## Catalytic hydrothermal liquefaction of municipal sludge in subcritical water

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In the last decades, the dwindling of the fossil sources of energy coupled with the growth of energy demand and of waste production prompted the research in developing novel industrial technologies for renewable energy production and waste valorization. Hydrothermal liquefaction (HTL) is a good alternative to transform wet biomasses as microalgae, macroalgae, agricultural residues, food waste, and municipal sludge (MS) into value-added products with high efficiency and decreasing the amounts that has to be disposed of.

HTL takes place in an aqueous environment, without the energy cost of drying the biomass, at 300-400°C and pressure of 10-40 MPa [1,2]. At these operative conditions, an integral degradation of wet biomass produces a bio-oil termed biocrude and other C-containing products i.e. a solid residue, a gaseous phase rich in  $CO_2$  and an aqueous phase with soluble organics.

The development of the process to the industrial scale is hindered by many challenges related both to the heterogeneous nature of the raw material and the complexity of the phase behavior downstream of the process and the poor quality of the biocrude produced as fuel precursor. This work aims to investigate the potentiality of catalytic HTL to obtain a biocrude more competitive as fuel precursor.

We have studied catalytic HTL of MS in a stirred AISI 316 high-pressure batch reactors at 325 °C and 30 min as reaction temperature and time using NiMo/Al<sub>2</sub>O<sub>3</sub>, CoMo/Al<sub>2</sub>O<sub>3</sub> and activated carbon felt as catalysts and formic acid (FA) as liquid hydrogen donor. Optimized work-out procedures were used to separate and quantify the products with the aim to decrease the amount of not detected mass [3]. With adopted methods the formation of an hydrocarbon fraction (HC) recovered from the biocrude, was detected in the presence of the catalysts. This result indicates that tested catalysts promote the in-situ up-grading of the produced biocrude.

Furthermore, the addition of FA as liquid hydrogen donor allowed us to achieve higher H/C and HHV of biocrude as it was possible to increase the biocrude yield at more than 50% with energy recovery approaching 100%.

Collected results suggest that use of catalysts can increase the yield and quality of biocrude in the HTL of municipal sludge.

[1] Yeh, T.M. et al., J. Chem.Technol Biotechnol., 2012, 88.

- [2] Biller, P., Ross, A.B., Bioresour. Technol., 2011, 102, 215-22.
- [3] Prestigiacomo, C., et al., Energy, 2020, 201, 117606.