

N°192 / OC

TOPIC(s) : Biomass conversion / Waste valorization

## Kinetics of biobased bitumen synthesis from microalgae biomass by hydrothermal liquefaction

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### PURPOSE OF THE ABSTRACT

Worldwide, about 100 million tons of bitumen are used per year. Mainly from petroleum refining, although bitumen can exist in natural form, this material is used because of its unique combination of properties: adhesion, impermeability to water and specific thermo rheological behaviour. Due to petroleum dependency, the future of petroleum-based bitumen is uncertain, especially in road construction field [1], [2].

In this context, alternative bitumen binders from renewable resources are most likely to be an issue [3]. The Algoroute project funded by the French National Agency for Research (ANR) tries to mimic the geological process of petroleum formation in a faster way. This process started with the sedimentation of microalgae biomass in oceans' depths which then turned progressively into petroleum by the increased of both temperature and pressure.

Algoroute partners have shown microalgae biomass can be converted via hydrothermal liquefaction into an hydrophobic product having similar rheological properties with petroleum bitumen [3], [4]. However the similitude between the geological formation and hydrothermal liquefaction also suffers from some distinctions. If reaction temperature and time seem to be important factors, some other less explored factors, such as heating/cooling rate, algae/water ratio or loading level of reactor might have a significant impact on quality and yield of the hydrophobic phase.

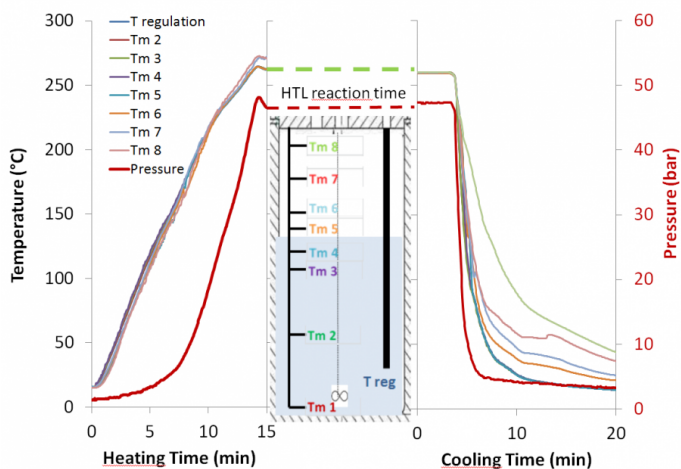
One of the aims of this project is to fully understand the physical and chemical phenomena taking place during hydrothermal liquefaction. To do so, hydrothermal liquefaction is studied with three different reactor scales: i) High pressure DSC crucibles (30  $\mu$ L.) are used to perform thermal analysis during hydrothermal liquefaction in a Differential Scanning Calorimeter. ii) A commercial stirred pressure reactor (300 mL) was instrumented with 9 thermocouples in different locations inside the reaction media, allowing to monitor the temperature fields together with global pressure, and stirrer's rotation torque. Fast heating and quenching of the reaction media are obtained with an induction coil and a mixed air/water spray cooler (figure A). iii) The same system is used with intermediate scale Swagelok non-instrumented reactors (30 mL.) allowing the screening of reaction temperatures and residence time on typically 3g of biomass batches.

These reactors were used to study the hydrothermal liquefaction of Spirulina residues. This microalgae is currently the main one produced worldwide, with identified residues from extraction of high added value molecules (pigments). Hydrothermal liquefaction of the microalgae biomass leads to three separate components: a gas phase, an aqueous phase and a hydrophobic phase. This hydrophobic phase, which mimics the rheology behaviour of petroleum-based bitumen, is made of a mixture of an oil phase, and insoluble solid residues. Oil and solid residues form a complex matrix, where the effects of both on the rheological response allow the potential formulation of different grades of bio-bitumen mimicking petroleum bitumen grades. (Figure B). Although previous studies have reported that the optimal reaction temperature is around 260°C [3]. Yet, no detailed kinetic studies have been made about the reaction time impact on the rheological behaviour. Therefore, the combination

of high heating/cooling rates and different reaction times was used to investigate the hydrothermal liquefaction kinetic of biomass waste conversion into bio bitumen.

That's what it's all about. Controlling the operating parameters to better understand the oil and solid residues formation's kinetic, and then understanding the contributions of these fractions in the bitumen-like behaviour.

## FIGURES

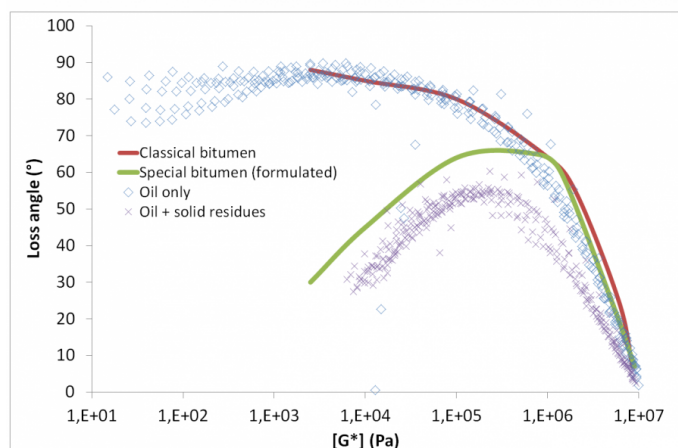


**FIGURE 1**

Temperature control of the instrumented stirred pressure reactor

This figure shows typical sequences for heating (induction) and quenching (spray cooling) allowing controlled hydrothermal liquefaction (HTL) reaction time for kinetic studies (here at 260°C).

The thermocouples are inside the reactor, and the blue square



**FIGURE 2**

Rheological behaviour of oil and oil/solid residues mixture obtained after 60 min at 260°C

This figure shows the comparison between bio-sourced bitumen and reference bitumen grades (classical petroleum bitumen, and special bitumen formulated with polymer additives)

## KEYWORDS

Biomasse conversion | Micro-algae | Hydrothermal liquefaction | Bitumen

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