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**Biobased bitumen analogue formation during hydrothermal treatment of microalgae residues, part 2: influence of residence time on reaction products.**

Antoine Rolland<sup>1</sup>. Alain Sarda<sup>1</sup>. Gaël Colomines<sup>1</sup>. Yannick Madec<sup>1</sup>. Clémence Queffelec<sup>2</sup>. Fabienne Farcas<sup>3</sup>. Emmanuel Chailleux.<sup>4</sup> and Eric Leroy<sup>5.\*</sup>

- 1) Université de Nantes. Oniris. CNRS. GEPEA. UMR 6144. F- 44470 Carquefou. France.
- 2) Université de Nantes. CNRS. CEISAM. UMR 6230. F-44000 Nantes. France
- 3) Université Gustave Eiffel / Ifsttar / Centre de Marne la Vallée. Département Matériaux. 14-20 Boulevard Newton. Champs sur Marne. F-77447 Marne la Vallée Cedex 2. France.
- 4) Université Gustave Eiffel / Ifsttar / Centre de Nantes. Département MAST/ Laboratoire Matériaux pour les Infrastructures de Transports. Route de Bouaye CS4. 44344 Bouguenais. France.
- 5) Université de Nantes. Oniris. CNRS. GEPEA. UMR 6144. F- 44600 Saint Nazaire. France.

\* corresponding author: [eric.leroy@univ-nantes.fr](mailto:eric.leroy@univ-nantes.fr)

**Abstract:** The hydrothermal conversion of industrial *Spirulina* sp. residues at 260 °C under autogenous pressure is investigated. This second part of the study, focuses on the influence of the residence time on the final reaction products. The hydrophobic phase obtained after 60 min. at 260 °C has a rheological behaviour similar to that of an elastomeric bio-binder. Removal of solid residues from the hydrophobic fraction by filtration leads to a pure conventional bitumen-like material pointing out their strong influence on rheology. The investigation of lower and larger residence times suggests that bio-bitumen formation first involves the formation of bio-char by hydrothermal carbonization during heating of the reactor to 260 °C followed by hydrothermal liquefaction during the isothermal plateau.

**Keywords:** hydrothermal conversion. microalgae. bitumen. residence time. rheology

**Highlights:**

- Bio-bitumen formation involves hydrothermal liquefaction of preformed biochar.
- Bio-bitumen rheology is strongly affected by the solid phase it contains.

## 1 Introduction

Hydrothermal carbonization (HTC) and Hydrothermal liquefaction (HTL) processes allow the conversion of wet biomass to fossil carbon feedstock analogues [1]. They mainly differ in terms of temperature (and resulting autogenous pressure) ranges and residence time (typically a few hours below 250°C (2-3 MPa) for HTC; and few minutes to an hour above 280°C (10-22MPa) for HTL). HTL was first applied to microalgae biomass in the 90's for the production of biocrude oil as a potential alternative to petroleum [2]. Concurrently, HTC was also investigated for microalgae biomass treatment [3], allowing the production of bituminous coal like products. More recently, the investigation of the 240 °C to 280°C temperature range (intermediate between typical HTC and HTL temperatures) with a fixed residence time of 60 min lead to the production of bitumen like products from two microalgae strain residues [4] [5]. For both microalgae biomasses, an optimal temperature close to 260 °C leading to autogenous pressures of 5 MPa, allowed obtaining a hydrophobic phase with rheological properties mimicking those of elastomeric bio-binders, with a yield of approximately 50% compared to initial biomass. The other reaction products were mostly CO<sub>2</sub> in the gas phase and water soluble organic compounds [4].

The first part of the present work was dedicated to the investigation of the thermic of this hydrothermal conversion process which takes place at the crossover region between HTC and HTL. In this second part, our objective is to study the influence of the residence time at 260 °C on the composition and rheological properties of the hydrophobic phase produced. Indeed, the process involves two main steps: First heating from room temperature (typically 25°C) to 260°C. During this step only HTC is likely to occur, while during the isotherm at 260°C, slow HTL can take place. The residence time at the isotherm is thus a key parameter, which happens not to have been investigated in previous studies [4] [5]. Moreover, for the fixed 60 min. residence time previously used, the bitumen like hydrophobic phase obtained typically

contained 80% of fatty acid based oil and 20% of solid particles (organic and inorganic) [5]. In the following, we will see that this composition depends on residence time, and significantly affects the rheology of the bio-bitumen.

## 2 Materials and methods

### 2.1 Materials

Petroleum bitumen samples used as references for rheological characterizations were provided by Ifsttar: one pure conventional bitumen (grade 50/70, this corresponds to a medium rigidity bitumen ) and one elastomeric bio-binder (Biophalt ®) [6]. The molecular mass distribution of the conventional petroleum bitumen is provided as supplementary data. (**supplementary Figure A**). It consists in two main populations: a maltene fraction with an average molecular mass of approximately  $1800 \text{ g}\cdot\text{mol}^{-1}$ , and an asphaltene fraction with a main peak around  $8700 \text{ g}\cdot\text{mol}^{-1}$  and a secondary peak at  $32000 \text{ g}\cdot\text{mol}^{-1}$  corresponding to aggregates.

Spirulina sp. biomass residues similar to those previously used to produce bio-bitumen [5] were supplied by AlgoSource (Alpha-Biotech. Asserac. France). It contains approximately 5% moisture, 39% of proteins, 9% of lipids and 8% of carbohydrates. For further details about production and these characterizations, please refer to the part 1 of the study.

The ash content (**Table 1**) was measured by thermo-gravimetric analysis: A TGA apparatus (STA 449. Netzsch) was used to heat a 25 mg sample from  $25 \text{ }^\circ\text{C}$  to  $600 \text{ }^\circ\text{C}$  at  $10 \text{ }^\circ\text{C}/\text{min}$ . under nitrogen atmosphere. The sample was then maintained at  $600 \text{ }^\circ\text{C}$  during 1 hour under oxygen atmosphere, leading to a stable final mass corresponding to ashes residues.

The carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) content were measured using a ThermoScientific FLASH 2000 Series CHNS Analyzer (samples were heated until  $980^\circ\text{C}$ ). The effective C. H. N and S contents in the organic phase were then calculated taking into account

the ash (inorganic) content. The oxygen (O) content was estimated as the remaining fraction to reach 100% ( $O = 100 - C - H - N - S$ ) (**Table 1**).

Dichloromethane (purity 99.9%) used for hydrophobic products recovery after hydrothermal conversion was purchased from Honeywell.

## 2.2 Hydrothermal conversion conditions

The HTL experiments were performed using a 300 mL stirred reactor with fixed head (4561 model from Parr Instrument Company, USA). For each hydrothermal conversion experiment, 45 g of Spirulina residues (dry mass 42.7 g) and 180 mL of osmosed water were introduced in the reactor at 25 °C. This corresponds to a biomass to water ratio of 0.25 (20 wt% of wet biomass). In order to remove the air still present in the reactor, nitrogen overpressure was applied 3 times and then flushed away. Then 1 bar nitrogen pressure was applied. A constant stirring rate of 100 rpm was applied during all experiments.

