HYDROTHERMAL LIQUEFACTION OF MICRO-ALGAE: INFLUENCE OF ALGAE SPECIE

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ABSTRACT

Hydrothermal processes are making use of the remarkable properties of water below its critical point. In those conditions, water is a solvent but also a reactant for the conversion of biomass. Algae biomass is made of different kinds of natural polymers (lipids, proteins, carbohydrates). Under hydrothermal conditions (250-350°C; 10-20 MPa), hydrolysis reactions will occur and the natural polymers will be deconstructed. This conversion is called hydrothermal liquefaction. The aim of this work is to produce a green crude for the production of biofuels.

Hydrothermal liquefaction of several micro-algae were performed in a batch reactor. Dunaliella salina, Spirulina platensis, Nannochloropsis occulata and Chlamydomonas reinhardtii were studied between 190 and 350°C for a pressure between 6 and 20 MPa according to the temperature. Biocrude high heating values between 20 and 36 MJ/kg were obtained regarding to the algae specie, the temperature and holding time during the experiment. The best carbon conversion yield into biocrude is 80% but a high conversion yield is not associated to the best heating value for the biocrude. In order to classify the experimental conditions in term of efficiency for energy production we calculate the Energy Recovery ratio. It shows that the best ER is 89% and the best temperature for hydrothermal liquefaction is around 300°C.

INTRODUCTION

Third generation of biofuels are considered as an interesting solution for the future in order to replace fossil fuels. Third generation means biofuels produced from an algae biomass. Micro-algae, with their high growing rates, are extensively studied. They offer several advantages among many, one can list: neither competition with food production, nor competition with land usage, high biomass productivity and accumulation of some energetic molecules as reserve (lipids and/or carbohydrates). However, this aquatic biomass is growing in highly diluted media (biomass concentration ~1 g/L). Classical routes for the conversion of micro-algae induce a lipid extraction step followed by transesterification to obtain biodiesel. But thoses routes need a drying step with a high energetic cost for water elimination. Hydrothermal processes offer an interesting alternative avoiding the drying step. In those processes, the native water is a solvent but also a reactant. The potentiality of this kind of processes in the region of the water critical point was first examined by M.Modell in the 80's [1] for forest residues. Hydrothermal liquefaction can be applied to the whole biomass or to the residue of biomass after a first extraction of valuable molecules.

This work is part of the Diesalg project. The aim of this project is to developed new technologies for each steps of the process route to third generation of biofuels from cultivation to wet extraction and biomass valorisation. Nannochloropsis oc. was selected by the DIESALG project as reference algae due to its good performance in term of lipid accumulation, and because it is relatively well known thanks to the previous Shamash project. The metabolism of accumulation by Chlamydomonas reinhardtii is extensively studied by the biologists as reference. Dunaliella Salina is an interesting algae growing in a natural environment with a high salinity. Spirulina pl. is a well-known alga for its high protein content and is relatively cheap.

MATERIALS AND METHODS

Nannochloropsis oculata. is produced in raceways by Alpha-Biotech SAS, near Saint-Nazaire, France, partner of the project. Spirulina (Arthrospira platensis) was produced by the EARL Carpio (Spiruline de Haute Saintonge). Dunaliella salina. and Chlamydomonas reinhardtii. were cultivated by Microphyt in photobioreactor. The elemental compositions and the main characteristics of the algae are presented in the table 1 below.

