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

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ABSTRACT

This study takes part of a larger program where the hydrothermal liquefaction (HTL) thermochemical process is used to produce an alternative bitumen from microalgal biomass. The objective is to compare the properties of non-water soluble fractions of two microalgae residues (*Scenedesmus sp*. and *Spirulina*) obtained after HTL. The process has been carried out in a batch reactor at 260 °C for 60 min with a biomass/ water ratio of 1:4 and maximum yields of 50% for *Scenedesmus sp*. and 48% for *Spirulina* were obtained for the non-water soluble fraction.

Characterization by nuclear magnetic resonance (NMR) has been performed on the non-water soluble fraction. More importantly, rheological properties have been investigated using a dynamic shear rheometer (DSR). The non-water soluble fraction obtained from *Scenedesmus sp*. showed rheological properties similar to a petroleum-based bitumen while non-water soluble fraction from *Spirulina* presented a viscoelastic behavior similar to bio-sourced binder loaded with a high percentage of elastomers.

Keywords: *Scenedesmus sp*., *Spirulina*, hydrothermal liquefaction, green-binder, rheological properties.

1. INTRODUCTION

Sustainability is an important topic since the past few decades. Resources management has to be found in order to satisfy the demand of the current generation without hindering the needs of future generations. Therefore, searching for alternative sources has become a priority at the world level and in all domains, so that, "sustainability" can be guarantee.

Petroleum crude oil is one of several natural non-renewable resources. Products derived from the distillation of petroleum are used in various fields (such as fuels, plastics products, solvents, roads…). Bitumen is a by-product resulting from the vacuum distillation of crude oil. It is a viscoelastic material mostly used in the fields of pavement construction and roofing membrane manufacture.

In a sustainable approach, different biomass have been used in an attempt to produce an alternative renewable binder. Fini [1] used swine manure to produce a bio-oil and used it as a partial replacement of bitumen. Raouf and Williams [2] produced bio-bitumen by pyrolysis of oakwood, switch grass and corn stover. Waste cooking oil was used by Sushanta and al., [3] to produce a bio-binder that can be used as a rejuvenating agent for aged bitumen.

Furthermore, micro-algae residues have been used to produce a road bio-binder with viscoelastic properties similar to that of a petroleum-based bitumen [4]. Microalgae are one of the most promising alternatives in the renewable energies field. In addition to its high photosynthetic yield and its high lipid content, micro-algal biomass is not in competition with human feeding.

The process used to transform *Scenedesmus sp*. residues (microalgae type) into a non-petroleum binder is the hydrothermal liquefaction (HTL). HTL produces a water-insoluble material composed of a mixture of an oil component and solid residues. This promising technology is able to mimic microalgae conversion conditions taken place naturally in an aqueous medium. Moreover, it can convert wet biomass avoiding thereby high-energy consumption [5].

To understand the influence of feedstock type on the bio-binder properties, the valorization of two microalgae biomass residues (*Scenedesmus sp*. and *Spirulina*) has been investigated in the present study.

Alternative binders obtained from HTL have been characterized with nuclear magnetic resonance (NMR). Dynamic shear rheometer (DSR) was used to investigate the rheological properties of bio-binders.

2. MATERIALS AND METHODS

2.1. Materials

A standard bitumen (35/50) and a binder enriched with 8 % in elastomer (Styrene Butadiene Styrene polymer) have been used as references.

Scenedesmus sp. and *Spirulina* residues are provided by AlgoSource (Alpha Biotech, Asserac, France). A major part of the water-soluble proteins was removed by centrifugation for other valorization. Both biomass, which contain about 80 wt % of water, were stored at -15 °C then freeze-dried for 1 week at -90 °C before use. The moisture content and ash content were analyzed as described in [6]. Table 1 gives an overview on the general composition both residues.