A vessel rigid mantle heater, fitting the reactor was used without additional thermal insulation. The advantage of this heating device is that it can be quickly withdrawn for the cooling of the reactor. Typically the reactor was heated from 25 °C to 260 °C at the highest heating rate possible, typically 5-6 °C/min. The thermally regulated temperature is actually that of the liquid phase inside the reactor (for more details, refer the part 1 of this work). Once the temperature of 260 °C was reached, the reactor was either cooled immediately, or maintained at 260 °C. Three residence times at 260 °C were used: 0 min (direct cooling to evaluate the influence of heating step on biomass), 60 min. (to reproduce the optimal conditions for bio-bitumen production described in literature, [5] and 400 min. (according to the results of the part 1 of this work, this long isothermal reaction time allows for a “complete reaction” in terms of heat released)

For the 0 min at 260 °C experiment, a high cooling rate was obtained by using both an internal and external cooling. The internal cooling is done by an internal cooling coil. In addition, a chamber was crafted, to fit dimensions of the reactor, fitted with two water/air sprays to quench the external surface of the reactor. For the two other reaction times (60 min and 400 min), the reactor was allowed to cool down slowly as described by Borghol et al. [5] in order to reproduce the conditions described for bio-bitumen production.

### 2.2.2 Recovery and analysis of the hydrothermal reaction products

After cooling at 25 °C, the residual pressure  $P_r$  was measured before opening the reactor. Assuming that the main gas product is CO<sub>2</sub>, as observed in previous works on bio-bitumen production by HTL of microalgae biomass [4], the mass of the gas phase product was estimated by applying the ideal gas law:

$$m_{CO_2} = M_{CO_2} \times \frac{P_r \times V}{R \times T_0} \quad \text{Eq. (1)}$$

Where:  $M_{CO_2}$  is the molecular mass of CO<sub>2</sub> equal to 44 g·mol<sup>-1</sup> ;  $T_0$  is the temperature equal to 298 K ;  $R$  is the constant of ideal gases equal to 8.314 J·K<sup>-1</sup>·mol<sup>-1</sup> ; and  $V$  is the initial gas volume (in m<sup>3</sup>) equal to 120 mL.

The gas phase yield  $Y_{gas}$  is then calculated as follows:

$$Y_{gas} = \frac{m_{CO_2}}{m_{biomass}} \quad \text{Eq. (2)}$$

Where:  $m_{biomass}$  is the initial dry biomass input equal to 42.7 g.

After opening the reactor, the aqueous phase (orange colored) was poured in a beaker. Assuming that the density of the aqueous phase density remains equal to 1 (density of the initial osmosed water), the aqueous phase yield  $Y_{aqueous}$  corresponding to water soluble products was estimated by:

$$Y_{aqueous} = \frac{m_{aqueous} - m_{water}}{m_{biomass}} \quad \text{Eq. (3)}$$

Where:  $m_{aqueous}$  is the mass of aqueous phase recovered, and  $m_{water}$  is the initial mass of water equal to 180 g.

The remaining hydrophobic phase was recovered by pouring dichloromethane into the reactor (approximately 100 mL of solvent) then closing the reactor and heating at 45-50 °C in order to ensure the complete dissolution of soluble products. After being cooled back at 25 °C, the reactor was again opened, and the dichloromethane phase containing soluble hydrophobic products and solid products in suspension was poured into a beaker. Residual hydrophobic products (mainly solid) present on the reactor's walls and inside steel parts (thermocouples, etc.) were recovered by washing with dichloromethane and pouring in the beaker. The dichloromethane was thus removed by using a rotational evaporator, leading to a dark phase. The black colored hydrophobic phase thus obtained was weighted to calculate the yield of hydrophobic phase  $Y_{hydrophobic}$ :

$$Y_{hydrophobic} = \frac{m_{hydrophobic}}{m_{biomass}} \quad \text{Eq. (4)}$$

Where:  $m_{hydrophobic}$  is the mass of the hydrophobic phase recovered after removal of dichloromethane.

The recovery loss was estimated as follows:

$$Y_{loss} = 1 - Y_{hydrophobic} - Y_{gas} - Y_{aqueous} \quad \text{Eq. (5)}$$

A first fraction of this hydrophobic phase was used for rheological characterization, while a second fraction was re-dissolved in dichloromethane and filtered using a cellulosic filter (3-5 µm porosity) in order to separate insoluble solid residues. In order to ensure that only solid particles remained in the filter, it was further rinsed with dichloromethane in order to remove

all dichloromethane soluble products. The solvent was then eliminated from both the filter (by evaporation in an oven at 50 °C for 10 hours) and the filtrate (by using a rotational evaporator).

This allowed estimating the yield in solid particles (of size higher than 3-5 µm)  $Y_{solid}$ :

$$Y_{solid} = \frac{m_{filter+solid} - m_{filter}}{m'_{hydrophobic}} \times Y_{hydrophobic} \quad \text{Eq. (6)}$$

Where:  $m'_{hydrophobic}$  is the mass of hydrophobic phase resolubilized in dichloromethane.  $m_{filter}$  is the initial mass of the cellulosic filter, and  $m_{filter+solid}$  is the mass of the filter after filtration, rinsing and evaporation of the solvent.

Concurrently, the evaporation of dichloromethane in the filtrate allowed the recovery of a hydrophobic oil phase, with the following yield:

$$Y_{oil} = Y_{hydrophobic} - Y_{solid} \quad \text{Eq. (7)}$$

### 2.2.3 Chemical characterizations of the hydrophobic fractions

The composition of the unfiltered hydrophobic fractions, and the isolated oil and solid residues fractions after filtration were analyzed. The inorganic ash content and the C. H. O. N. S contents in the organic part of each sample were obtained by TGA and elemental analysis following the same procedure used for the initial *Spirulina* sp. biomass.

Samples were also characterized by infrared spectroscopy. ATR-FTIR spectra were obtained in the 600- 4000  $\text{cm}^{-1}$  range with a Bruker Vector 22 FTIR spectrometer.

The unfiltered hydrophobic fractions were also used for further characterization of the oil phase by size exclusion chromatography (SEC) analyses, using a Waters 510 solvent delivery system, a 4214 differential refractive index (DRI) and a 486 Waters UV-detector with a wave length of 254 nm. Two series of "PL Mixed-D 5 µm" columns with a guard column "PLgel 5µm" provided by Polymer Laboratories were used. Acquisitions were performed with the AZUR V4.6 software provided by Datalys. Analyses were carried out at 25°C using a high performance

liquid chromatography grade tetrahydrofuran (THF) as eluent at a flowrate of 1 mL.min<sup>-1</sup>. Samples of 5 µL of oil-phase diluted at 1 wt% in THF, filtrated at 0.45 µm, were injected. The SEC system was calibrated with polystyrene standards with molecular weights from 162 to 371 100 g.mol<sup>-1</sup>. MagicPlot<sup>TM</sup> software was used for elution peaks deconvolution.

