

Hydrothermal liquefaction of microalgae in the presence of transition metal salts

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Biofuels represent an interesting alternative to fossil fuels as an ecologically sustainable form of energy. In recent years, the production of liquid biofuels by different biochemical or thermochemical processes has been the object of many studies.

Several pilot- and demo-scale projects for hydrothermal liquefaction (HTL) of terrestrial biomass started but different technological hurdles are still to be overcome to reach good efficiency of the processes. For example, problems must be solved concerning the effect of biomass impurities and inhomogeneity, the pumping of the water-biomass mixture, the necessity to use corrosion resistant materials [1].

However, the continuous raise in the prices of fossil fuels and the awareness of the society challenges related to their use has recently driven a strong growth of interest on HTL processes performed using as feedstock microalgae with high lipid content.

In this context hydrothermal processes are suggested to be particularly apt to convert thermochemically the microalgae avoiding the energetically expensive step of the biomass drying. Several studies have shown that the biocrude obtained from thermochemical liquefaction of microalgae has a high heating value [2], although the oxygen and nitrogen content of the obtained bio-oil are significant.

In this study, experiments of hydrothermal liquefaction of microalgae in the presence of transition metal salts were carried out to estimate their influence on the product yields.

Experiments were carried out in batch reactor of 28 mL, filled at 70% with an algal slurry at 10 wt% of biomass. The used algal biomass was constituted by a 70% *Nannochloropsis* sp. and 30% *Tetraselmis suecica* mixture. Tests were carried out in subcritical condition at 325 °C with a reaction time of 15 minutes and RhCl₂, NiCl₂ and CoCl₂·6H₂O were tested as catalyst initially dissolved in the aqueous slurry at 5 mmol/L concentration. Control tests without any added transition metal salt were also performed for comparison.

Products collected at the end of each batch liquefaction experiments were distributed in four different phases: a solid residue, an aqueous phase, a biocrude oil and a gaseous mixture. The amount, the yield and the organic content of each phase were estimated. Moreover, chromatographic analyses of gaseous phase were performed to estimate their composition.

All investigated transition metal salts exhibited some influence on the yields of the different obtained phases. The best results obtained till now were achieved using RhCl₂ that allowed us to decrease the yields in the aqueous phase from 55 to 51 % w/w and to increase that in bio-crude from 17 to 22 % w/w. More interestingly, when RhCl₂ was used, the detected amount of hydrogen and methane in the gas mixture was about five time higher than that obtained in all other performed experiments.

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A continuous reaction system

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Among oleaginous crops for the production of biofuels, microalgae are particularly interesting due to their high lipid content, high yields in terms of biomass and the possibility to be cultivated in industrial systems. The use of microalgae as feedstock for the production of biofuels by torrefaction and gasification, hydrothermal liquefaction (HTL) and pyrolysis, the possibility to avoid the feedstock can be avoided [2]. In the last few years, the use of whole microalga as feedstock, instead of the biomass obtained from the starting matrix. Alternatively, a common approach is to use the biomass then hydrothermal treatment of the residue obtained from the starting matrix [3]. Due to the strong dependence of the product yields on species as well as on the growth conditions, the choice of the species, concentration, temperature, possible contaminants, and the need to guarantee a conversion plant suitable to process large quantities of biomass. This aspect is still more important if considered from the point of view of the desirability for biofuels production in general.

However, the use of microalgae as feedstock for the production of biofuels has been used for hydrothermal liquefaction (HTL) and pyrolysis. In fact, microalgae and there are only few examples of continuous layout for the hydrothermal conversion of microalgae under these conditions. To achieve the desired continuous layout, it is necessary to take into account, such as the use of materials resistant to corrosion, the need to perform the same time, the use of a preheating system for the feedstock, and the use of a catalyst with that containing the biomass to be converted. The use of a continuous layout (gas mixture, aqueous and organic liquid phases) for the production of biofuels by performing experiments with real biomass. The use of a continuous layout for the production of biofuels by feeding glucose and glycerol as model feedstocks for the production of microalgae respectively.

In the present work we will also show the results of the experiments performed with *Nannochloropsis gaditana* as feedstock. The results of the experiments performed in the different phases were obtained and the effect of the different parameters on the yields and on the composition of the produced phases were estimated.

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