**Hydrothermal liquefaction of sewage sludge: towards the effects of transition metals in the presence of homogeneous hydrogen producers**

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**1.Introduction**

Waste carbonaceous matrices, such as sewage sludge (SS) seem to have a great potential, because they are namely costless matrices compared to the microalgae and hydrothermal liquefaction (HTL) can be considered an interesting route to dispose and valorize them [1-5]. However, SS are characterized by high amount of non-biogenic fractions, such as plastics, salts and metals. In particular SS contains a high amount of inorganics [5], such as Al, Ba, Ca, Cr, Cu, Fe, Ni, K, Mg, Mn, Na, P, S, Ti, Zn, Si which are distributed in the products at the end of the reaction. The presence of heavy metals represent a big challenge for the implementation of HTL on the industrial scale as they can affect product quality and/or the performances of the process. One of the hurdles of the transfer of the HTL from the lab to an industrial plant fed by SS is represented by the fact that the metals in the feedstock can be transferred to the biocrude (BC) affecting its placing on the market [6]. Some studies analyzed the distribution of metals in the phases produced by HTL of real SS and the main evidence was that the higher the reaction temperature, the higher is the fraction of metals entrapped in the produced BC [5, 7]. However, metals can positively affect the process behavior acting as catalysts [5]. Among the metals contained in residual biomass [6-8], Ni, Zn and Fe were selected as model compounds in this work and a systematic investigation was conducted to study their effect, individually and combined with homogenous hydrogen producer as formic acid (FA) and KOH, on the biocrude yield and quality.

**2. Methods**

SS provided by the wastewater treatment plant of Karlsruhe, Germany were used in HTL experiments. FA and KOH were selected as homogeneous additives. A slurry at 10%w/w of dry SS was used as feedstock and the metal powders of Ni, Fe and Zn and the homogeneous additives were added at 10%w/w (based on dry SS). Batch runs were performed at 350°C for 10 min in an AISI 316Ti high-pressure reactor with an internal volume of 25mL, processing 10 g of slurry in each experiment. A sand bath was used to heat the reactor until 350°C. The procedures adopted to separate the products downstream of HTL experiments were an optimization of those used in a previous work [2].

**3. Results and discussion**

Interesting results were obtained with Zn that when used alone or in the presence of KOH increased the cumulative biocrude yields from 29 to 42 and 46 % w/w respectively and resulted in energy recoveries (ER) higher than 100%. These results were accompanied by an improvement of the values of H/C and O/C of BC from 1.61 to 1.81 and from 0.13 to 0.06 respectively when Zn was added to the reaction mixture. Moreover when Zn was used with FA it strongly enhanced gas yield from 10 to 66% w/w leading to a significant hydrogen production that was determined to be generated mainly from SS or water. In fact, it is known that Zn could react with sub/supercritical water promoting the production of molecular hydrogen inside the reactor [9].Ni chips were used in two consecutive HTL experiments with no decrease of BC yields and ER.

**4. Conclusions**

According to results obtained in our study Zn, Ni and Fe powders used alone do not affect negatively the quality of BC and their effect can be improved by adding KOH or FA.

More in detail, it was found that:

- Zinc alone and in the presence of KOH, can promote improvement of BC yield and quality in terms of ER, H/C and O/C,

- Iron added in the presence of FA, was active in producing a BC with higher H/C and lower O/C, even it does not exhibit any positive effect on BC yield;

- Nickel in the metallic form was found stable in the HTL reactor after two HTL cycles.

Collected results suggest that metallic powders can be good catalyst to improve yield and quality of BC in the HTL of SS.

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