#### 2.2.4 Rheological characterizations

Both the hydrophobic phase and the isolated oil phase obtained after filtration were characterized in dynamic shear rheometry. A rotational rheometer (Haake Mars III. Thermo Fischer Scientific) with plate-plate geometry (∅ 8mm) was used with a 0.5mm gap, in controlled strain (0.01%. linear domain) and frequency sweep mode (from 0.01 to 100Hz). A Peltier heating system allowed following the norm NF 14770 in terms of temperature cycle. The sample was introduced between the rheometer plates at 25 °C and heated to 80 °C for 2 hours within the 0.5 mm gap. The system was thus slowly cooled down to 0 °C (typically at a 2 °C/min cooling rate). Isothermal measurements were then performed at increasing temperatures (0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75 and 80 °C)

The complex modulus  $|G^*|$  and the loss angle  $\delta$  were recorded as a function of temperature  $T$  and frequency  $f$ :

$$G^*(T, f) = G' + i \times G'' \quad \text{Eq. (8)}$$

$$\tan \delta = \frac{G''}{G'} \quad \text{Eq. (9)}$$

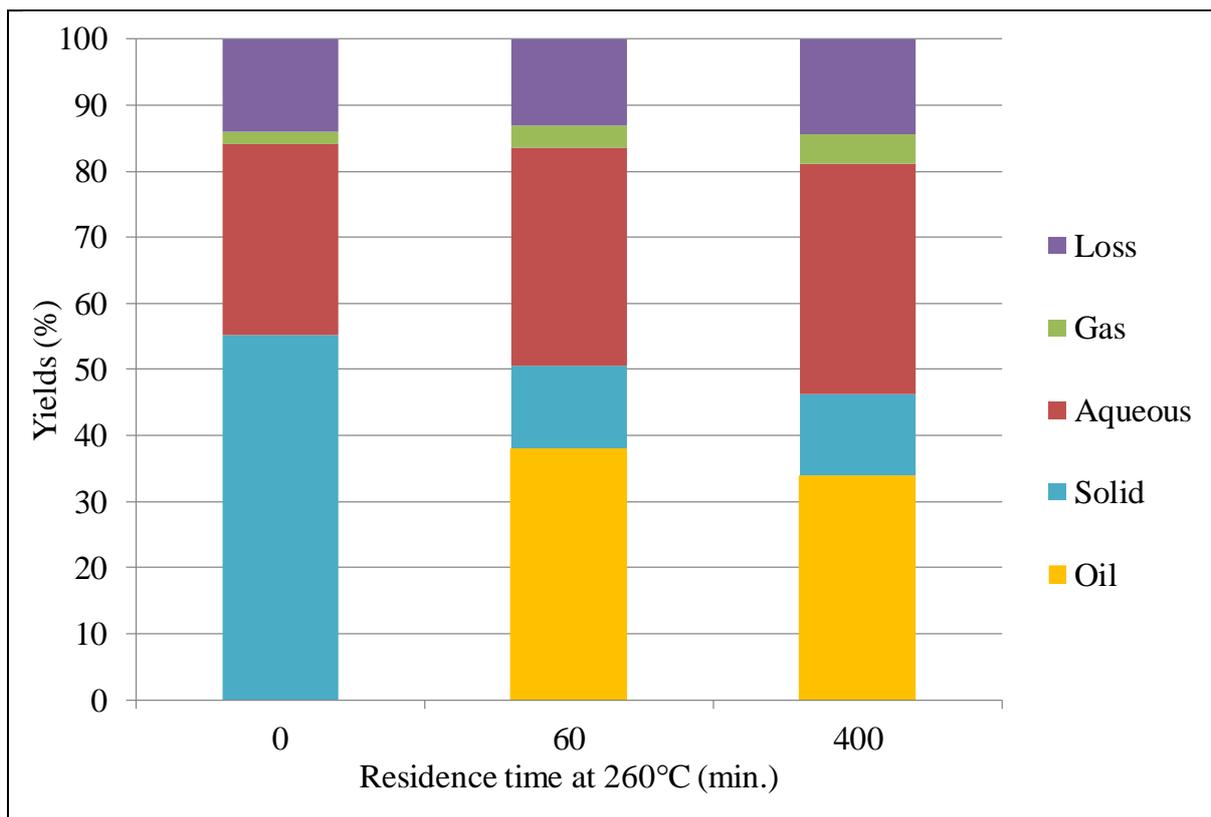
Where:  $G'$  is the storage modulus and  $G''$  is the loss modulus.

## 3 Results

### 3.1) Composition of the hydrothermal conversion products

#### 3.1.1) *Ash content and elemental analysis*

The evolution of the composition of hydrothermal conversion products as a function of the isothermal reaction time at 260 °C is presented on **Figure 1**. The recovery loss is fairly constant ( $\approx 10\%$ ). When the reactor is quenched just after reaching 260 °C (0 min isotherm), the hydrophobic phase only contains char like solid particles. No oil phase could be isolated for characterizations probably due to very low oil content. However, the SEC results show that an oil phase soluble in tetrahydrofuran is present (**Figure 3(a)**). see below). This result is consistent with the assumption that below 260 °C, almost only HTC occurs. The yield in solid bio-char is 59%, while yields for water soluble products and gas products are of 29% and 1% respectively. For the two other experiments involving isothermal plateaus at 260 °C, the hydrophobic phase could be separated into an oil phase and solid residues. The ratio  $Y_{oil} / Y_{solid} \approx 3$  is not influenced by the residence time, but the total hydrophobic phase yield  $Y_{hydrophobic}$  decreases to 54% after 60 min and 49% after 400 min. In the meantime, the yields in gas  $Y_{gas}$  and water soluble products  $Y_{aqueous}$  increase.



**Figure 1:** Composition of the different hydrothermal conversion products of *Spirulina* sp. residues as a function of residence time at 260 °C after heating from 25 °C. (Yields calculated with equations Eq. (2) to Eq. (7)).

The results of chemical analysis of the hydrophobic phases (unfiltered oil and solid residues) are shown on **Table 1**. The ash content is fairly constant for unfiltered products (15-17%) and very low for the isolated oil fractions (0-2%). A much higher ash content is observed for the solid residues (37% after 60 min and 55% after 400 min) suggesting that the solid particles contain a significant part of the initial inorganic fraction present in the *Spirulina* sp. biomass. The C content increases with residence time at 260 °C from 55% (close to C content in initial biomass: 51.5%) to 74.7%. A similar increasing trend is observed for H content. In the meantime, the O content decreases from 29.6 % (close to O content in initial biomass: 28.5%) to 8%. The N content is fairly independent of residence time (5.8 - 6.4%) but significantly lower

than that of initial biomass (11.1%) suggesting that the proteins are solubilized in the water phase during the heating step. S content is almost the same for all samples (1.3 - 2.7%).