Algae species	**Dunaliella salina**	**Spirulina platensis**	**Nannochloropsis oculata**	**Chlamydomonas reinhardtii**
Dry matter content (w%)	31.24	23.13	24.97	14.00
C (w% dry)	49.1	48.5	52.7	52.7
H (w% dry)	6.37	6.59	6.93	7.25
N (w% dry)	3.38	9.49	9.28	9.02
O (% dry)*	14	31	24	22
HHV (MJ/Kg)	23.23	20.8	23.6	24.34
Ash (% dry)	16.7 (815°C)	8.8 (550°C)	7.09 (550°C)	10.6 (550°C)
Ca (mg/Kg)	1002	1830	2021	2826
Mg (mg/Kg)	47094	2387	4487	6792
P (mg/Kg)	1700	9687	19802	26842
K (mg/Kg)	8517	13823	15245	4335
Na (mg/Kg)	41249	6821	7956	2323

***Oxygen content is calculated by difference**

Table 1 . Elemental composition and High Heating Value (HHV) of the different algae

Hydrothermal experiments were performed in a batch reactor (Parr instruments). Reactor volume is 600 ml. 240 g of the algae solution is introduced initially. In most cases the algae solutions were used directly without any dilution. An initial N_2 pressure of 10 bar is applied after elimination of residual oxygen. Temperature setpoints were between 190 and 350°C. The resulting pressure depends on the selected temperature (60-200 bar). The heating rate is 7°C/min. Figure 1 presents the temperature/pressure time profile. At the end of the temperature plateau the reactor is rapidly cooled down. The gas phase is analysed on line via a micro-GC (Varian CP-4900). Biocrude is recovered directly by skimming or filtration on a Buchner. No solvent was used for the separation of biocrude from the aqueous phase nor extraction. This was especially done to avoid the influence of the nature of the solvent on the quantification of the biocrude obtained [2]. For each experiment, the carbon balance is done. The carbon content of the aqueous and organic or solid phases are determined with TOCmeter Shimadzu (TOC-L CSH / SSM). The higher heating value (HHV) of the biocrude is determined by a calorimetric bomb (Parr 6200 calorimeter).

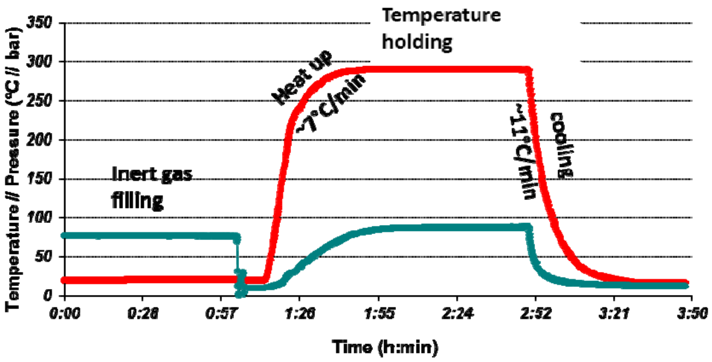


Figure 1 Example of temperature/pressure time history for an experiment at 290°C

Some GCMS analyses were done on ethylacetate extract from the aqueous phase or for biocrude solubilized in ethylacetate.

RESULTS

Hydrothermal liquefaction of Nannochloropsis oc.

A typical result for hydrothermal liquefaction of Nannochloropsis oc. is given below. A biocrude with a HHV of 35 MJ/Kg is obtained. 51,3% of the initial carbon is converted into biocrude. The gas produced is mainly composed of CO_2 (99%vol). The carbon distribution in the different phases is given in the figure 2 with a picture of the biocrude. This “green crude” looks like petroleum.