TABLE 1 General composition of *Scenedesmus sp*. and *Spirulina* residues (% of dry matter)

Species	Lipids content*	Protein content [7]	Polysaccharides content [8]	Moisture content	Ash content
Scenedesmus sp. residues	-	20	30	7.8	6,1
Spirulina residues	-	20.48±0.37	16.30±5.26	7,7	7.3

* To be determined

2.2. Experimental procedure

2.2.1. Hydrothermal liquefaction (HTL)

The experiments were carried out in a 300 mL non-stirred batch stainless steel reactor (model 4760, Parr Instrument Company, Moline, Il, USA). The reactor was loaded with 39 g of freeze-dried microalgae residues and 156 mL of distilled water. The reactor was closed and purged three times with nitrogen in order to remove air. The temperature was increased to 260 °C, and then kept constant during 60 min based on previous study [4].

After cooling down the reactor to room temperature, the gas was released. The water-soluble fraction was poured out from the reactor, the water insoluble fraction was removed using a spatula, and then the reactor was washed with CH_2Cl_2. The solvent was then evaporated under vacuum and the viscoelastic fraction was finally obtained.

Aqueous fraction and non-water soluble fraction yields are determined according to Eqs. (1, 2) and expressed in % w/w on the basis of the dry biomass:

$$Aqueous\ fraction\ (\%) = \frac{Mass\ of\ aqueous\ fraction}{Initial\ mass\ of\ microalgae} \times 100 \quad (1)$$

$$Water\ insoluble\ fraction\ (\%) = \frac{Mass\ of\ water\ insoluble\ fraction}{Initial\ mass\ of\ microalgae} \times 100 \quad (2)$$

2.2.2. Analytical methods

- **NMR** (nuclear magnetic resonance): The ^1H NMR of bio-binder sampleshave been collected on a Brucker Avance operating at 300 or 400 MHz. Samples are prepared by dissolving about 10 mg of HTL fraction in deuterated chloroform ($CDCl_3$).

- **DSR** (Dynamic shear rheometer): Rheological properties of bio-binders are measured with a Kinexus pro+ rheometer in the shear mode and according to the European Standard EN 14770. Non-water soluble fraction is loaded on a plate-plate geometry (with a diameter of 8 mm and/or 25 mm) with 1 mm gap. DSR takes measures of phase angles δ (°) and of norm of complex modulus (│G*│) at different temperature values: at high temperatures (from 20 °C to 80 °C) and low temperatures (from 20 °C down to -20 °C), in various frequencies (from 0,01 Hz to 10 Hz). Black diagram (phase angle (δ) against the norm of complex modulus (|G *|) reflects the viscoelastic behaviour of bitumen.

3. RESULTS AND DISCUSSIONS

Scenedesmus sp. and *Spirulina* HTL water insoluble fraction yields and its chemical and rheological characterization are provided in this section.

3.1. Yields of HTL different fractions

Table 2 shows *Scenedesmus sp*. and *Spirulina* HTL fractions yields. The water insoluble fraction yields represent the average of at least, three HTL experiments for each microalgae. Yields are calculated according to equations presented in *2.2.1*. The water insoluble fractions yields seem to be unaffected by the microalgae feedstock type. The *Spirulina* aqueous fraction yield is higher than that of *Scenedesmus sp*.

Gas fractions represent the rest of the total fractions. It was characterized for the *Scenedesmus sp.* HTL by gas chromatography with thermal conductivity detection (GC-TCD) in a previous work [4]. Its main gas components are CO_2 (90,3%) and CO (1,5%).

TABLE 2 Yields of HTL product fractions of *Scenedesmus sp*. and *Spirulina*

	Spirulina	*Scenedesmus sp.*
Aqueous fraction (%)	32	21
Water insoluble fraction (%)	48±1	50±0.5

3.2. Physicochemical characterization

- **NMR**: ^{1}H NMR spectrum of *Scenedesmus sp*. and *Spirulina* water insoluble fractions are presented in figure 1. ^{1}H NMR spectra shows a high contribution of aliphatic functional groups (around 0,5- 1.5 ppm) for the two bio-binders. Unsaturated functions (around 4.5- 6.0 ppm) may be due (i) to the large number of nitrogenous and oxygenated molecules resulting from the degradation of proteins present in the feedstock or (ii) to unsaturated free fatty acids or alkenes obtained after decarbonylation. Aromatic protons are as well observed in the two samples (6.0- 8.0 ppm) [9] by contrast with a standard bitumen spectrum.

a.

b.

