**Hydrothermal co-liquefaction of sewage sludge and formic acid**

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**Highlights**

* Addition of HCOOH allows achievements of higher biocrude yields at higher biomass loadings.
* Addition of HCOOH increases the H/C molar ratio of biocrude.
* Detected production of light hydrocarbons from hydrothermal co-liquefaction of sewage sludge and formic acid.

**1. Introduction**

The biocrude produced by non-catalytic hydrothermal liquefaction (HTL) has a too high heteroatom content to be used directly as a fuel [1-3]. Several studies found that different H2 initial pressures during HTL experiments were ineffective in improving the biocrude yield [4-6], nevertheless it was observed that higher initial pressures of H2 brought an improvement of the concentration of light compounds in the biocrude, decreasing the average molecular weight of biocrude oil. To date H2 is mainly generated from fossil sources and realization of a possible hydrogen economy from alternative sources presents many challenges. The use of a liquid hydrogen storage media could represent for the HTL process an alternative solution to avoid the mass transport resistance associated to gaseous H2, furthermore Biller and Ross [7] observed that the addition of selected organic acids had similar effects than the addition of molecular H2. According to these premises, we studied the influence of formic acid as hydrogen donor on the yield and quality of the biocrude produced by HTL of sewage sludge (SS). Formic acid was selected because it can decompose to hydrogen and carbon dioxide under mild conditions [8] and it can be produced by electrochemical reduction of carbon dioxide, an appealing process to capture atmospheric carbon dioxide under the form of a useful chemical [9].

**2. Methods**

SS provided by WWTP of Palermo, Italy (A.M.A.P. spa) and formic acid (Alpha Aesar 97 vol%) were used in HTL experiments. CoMo/Al2O3 (Albemarle, KF1022 cylindrical units) was used as catalyst. Acetone and cyclohexane (Sigma Aldrich, analytical grade) were used to recover the biocrude. A stirred stainless steel reactor with a volume of 30 mL was filled with 10 g of slurry changing the SS loading from 10 to 20 and 30 % w/w, formic acid loading was fixed at 1.8 % w/w. When used catalyst was added with a concentration of 10 %w/w with respect to SS. Set point temperature was reached by a software controlled ceramic heater with a typical heating rate of 13 °C/min and the reaction time was considered to start when the set-point temperature was reached. The procedures adopted for products separation after HTL tests are the result of the optimization of the methods reported in our previous work [10]. The yields of the products were expressed in dry ash free (daf) form (i.e. referred to the organic content of the feedstock) as reported in the literature [10,11]. All experiments were repeated twice and mean values are reported. Elemental analyses of the biocrudes was performed in a Perkin Elmer 2400 series II elemental analyzer. Biocrude yield was determined after stripping of recovery solvents (daf %vw/w). Light hydrocarbons evaporated during stripping were condensed in a cold trap. Their relative amounts were estimated in term of fractional chromatographic areas (A%) after gas–chromatography analyses of the liquid (GC AutosystemXL Perkin Elmer equipped with a column Zebron ZB-FFAP).

**3. Results and discussion**

At a SS loading of 30% w/w, the biocrude yield increased from 39±2% w/w to 55±2% w/w when formic acid was added. Furthermore an increase of H/C molar ratio (from 1.54 to 1.96) was observed in the biocrudes produced in the presence of formic acid. The work herein, starting from the observed results found in literature, tried to evaluate the effect of formic acid on the performances of the hydrothermal co-liquefaction process characterizing also the produced light compounds. A technique to recover and to to trap solvent vapours during the stripping process of the biocrude phase was optimized and light hydrocarbons (C10-C18) were effectively detected by gas-chromatography analyses of the trapped phases. By means of this technique cumulative chromatographic area associated to light hydrocarbons increased from 7 to 32% when HCOOH was added at 10% w/w loading of SS.

**4. Conclusions**

Formic acid, obtainable from electrochemical reduction of carbon dioxide, showed promising result in improving the yield and the quality of biocrude generated from HTL of SS. Furthermore in the presence of formic acid, an increase of produced light hydrocarbons compounds was observed, and a better closure of the mass balance was obtained.

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