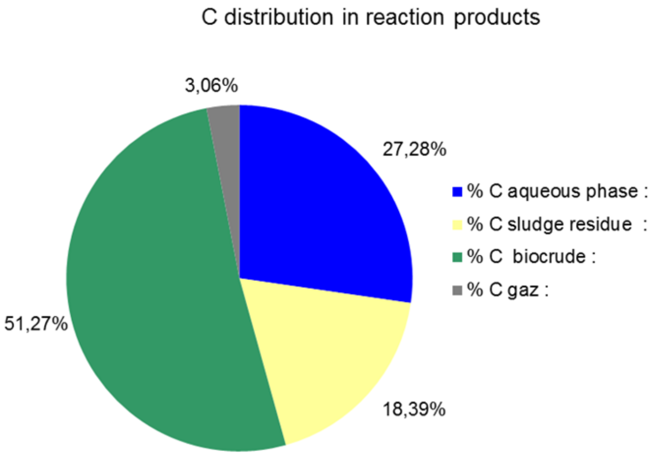
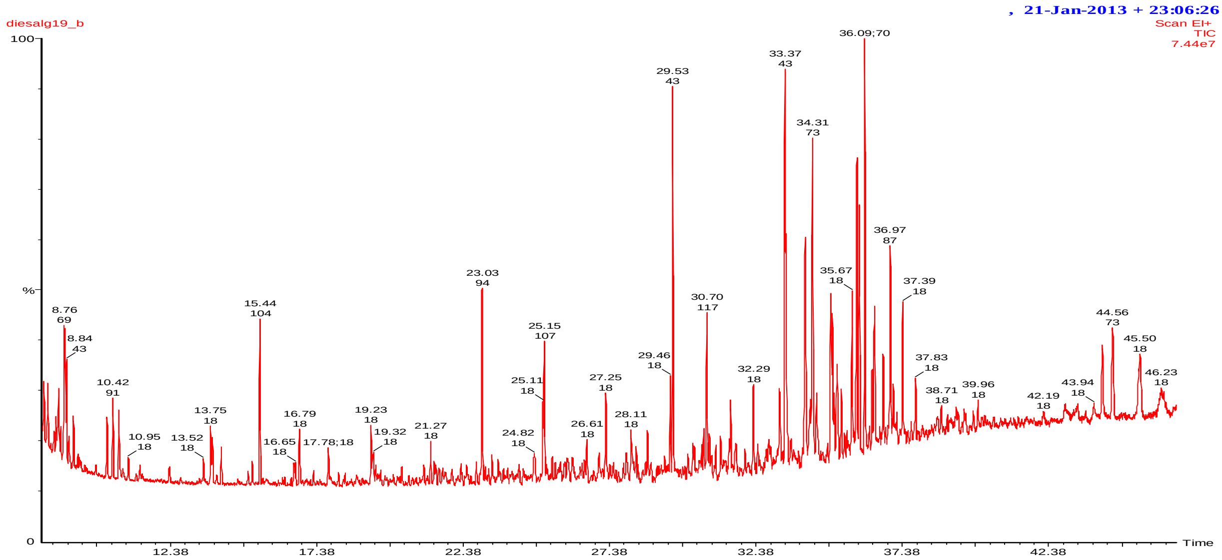


Figure 2 carbon distribution (left) and picture of biocrude (right), Nannochloropsis oc. 290 °C, holding time 60 min

A fourth phase is observed at the bottom of the flask. This kind of sludge still contain 18.39% of the carbon and has to be separated from the biocrude. GCMS analysis of this biocrude gives a wide range of organic molecules (see figure 3) from aromatics with phenol to long aliphatic chains, aldehydes, amides from the condensation of lipids fragments with amines.



	Formula	Tr	Area%
2-Methyl-2-heptene	**C8H16**	**8,76**	**2%**
Styrene	**C8H8**	**15,44**	**1%**
Phenol	**C6H6O**	**23,03**	**2%**
7-hexadecene	**C16H32**	**29,53**	**3%**
Nonadecane	**C19H40**	**33,37**	**5%**
Dodecanamide		**34,06**	**3%**
Hexanal		**34,94**	**2%**
2-hexadecene, 3,7,11,15-tetramethyl	**C20H40**	**35,83**	**3%**
2-hexadecene, 3,7,11,15-tetramethyl	**C20H40**	**35,91**	**2%**
2-hexadecene, 3,7,11,15-tetramethyl	**C20H40**	**36,09**	**3%**
9-Octadecenamide, N,N-dimethyl-dimethyl-		**36,43**	**2%**
2-Nonadecanone, O-methyloxime		**36,97**	**2%**
Dodecanamide, N,N-diethyl-		**45,5**	**2%**

Figure 3 GCMS analysis of a biocrude obtained from hydrothermal liquefaction of Nannochloropsis oc. 290 °C, holding time 60 min, table of main species identified among 140 pics

Liquefaction Temperature influence for Nannochloropsis oc.