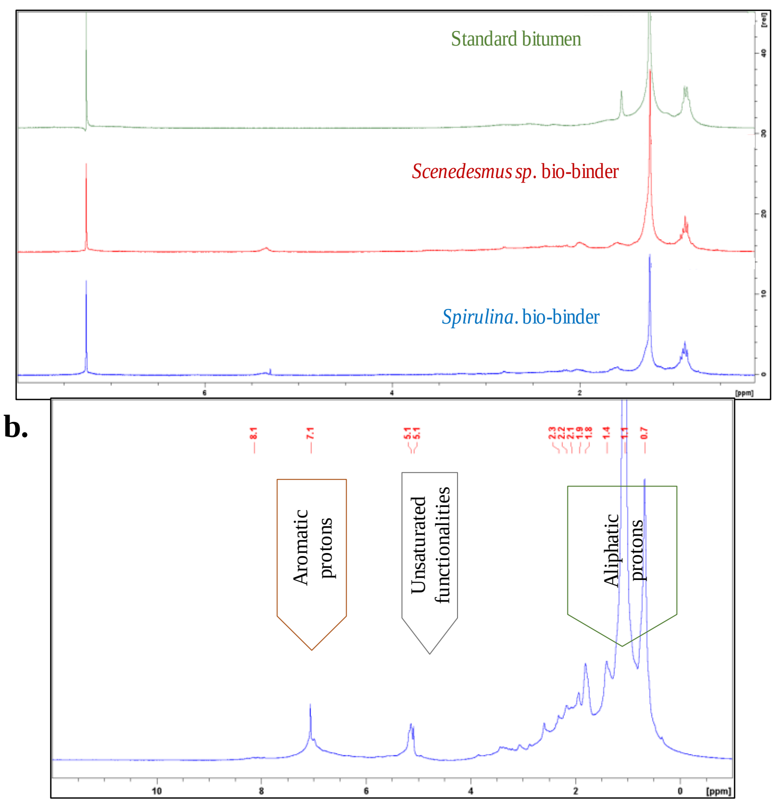

FIGURE 1 a.^{1}H NMR (300 MHz) spectra of *Scenedesmus sp*. and *Spirulina* bio-binders b. Detailed ^{1}H NMR spectrum of the water insoluble fraction for *Scenedesmus sp*.

3.3. Rheological properties

The rheological behaviour of both bio-binders compared to those of a standard bitumen and an elastomer-rich binder are illustrated[2] in figure 2 through the Black diagrams.

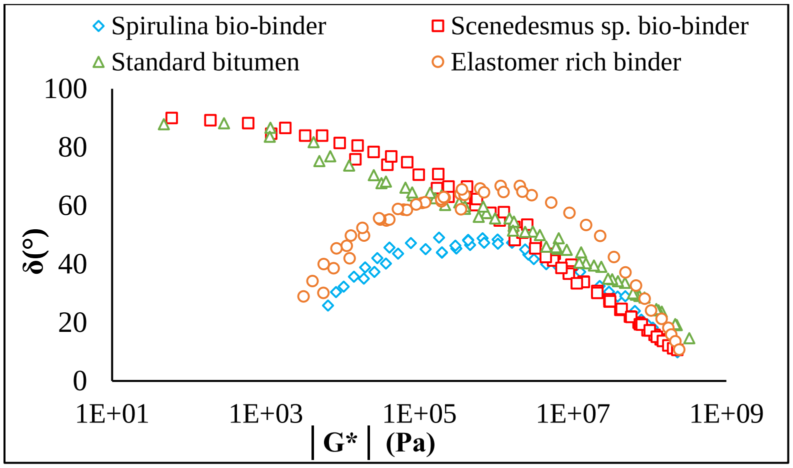

FIGURE 2 Complex modulus of the water-insoluble fractions obtained from HTL of *Scenedesmus sp.* and *Spirulina* compared to a standard bitumen and an elastomer rich binder plotted in the Black space

As seen in figure 2, the *Scenedesmus Sp*. bio-binder presents a similar behaviour as a standard bitumen. At low temperatures (below -20°C), petroleum bitumen is an elastic solid characterized by a constant value of complex modulus (1 GPa) and a low phase angle (nearly 0 °) whereas at high temperatures, bio-binder is a viscous Newtonian liquid with low complex modulus values and high phase angles (nearly 90 °). Between these two behaviours, the bitumen presents an intermediate response between a viscous liquid and an elastic solid which is called the viscoelastic behaviour.

