Production of fuels and chemicals by hydrothermal liquefaction of microalgae

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Abstract:
Microalgae are considered as one of the main renewable fuel crop in the future. Among several valorization pathways, the whole algae hydrothermal liquefaction and further hydrotreatment is an attractive one using all algal biomass and preventing costly drying and extraction methods. In the present study, HTL reaction was optimized for bioliquid production with Spirulina and then applied to the conversion of 4 other microalgae: Ourococcus sp., Porphyridium cruentum, Nannochloropsis occulata and Dunaliella salina. The bioliquids were further hydrotreated in order to get fuel like hydrocarbons. Comprehensive characterization of the products was obtained by HT GCXGC FID.

Keywords: *Biofuels; microalgae; Hydrothermal*

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1. Introduction

(micro)Algae are considered the most optimal feedstock for biofuels and represent the third generation of alternative fuels to substitute fossil fuels. These algae present multiple possibilities for fuel end-products – biodiesel, ethanol, methane, jet fuel, biocrude and more – via a wide range of process routes (Wang et al., 2008). Each of these process routes presents its own set of opportunities, parameters, dynamics and challenges. Among these routes hydrothermal liquefaction (HTL) is regarded as a highly promising technology for treating the whole biomass and algae (Behrendt et al., 2008; Duan and Savage, 2011). Dote et al. (1994) were among the first to apply HTL to *Botryococcus braunii* with and without catalyst (Na_2CO_3). Later on, various microalgae were investigated. However, the complexity of the bio liquids and their further hydroconversion has not yet be investigated in details. Therefore, we propose to study the combination of HTL and further HDT with a series of microalgae and to get an in depth characterization of the liquid products by GC XGC chromatography.

2. Experiment

Table 1 summarizes the composition of the algae investigated in this study.

Tableau I – Composition of investigated µalgae

	Elemental Analysis						Biochemical composition			Proximate	
	% N	%C	%H	%S	%O	PCS (MJ/kg)	Proteins	Lipids	Glucids	Ashes	Water
Spirulina	9,7	43,8	6,4	0,4	28,9	19	50-70	6-9	20-25	14,7	8,0
Chlorella	2,5	21,0	3,2	0,0	17,3	9	51-58	14-22	12-17	60,5	7,0
Nannochloropsis	6,5	49,0	7,4	0,3	26,5	22	52	28	12	8,5	6,0
Dunaliela Salina	2,2	30,0	4,1	0,4	16,5	13	57	6	32	46,7	8,0
Porphyridium	4,8	33,5	5,0	1,0	27,7	14	44	9	47	34,1	6,0
Ourococcus	7,4	30	7,2	0,3	28,8	15	-	31	-	53,5	14,0

The HTL experiments were carried out in a mechanically stirred autoclave (Parr 300 mL reactor). For each experiment, 5 g of dried of microalgae and 20 g of water were loaded into the reactor. The autoclave was pressurized to 0.7 MPa with N_2 and heated at 320°C (P_T: 14MPa) for 1h. Bio-oil was recovered from the liquid phase with dichlomethane. HDT reactions were performed in a similar batch system with a smaller volume (100 ml). In this case, 40g of dodecane was mixed with 3-5 g of algal bio-oil and pressurized under H_2 at 350°C (P_T : 8MPa) for 5h.

3. Results and discussion

Depending on the nature of the algae, the yield in bio-oil (ash-free) varies between 9% Porphyridium) and 37% (Ourococcus). HTL conversion allows to remove a large part of O contained in the microalgae as illustrated by Fig. 1. HT GCxGC-FID was used to investigate the nature of the molecules contained in the bio-oil.

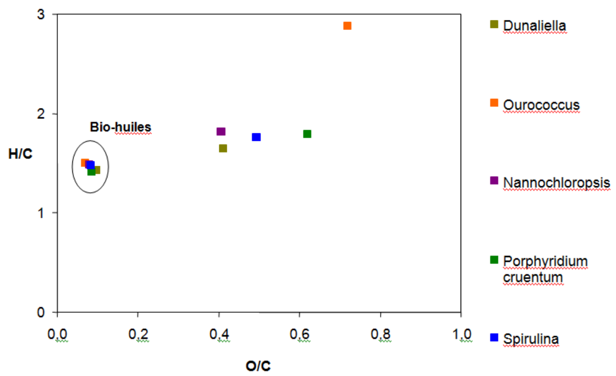

Fig. 1 van Krevelen diagram of iniial composition and after HTL of various algae.

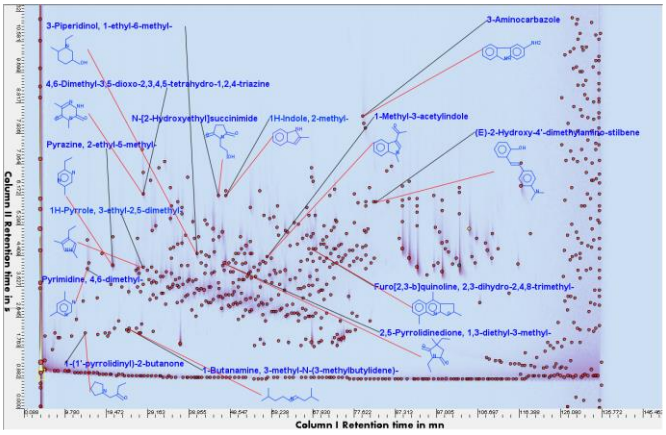

Fig. 2 GC x GC chromatogram of bioliquid obtained from HTL of spirulina.

The nitrogen originating from proteins still remained in a large amount in the bio-liquid as illustrated by Fig. 2. Further hydrogenation at 350°C with sulfide ($NiMoP/Al_2O_3$, $CoMo/Al_2O_3$, $NiMoP/Al_2O_3$-Y) or nitride catalysts (Mo_2N, prepared from Sheelites) can provide high alkanes yields (C_6-C_{17}, up to 70%), aromatic compounds (~10%),nitrogen and oxygenated compounds (~30%). Considering the large amount of N compounds and ammonia produced, the use of a nitride catalyst is an interesting option.

4. Conclusion

The two stage conversion (HTL and HDT) of various micro-algae has been performed at 320 and 350°C respectively in batch reactors. Considering the nature of the algal biomass, large amount on N compounds are recovered in the liquid oil whereas O compounds have been well converted by HTL. Conversion of the bio-oil into fuels requires a further hydrotreatment which can potentially lead to alkenes. This conversion pathway is particularly suitable for the conversion of algal wet feedstocks.

5. References

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