Hydrothermal liquefaction of Nannochloropsis was performed for temperatures between 250 and 315°C. No strong dependence can be observed on the higher heating values of the biocrude obtained (see figure 4). At 260°C, no real biocrude was obtained. The carbon conversion showed a clear maximum at 290°C. For Nannochloropsis it is then easy to define 290°C as the best temperature for hydrothermal liquefaction. The best results are obtained with a reacting time of only 15 min ((57,7 % Carbon conversion at 290°C) and a faster reactor heating rate (20°C / min) with 64,4% Carbon conversion at 290°C. This is in favour of a future continuous process. A test of liquefaction has been done with Nannochloropsis after extraction of lipids by soxhlet (8 hours, ethyl acetate). A biocrude is still obtained but with a lower HHV (20,2 MJ/Kg, 57,9 %conversion C, 290°C).

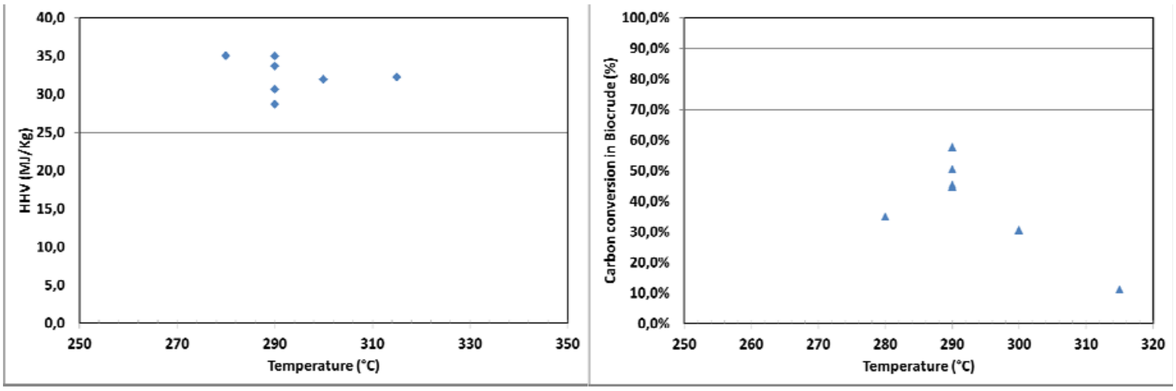


Figure 4 Temperature influence on the biocrude HHV (left) and the conversion of carbon into biocrude (right) for Nannochloropsis

Results comparison for the different algae

Those trends are not seen for the others algae (see figure 5). Generally, HHV seems to be improved at a higher temperature (300-310°C) but there is a large scattering regarding results for carbon conversion into biocrude. The best conversion is obtained with Dunaliella and Chlamydomonas near 300°C.