Spirulina bio-binder presents different rheological propeties and reveals an elastomeric non fusible behaviour. While heating the sample, the phase angles increase up to almost 50 ° and decrease down to almost 20 °.

Isochronous curves can be used to compare samples rigidity. In fact, the most rigid samples have the higher complex modulus and the lowest phase angle. Isochronous curves of both bio-binders were compared to those of a standard bitumen and an elastomer-rich binder.

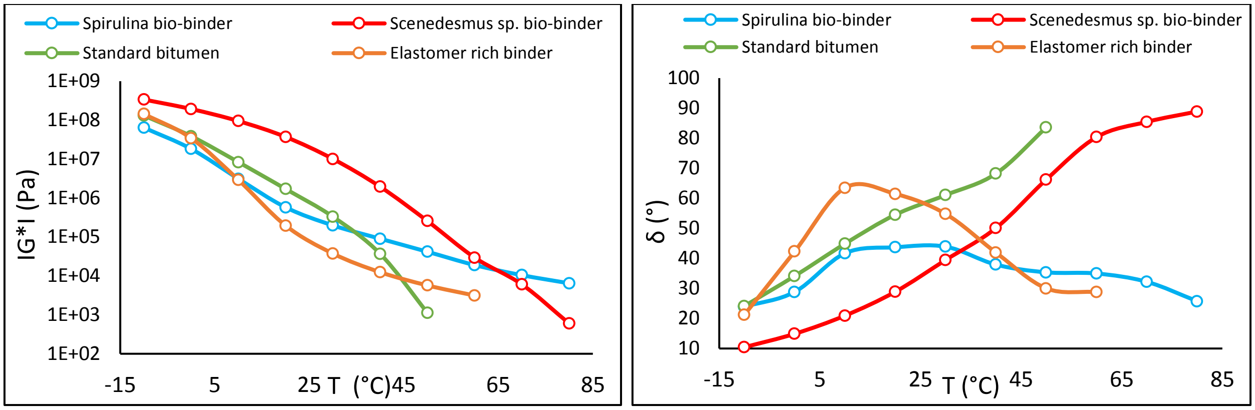

FIGURE 3 Isochronous curves, at 1 Hz, of the water-insoluble fractions obtained from HTL of *Scenedesmus sp.* and *Spirulina* compared to a standard bitumen and an elastomer rich binder

The *Scenedesmus sp*. bio-binder seems to be the most rigid of all binders (Figure 3). Furthermore, *Spirulina* bio-binder is more rigid than the standard bitumen and the elastomer rich binder. Its phase angle varies from 20 ° to 42 ° reflecting its elastomeric behaviour.

4. CONCLUSION: INFLUENCE OF FEEDSTOCK TYPE ON BIO-BINDER PROPERTIES

Two types of microalgae residues with different initial composition were converted into bio-binders by hydrothermal liquefaction at 260 °C. The different feedstock compositions slightly influenced HTL fractions (aqueous fraction, gas fraction and water insoluble fraction). The maximum bio-binder yield was observed for *Scenedesmus sp.*

NMR ^{1}H did not reveal a significant chemical difference between *Scenedesmus sp.* and *spirulina* binders. However, rheological results showed that *Scenedesmus sp*. presented rheological properties similar to a petroleum-based bitumen while *Spirulina* had a viscoelastic behavior similar to binder loaded with a high percentage of elastomers.

Scenedesmus sp. bio-binder may be used as a “direct alternative” to bitumen binder. Spirulina bio-binder may be used as an additive in the asphalt substituting SBS (Styrene Butadiene Styrene polymer) [10] in order to modify road binder rheological properties.

5. REFERENCES

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