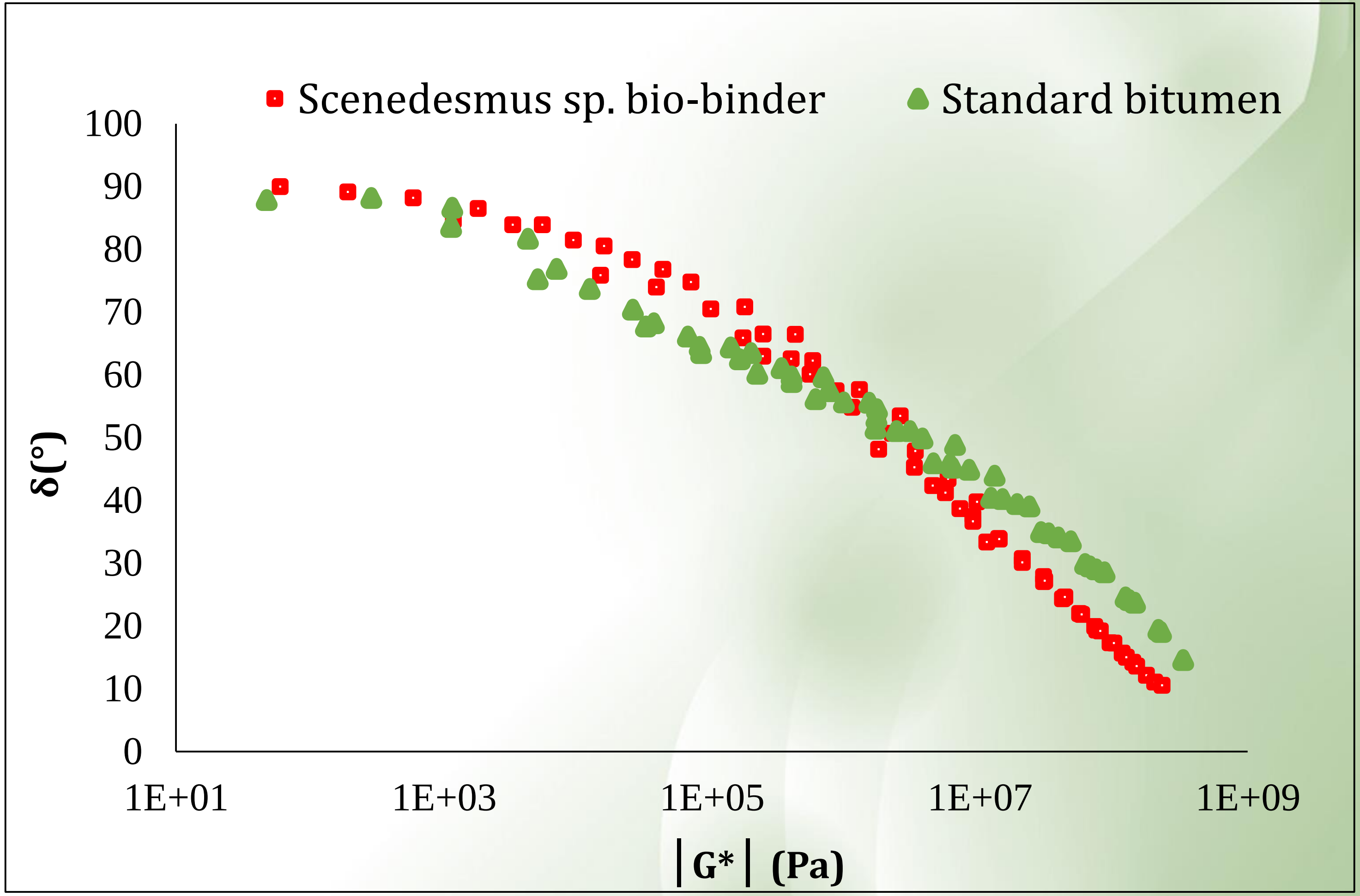
high temperatures, low frequency domain

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)*



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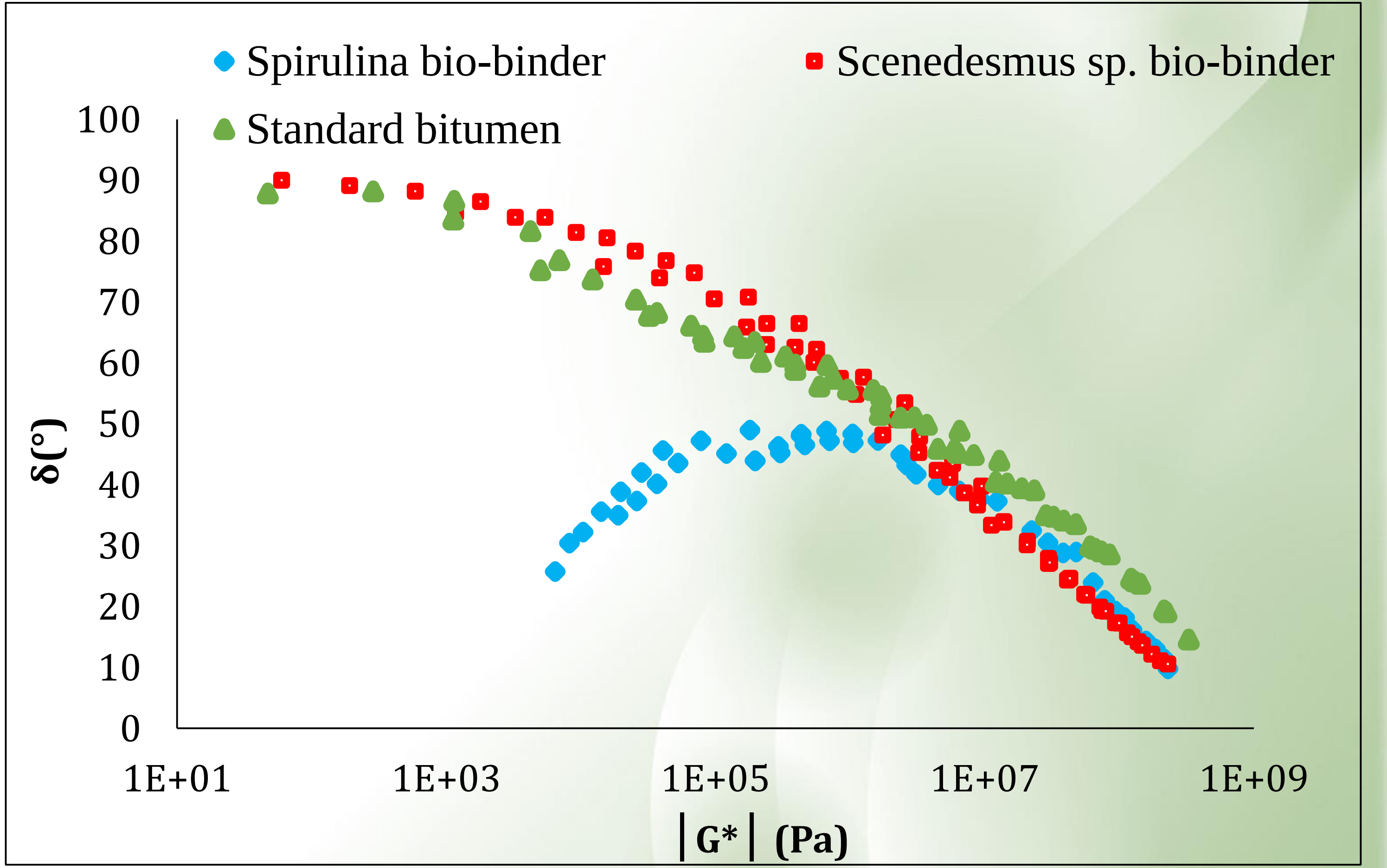
Scenedesmus sp. bio-binder*: A viscoelastic behavior similar to a standard petroleum bitumen (35/50)*

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 → 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 → production using a continuous process pilot

Towards continuous hydrothermal liquefaction (HTL)

- 1 to 2 L/h maximum
- Up to 350 °C

Acknowledgments

algosource technologies

GEPEA

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IRCELYON

Fundings

Région PAYS DE LA LOIRE

ANR AGENCE NATIONALE DE LA RECHERCHE

Thank you for your attention