Microalgae hydrothermal liquefaction process optimization and comprehension to produce high quality biofuel

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The microalgae hydrothermal liquefaction (HTL) process is a promising solution to produce biofuel. The aim of the RAFBIOALG project is to study a full biofuel production chain using this technology. This project engages five research centers, CEA Cadarache for the microalgae cultivation and the HTL aqueous phase reuse, CEA Grenoble for the HTL process and the combustion properties of the product will be evaluated by CORIA. Finally, the full process chain will be evaluated for sustainability by the LBE to guide choices during the process optimization.

Microalgae are treated by the hydrothermal liquefaction process where reactions occur between 270-350°C, at approximately 100 bar and at 10% by weight organic matter concentration in water. After 30 min, we obtain a gaseous phase (90% of CO_2), an aqueous phase and a biocrude (considered as a mix of bio-oil and char) which will be our product of interest. Finally, an extraction step is necessary to obtain the non-upgraded bio-oil composed of 75% carbon (Fig.1). Today, the chosen resource, *Chlorella sorokiniana*, composed of 23.2% lipids, 22.1% polysaccharides and 54.7% proteins, has never been studied in hydrothermal liquefaction, so the process optimization is necessary to obtain both a high yield and high bio-oil quality.

The principal quality parameter targeted is the nitrogen and oxygen content which can be represented as H/C, N/C and O/C ratio in the Van Krevelen diagram. In the bio-oil, these heteroatoms can damage catalysts during hydrotreatment upgrading and prevent their use as fuel due to toxic gas emission.[1] Moreover, the control of the HTL aqueous phase quality is important because of the possibility to be recycled in the microalgae cultivation step. Compounds like phenol, aromatic and nitrogen molecules are toxic for algae growth so a special attention will be held on that criteria too.[2]

Consequently, an important part of the project is to understand reactions implied during the hydrothermal liquefaction and to identify the best way to avoid or limit heteroatoms compounds in the bio-oil and toxic compound in the aqueous phase, like phenol derivatives or nitrogen containing molecules. Degradation reactions like decarboxylation, deamination, dehydration are well-known but no detailed reaction scheme is described for *Chlorella sorokiniana*. A model predicting the yield and the quality of the bio-oil will be necessary to have a first overview of the degradation of *Chlorella sorokiniana* during HTL. In order to build this model, the yield variations are studied experimentally, and precise analyses of the bio-oil composition by GC-MS are performed to know which molecules are produced in function to the HTL conditions and the biomass composition.

The global objective is to build a mechanistic and kinetic study based on these observations. This model will be useful to analyse and predict conversion of other *Chlorella* microalgae through HTL for biofuel production as well as helping in the design of a future industrial process at a larger scale.

Fig. 1. Bio-oil from *Chlorella sorokiniana* hydrothermal liquefaction

(1) Obeid, F. et al. Nitrogen and Sulphur in Algal Biocrude: A Review of the HTL Process, Upgrading, Engine Performance and Emissions; **2019**
(2) Chernova, N. I. et al. Hydrothermal Liquefaction of Microalgae for Biofuel Production: The Recycling of Nutrients from an Aqueous Solution after HTL; **2019**