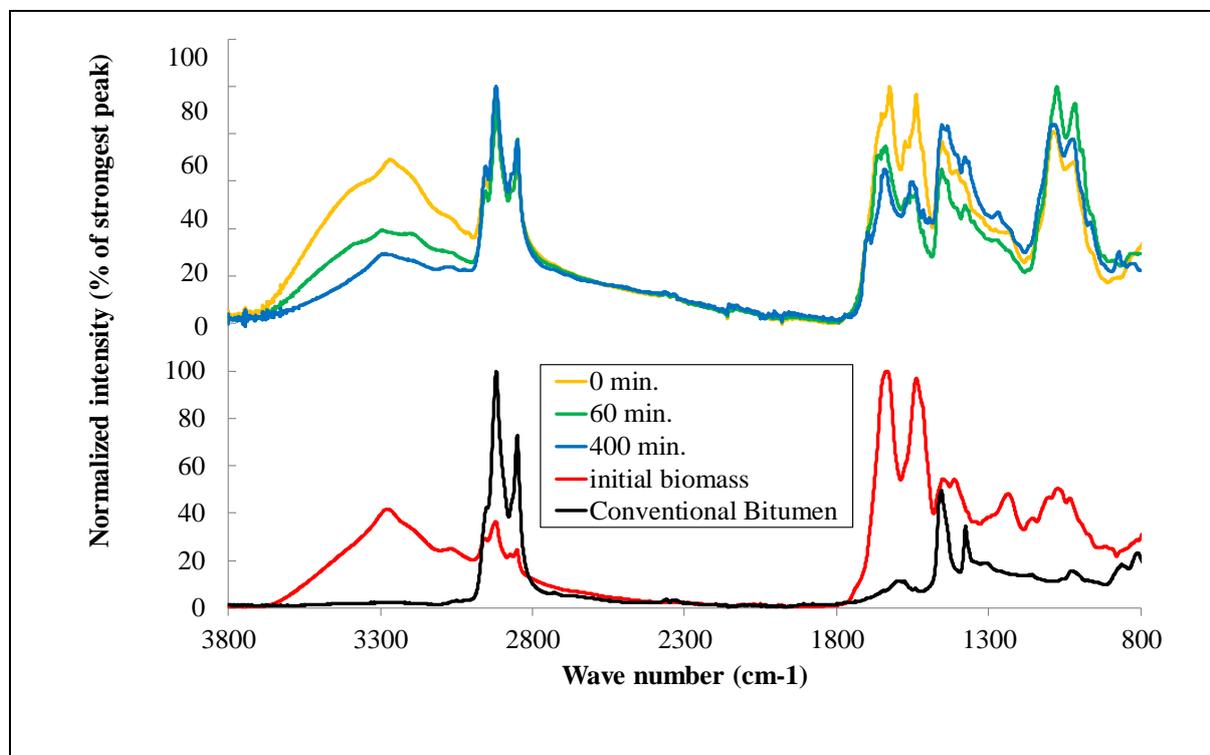
The pure conventional bitumen used for rheological characterizations was also analysed (**Table 1**). The total absence of ash and oxygen and the scarce nitrogen content show that its composition is very different from that of hydrothermal conversion products.

**Table 1:** Chemical composition of pure conventional bitumen and hydrophobic products: inorganic ash content and elemental analysis of the organic phase <sup>(a)</sup>

Residence time at 260°C	Initial biomass	Pure Conventional Bitumen	0 min.	60 min.			400 min.		
			Unfiltered	Unfiltered	Oil	Solid	Unfiltered	Oil	Solid
Ash (%)	<b>8.0</b>	<b>0</b>	<b>16.8</b>	<b>17.6</b>	2.1	37.0	<b>14.5</b>	0	55.2
C <sup>(a)</sup> (%)	<b>51.5</b>	<b>85.5</b>	<b>55.7</b>	<b>66.7</b>	72.0	59.8	<b>74.7</b>	74.7	60
N <sup>(a)</sup> (%)	<b>11.1</b>	<b>1.0</b>	<b>6.2</b>	<b>6.4</b>	6.3	6.8	<b>5.8</b>	5.6	3.6
H <sup>(a)</sup> (%)	<b>7.2</b>	<b>9.9</b>	<b>7.1</b>	<b>8.8</b>	9.1	7.1	<b>9.6</b>	9.4	7.2
S <sup>(a)</sup> (%)	<b>1.7</b>	<b>3.6</b>	<b>1.3</b>	<b>1.7</b>	2.2	2.3	<b>2.0</b>	2.6	2.7
O <sup>(a)</sup> (%)	<b>28.5</b>	<b>0</b>	<b>29.6</b>	<b>16.4</b>	10.3	24.0	<b>8.0</b>	7.7	25.8
O/C	<b>0.55</b>	<b>0.00</b>	<b>0.53</b>	<b>0.25</b>	0.14	0.40	<b>0.11</b>	0.10	0.43

### 3.1.2) Infrared spectroscopy

The spectrograms obtained by FT-IR are shown on **Figure 2**. Each curve has been normalized to the highest absorption peak intensity.



**Figure 2:** Infrared spectrograms of the pure conventional petroleum bitumen, the initial biomass and the hydrophobic hydrothermal conversion products obtained for different residence times at 260 °C

For pure conventional bitumen, the highest absorption is observed at 2917 cm<sup>-1</sup>. This band and the one at 2848 cm<sup>-1</sup> are related to C-H stretching vibrations, indicating the presence of alkyl C-H. The band at 1468 cm<sup>-1</sup> correlated to 1374 cm<sup>-1</sup> are attributed to C-H bending modes. As expected, the pure conventional bitumen is mostly aliphatic due to its high hydrocarbon composition.

However, for the initial biomass (spirulina microalgae residues) the strongest bands are observed at 1639 and 1535 cm<sup>-1</sup>. Intense absorption bands between 3000 to 3500 cm<sup>-1</sup> and at

1070  $\text{cm}^{-1}$  are also observed. Such a profile is consistent with aliphatic oxygenated or nitrogenated compounds.

The hydrophobic hydrothermal conversion products present a profile similar to microalgae residues. The intense absorption between 3000 and 3500  $\text{cm}^{-1}$  corresponds to O-H or N-H stretching vibrations indicating the presence of water or alcohol or carboxylic acid or primary or secondary amides or amines. It is noteworthy that the intensity of these bands tends to decrease as the residence time at 260 °C increases. A similar trend is observed for the C=O or C-N and C=C stretching vibrations at 1667, 1639 and 1535  $\text{cm}^{-1}$  which indicates the presence of ketones, aldehydes, esters, or secondary amides and unsaturated compounds.

