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 $RhCl_2$, $NiCl_2$ and $CoCl_2 \cdot 6H_2O$ 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 $RhCl_2$ 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 $RhCl_2$ 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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[2]. T.M. Brown, P. Duan and P.E. Savage, *Energy e Fuel 24*, **2010**, 24, 3639-3646.

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A continuous reaction

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Among oleaginous crops for
their high lipid content, high
possibility to be cultivated in
torrefaction and gasification,
the feedstock can be avoided [2].
whole microalga as feedstock,
from the starting matrix.
then hydrothermal treatment
matrix [3]. Due to the strong
species as well as on the
concentration, temperature,
guarantee a conversion plant
This aspect is still more
desirable for biofuels production
been used for hydrothermal
microalgae and there are
continuous layout for the
conditions. To achieve the
account, such as the use of
the same time, the use of a
with that containing the biomass
(gas mixture, aqueous and
performing experiments with
by feeding glucose and glycerol
microalgae respectively.
In the present work we will
Nannocholoropsis gaditana as
phases were obtained and
and on the composition of

[1]. L. Gouveia, A.C. Oliveira,
[2]. J. Cheng, R. Huang, T.
[3]. V. Patil, K.-Q. Tran, H.R.

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