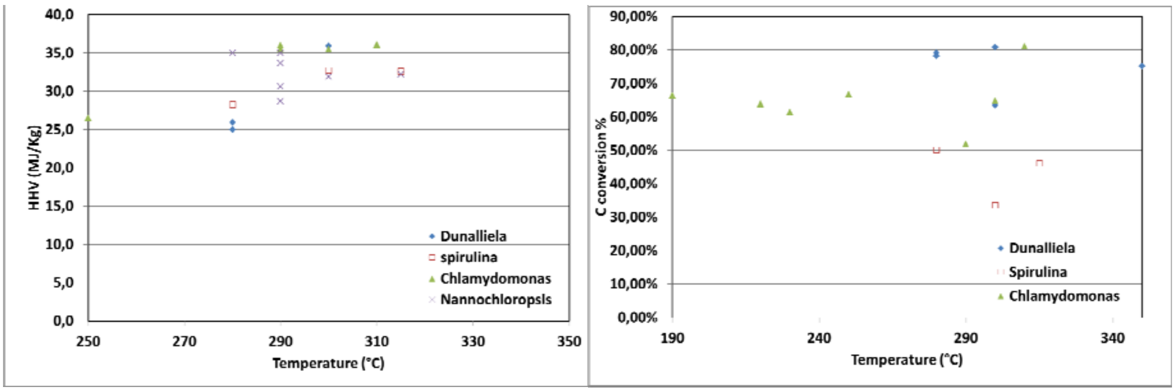


Figure 5 Comparison of the bicrudes HHV and carbon conversion into biocrude for the different algae

In order to compare the conversion efficiencies for the various algae we calculated the Energy Recovery ratio. This ratio takes into account the initial HHV of the algae, the percentage of conversion (by weight) and the final HHV of the biocrude : it represents the proportion of energy recovered finally in the biocrude.

ER=%conversion (%w)*HHV biocrude/HHValgae Eq (1)

ER values are presented in the figure 6. The best alga is always Chlamydomonas, giving a biocrude with a good HHV and an interesting conversion efficiency. The best ER observed is 89% , 310°C. The best temperature is slightly different according to the alga. Those results can be explained by the differences in the algae composition and also the differences in the cultivation methods. Chlamydomonas and Nannochloropsis are known to accumulate lipids. Dunalliela salina and Spirulina platensis are rich in proteins [3]. Dunalliela has also a high sodium content (see table1).

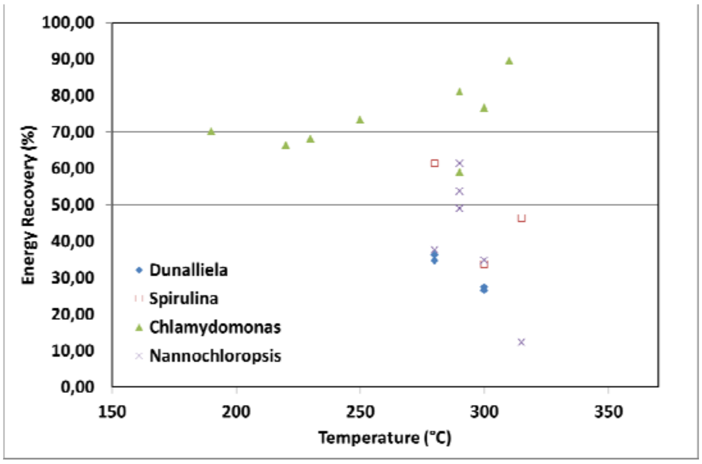


Figure 6 Energy recovery calculated for the different algae

The process parameters have hence to be optimized for each biomass.

CONCLUSION

A lot of parameters have to be taken into account to design an hydrothermal liquefaction process for micro-algae : algae specie, composition, conditions of growth. A temperature between 290-310°C seems to be in all cases an interesting choice. This could be related also to the water properties just below the critical point with a dissociation constant at its maximum. A rapid heating and a residence time of 15 min gives best results for Nannochloropsis. Chlamydomonas gave the best results in term of Energy Recovery.

For a third generation production of biofuel, the technico-economical evaluation has to considered the full chain of the process taking into account the growth speed of the alga and its conversion efficiency, quality of biocrude.

The experiments in this work were performed on a batch reactor. The next step is to work on a continuous pilot.

ACKNOWLEDGEMENT

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REFERENCES

[1] M. Modell, Fundamentals of thermochemical biomass, Chap.6, E. a. publishers. London, **1985**. 1:p. 95

[2] Peter J. Valdez, Michael C. Nelson, Henry Y. Wang, Xiaoxia Nina Lin, Phillip E. Savage , biomass bioenergy , vol. 46, **2012**, p.317

[3] Yeh, T. M., J. G. Dickinson, et al., J. Chem. Technol. & Biotechnology 88(1) **2013**, p. 13