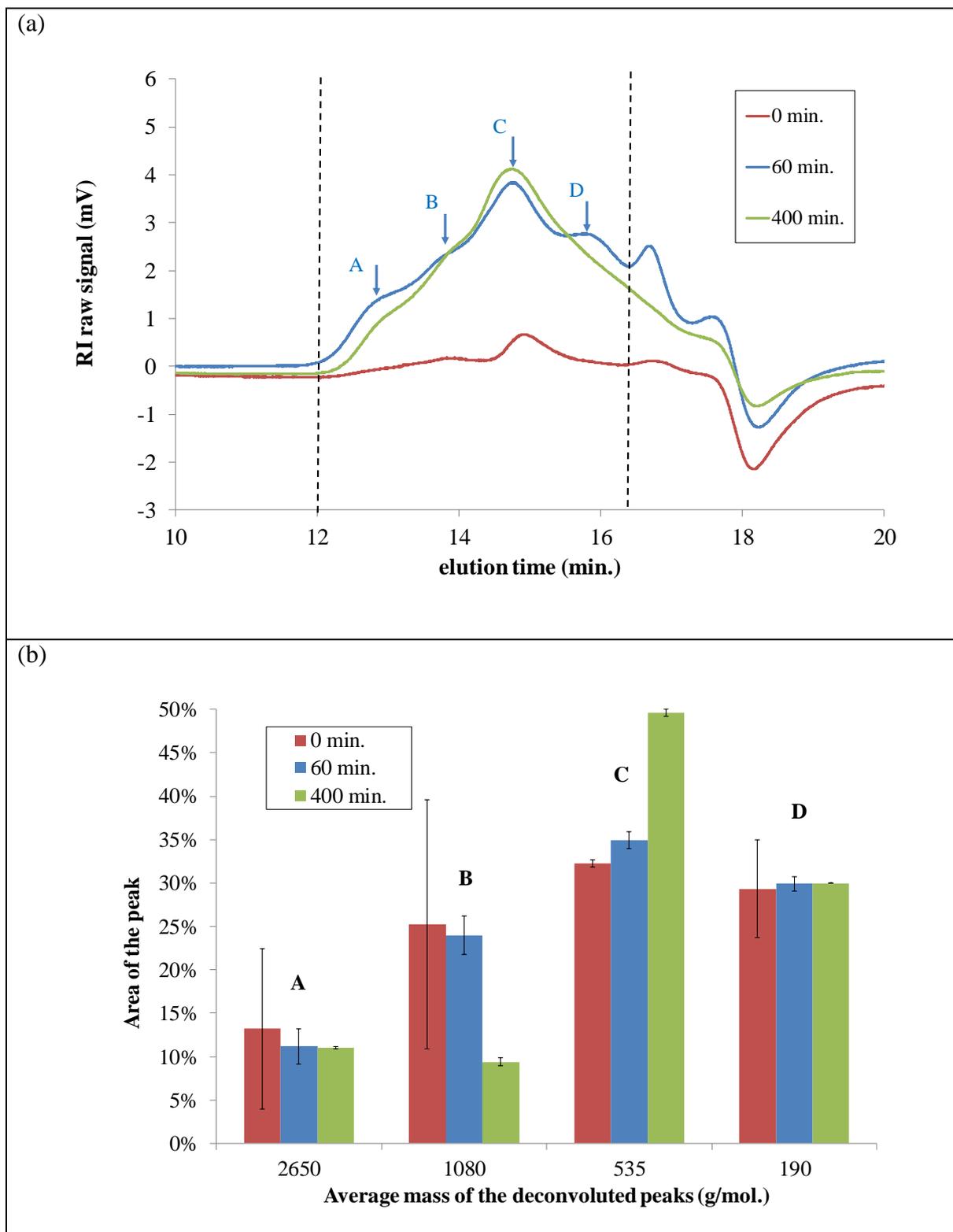
### *3.1.3) Molecular mass distribution of the oil phase*

The SEC elution curves obtained for the hydrothermal conversion products are shown on **Figure 3(a)**. The signal is much lower for the sample obtained after 0 min. at 260 °C. Assuming that the chemical nature of the molecules (and so their UV absorption) is not influenced by the residence time at 260 °C. This could be ascribed to very low oil content in the biochar. This is consistent with the impossibility to isolate an oil phase by filtration of this 0 min sample (**Figure 1**).

For all samples, the elution times corresponding to molecular mass distribution are between 12 and 16.7 min (the right dotted black line represents the elution of the THF solvent so no peak could be analysed after 16.7 min). Four main peaks (indicated by arrows on Figure 7a) could be detected by deconvolution for the three residence times at 260 °C. The maximums of these peaks correspond to the following molecular masses in polystyrene equivalent: A (2650  $\text{g}\cdot\text{mol}^{-1}$ ), B (1080  $\text{g}\cdot\text{mol}^{-1}$ ), C (535  $\text{g}\cdot\text{mol}^{-1}$ ) and D (190  $\text{g}\cdot\text{mol}^{-1}$ ). The evolution of the balance between these 4 peaks/populations with residence time at 260 °C is shown on **Figure 3(b)** (Note that for

the 0 min sample, the low signal leads to high standard deviation of the percentages of the 4 populations). On one hand, the highest (A) and lowest (D) molecular weight populations are not significantly affected by the residence time at 260 °C. On the other hand, the population B strongly decreases while C strongly increases, representing the major population (up to 50% after 400 min).

This molecular mass distribution roughly corresponds to the lower end of that of the conventional petroleum bitumen, with a similar continuity of molecular mass distribution if we consider the main maltene fraction of average molecular mass close to 1800 g.mol<sup>-1</sup>. (**supplementary data**). However, the petroleum bitumen also presents a higher molecular weight asphaltene fraction. It may be assumed that some of the solid residues present in the hydrophobic phase (that are not soluble in the elution solvent) can have a similar influence on rheology than that of this asphaltene fraction.



**Figure 3:** SEC results: (a) Elution curves. The positions of the 4 convoluted peaks A, B, C and D observed for the hydrothermal conversion products are indicated) (b) Molecular mass at the apex and relative area of the A, B, C, D peaks for the different residence times at 260 °C.

### 3.2) Rheology of the bio-bitumen hydrophobic phase and isolated oil phase

The rheological signature of the unfractionated hydrophobic phases (oil + solid residues) and the isolated oil phases obtained after 60 min and 400 min at 260 °C is illustrated by **Figure 4** showing Black diagrams and **Figure 5** showing temperature dependence of the modulus at 1Hz.

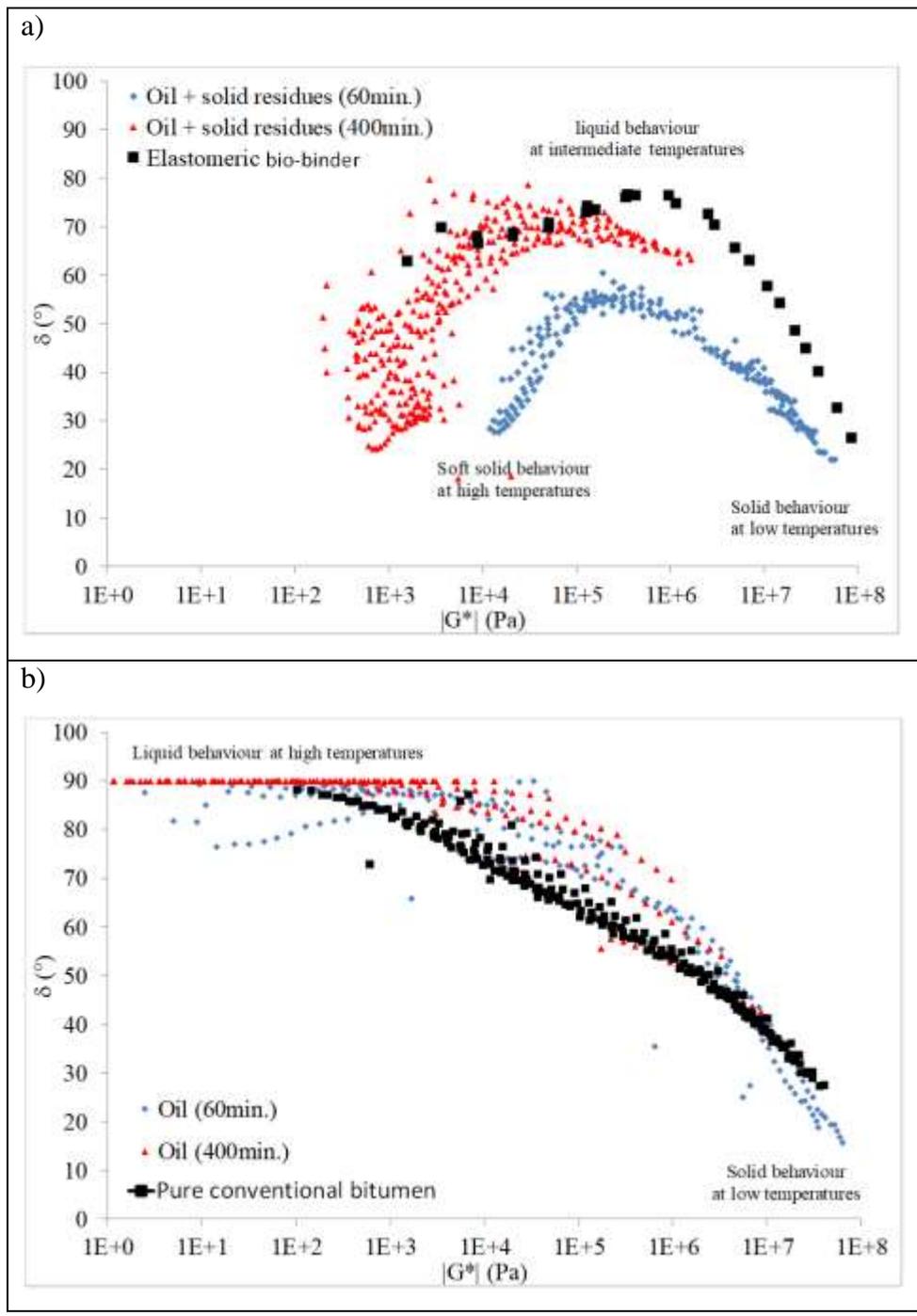
The Black diagram consists in plotting the measured loss angle  $\delta$  as a function of the measure complex modulus  $|G^*|$  for each temperature-applied shear frequency couple. In practice the lowest values of  $G^*$  for each sample are those measured at the highest temperature (80 °C) and for the lowest frequency (0.01 Hz).

The behaviour of hydrothermal conversion products were compared with the pure conventional bitumen, and the elastomeric bio-binder. In the case of the unfractionated hydrophobic phase obtained after 60 min at 260 °C, the rheological behaviour is qualitatively similar to that of an elastomeric bio-binder (**Figure 4 (a)**). The material is a rigid solid at low temperature (at 0 °C  $|G^*| \approx 10^8$  Pa;  $\delta \ll 45^\circ$ ), becomes liquid upon heating ( $\delta > 45^\circ$ ) and has a soft solid behaviour at high temperature (at 80 °C  $|G^*| \approx 10^4$  Pa;  $\delta < 45^\circ$ ). This result is consistent with those reported for the same hydrothermal conversion conditions by Borghol et al [5]. However, as shown on **Figure 5 (a)**, the modulus at 1Hz is significantly higher than that of the elastomeric bio-binder. The similarity is thus only qualitative, probably due to the high ash fraction.

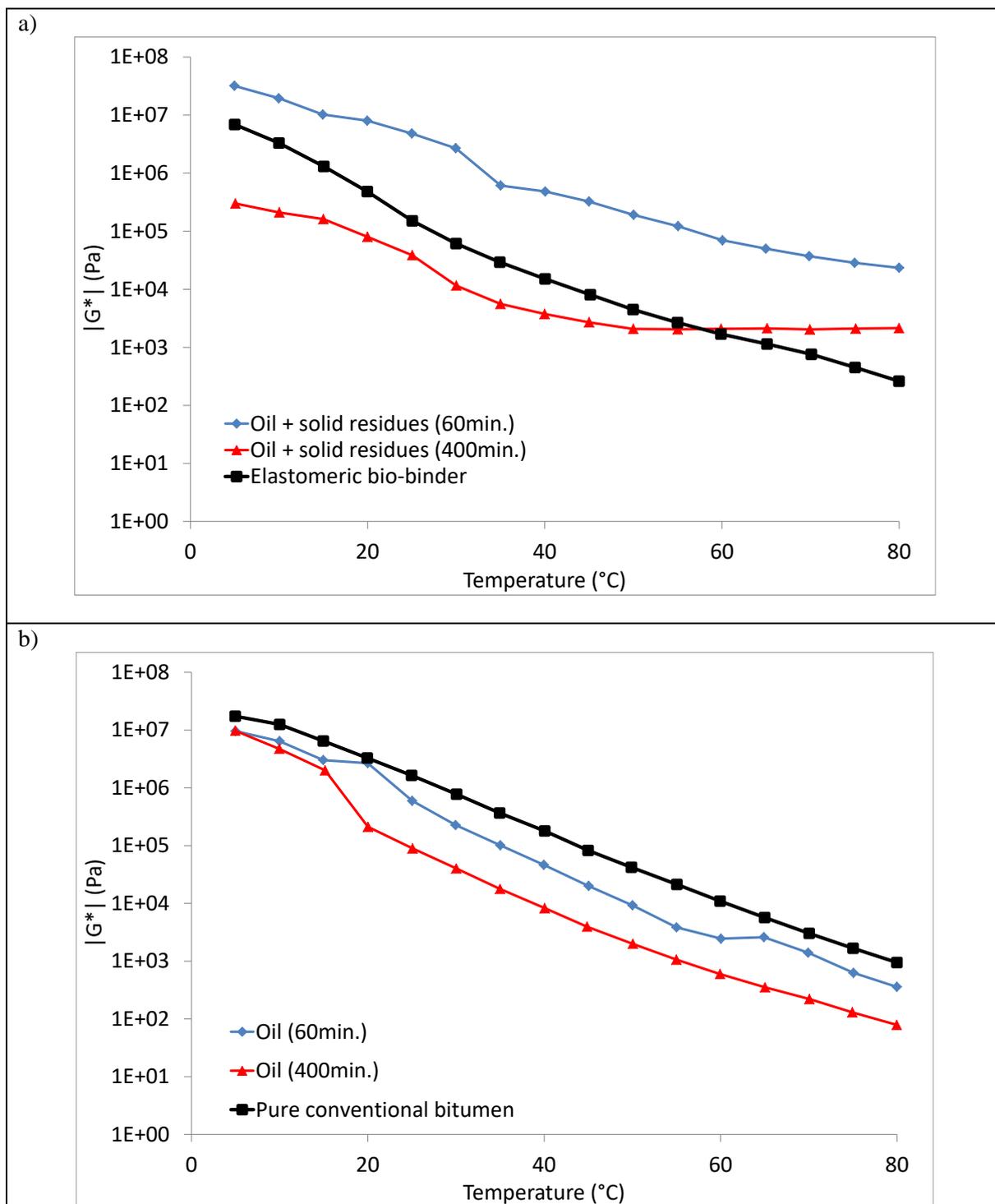
Indeed, for the same residence time at 260 °C, the rheological behaviour of the isolated oil phase is similar to that of a pure conventional bitumen (**Figure 4 (b)**). The material is a rigid solid at low temperature (at 0 °C  $|G^*| \approx 10^8$  Pa;  $\delta \ll 45^\circ$ ), becomes liquid upon heating ( $\delta > 45^\circ$ ) and has no residual elasticity at high temperature (at 80 °C  $|G^*| \approx 10^1$ Pa;  $\delta \approx 90^\circ$ ). This behaviour is similar to that of unfractionated hydrophobic phase obtained by hydrothermal conversion in the same conditions, but for a different microalgae biomass (*Scenedesmus* sp.) [4]. As can be seen on **Figure 5 (b)**, the temperature dependence of the modulus at 1Hz is also

very close to that of the reference pure conventional bitumen. As indicated in the materials section, this pure conventional bitumen is a 50/70 grade which corresponds to a medium rigidity bitumen. So the isolated oil phase would be considered as a soft bitumen analogue from the rheological point of view. This may be ascribed to the lower molecular masses of the oil phase observed in SEC, compared to the conventional petroleum bitumen. However, the presence of oxygen containing functional groups detected by FTIR in the bio-bitumen may in turn increase intermolecular interactions and so the rigidity.

For the 400 min residence time at 260 °C, the unfractionated hydrophobic phase does not present a rigid solid state at low temperature (at 0 °C  $|G^*| \approx 10^6$  Pa ;  $\delta > 45^\circ$ ) (**Figure 4 (a)**). In terms of application, such a material cannot be used as a road binder. Therefore, it should be considered more as a bio-crude than a bio-bitumen. However, when the oil fraction is isolated, it still presents pure conventional bitumen like signature (**Figure 4 (b)**). As shown on **Figure 5 (b)**, its modulus is much lower than that of the reference medium rigidity bitumen. Consequently, this oil fraction may be considered as a very soft bitumen analogue. Such a difference of behaviour with the oil fraction obtained after 60 min. may be related to the different distribution of the peak areas in SEC (**Figure 3 (b)**). More low molecular compounds are present after 400 min., leading to a softer material.



**Figure 4:** Rheological behaviour of viscoelastic hydrophobic products obtained from hydrothermal conversion of *Spirulina* sp. biomass for different residence times at 260 °C: Black diagram for the entire hydrophobic fraction (oil + solid residues) (a) and for the isolated oil fraction (b). For comparison, the Black diagrams obtained for references are plotted: elastomeric bio-binder (a) and pure conventional bitumen (b).



**Figure 5:** Rheological behaviour of viscoelastic hydrophobic products obtained from hydrothermal conversion of *Spirulina sp.* biomass for different residence times at 260  $^{\circ}\text{C}$ : evolution of the complex modulus as a function of temperature for a frequency of 1Hz. Plot for the entire hydrophobic fraction (oil + solid residues) (a) and for the isolated oil fraction (b). For comparison, the data obtained for references are plotted: elastomeric bio-binder (a) and pure conventional bitumen (b).

## 4 Discussion

During HTC and HTL processing of biomass, a general trend is often seen such as first a depolymerization of the biomass, then decomposition of the biomass by cleavage, dehydration, decarboxylation, or deamination and finally reaction of reactive fragments [7,8]. Thus, during hydrothermal conversion, biomass releases some oxygen through dehydration (water molecule released) or decarboxylation (carbon dioxide released). All those mechanisms will lead to the decrease of the O/C and H/C ratio (a reported advantage of the HTC/HTL processes) of the biochar, bio-crude or bio-bitumen products compared to the initial biomass.

These ratios have been calculated in **Table 1**. The O/C value is important for estimating the degree of deoxygenation taking place during the conversion of the microalgae residue. Despite a decrease observed with increasing residence time at 260 °C, the lowest value of O/C=0.11 after 400 min is still far from the value for the conventional petroleum bitumen (O/C  $\approx$  0).

Even though these elemental analysis results demonstrate that the process is an effective process to harvest carbon and hydrogen and redistribute other elements (oxygen, nitrogen, etc.) into other products (aqueous and gaseous products), oxygen and nitrogen contents in the hydrophobic fraction are still high and it is confirmed by FT-IR. The functional groups involving N and O that are detected are likely to make the biobased bitumen analogue more sensitive to moisture and oxidation than petroleum bitumen. However, this should be strongly dependent on the initial composition of the biomass. Higher protein content for example may result in higher N content in the products.

The previously published works on bio-bitumen [4] [5] focused on unfractionated hydrophobic phases (oil + solid residues) and have shown the possibility to obtain pure conventional bitumen like products [4] or elastomeric bio-binder products [5] depending on the microalgae biomass used (industrial residues of *Scenedesmus* sp. or *Spirulina* sp. respectively). In the present work, we observed that the fractionation of the hydrophobic phase is an important parameter: it allows

obtaining conventional bitumen like oil fraction starting from *Spirulina* sp. biomass. Thus for a same biomass, playing on the solid residue content by filtration could allow modulating the properties of bio-bitumen between those of conventional and elastomer containing petroleum bitumen.

It's also worth noticing that the isolated solid residues show a huge inorganic ash content (37% at 60 min and 55.2% at 400min) while the corresponding isolated oil phases almost ash-free (2.1% at 60 min and 0% at 400 min). This inorganic matter that has a huge impact on rheology of the hydrophobic products is necessarily related to the inorganic salts present in the *Spirulina* culture medium. Therefore, it can be inferred that variations of salinity of the microalgae culture medium may affect the bio-bitumen hydrothermal products properties.

The evolution of the composition and rheological properties of the unfractionated hydrophobic phase (oil + solid residues) and the other hydrothermal reaction products with residence time at 260 °C suggest that bio-bitumen formation involves first the formation of solid bio char by HTC during the heating step, which is then progressively liquefied by HTL during the isothermal plateau leading to a bitumen like product after 60 min and bio-crude like product after 400 min.

The formation of biochar by HTC from *Spirulina* biomass is described in literature [3]. For a hydrothermal treatment at 213 °C during 3 hours, a biochar containing 58.4% C. 6.7% H and 6.6% N was obtained. The composition we obtain for a residence time of 0 min at 260 °C is almost the same. However, the authors calculate a percentage of carbon recovered in the char product of 35%. In our case this percentage is equal to 59% due to a much higher yield in biochar (55% in our case against 27% reported in [3]).

A similar comparison can be made with the previously reported production of biocrude from *spirulina* biomass [9] : HTL at 300 °C during 30 min. was used with bio-crude yield 32.6% which is close to the value  $Y_{oil} = 34\%$  we obtain after 400 min at 260°C. Vardon et al. [9]

described their material as a bio-crude oil. However, these authors did not perform rheological characterizations. In future work, with the perspective of upscaling the process, it would be interesting to study the impact of such higher temperature conversion conditions typical of HTL (300 °C and short residence time) on the rheology of the hydrophobic phase, in order to see if bitumen like behaviour can be obtained. However, this requires a better control of the residence time by fast heating/cooling up to the isothermal treatment temperature.

## **5 Conclusions**

The hydrothermal conversion of industrial *Spirulina* sp. residues to bio-bitumen at 260 °C was studied with a 300ml instrumented reactor (45 g of biomass scale).

The characterisation of the hydrothermal products suggests that bio-bitumen formation first involve the formation of bio-char by hydrothermal carbonization during heating of the reactor to 260 °C, followed by hydrothermal liquefaction during the isothermal plateau.

The rheological behaviour of the hydrophobic phase strongly depends on both residence time at 260 °C and fractionation into solid and oil components. Materials with behaviours to that of elastomeric bio-binder or pure conventional bitumen could be obtained by removing solid particles.

In order to further investigate the process, the development of a reactor equipped with faster heating (induction) and cooling system for controlled kinetic studies will be the subject of a future work.

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## Declaration of interest

None

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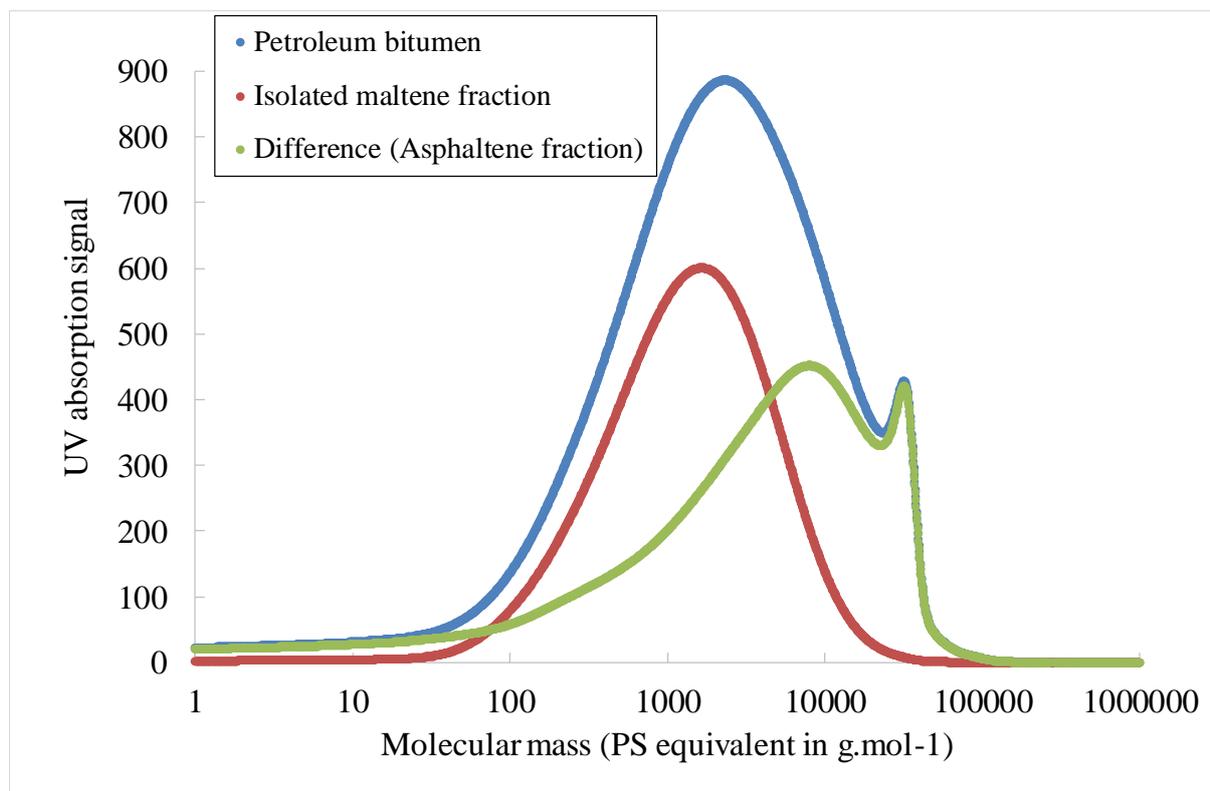
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## Supplementary data



**Figure A** : Conventional petroleum bitumen molecular mass distribution obtained from SEC expressed in PS equivalent mass.

NB: Size Exclusion Chromatography data was obtained for the raw petroleum bitumen (blue curve) and after solubilisation in pentane, which results in isolation of the maltene fraction which presents an average molecular mass of approximately 1800 g.mol<sup>-1</sup>. The difference of the two curves roughly corresponds to the asphaltene insoluble fraction which presents a main peak around 8700 g.mol<sup>-1</sup> and a secondary peak at 32000 g.mol<sup>-1</sup> corresponding to aggregates.