

Real sludge from a wastewater treatment plant as alternative to microalgae as feedstock of hydrothermal liquefaction of biomass to biocrude.

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ABSTRACT

In this work *Chlorella vulgaris* and real sewage sludge (SS) were compared in batch hydrothermal liquefaction (HTL) experiments performed at 598 and 648 K with 0 and 30 min as reaction time. Even if *C. vulgaris* and SS are different in terms of organic content and higher heating value (HHV) they gave similar biocrude yields. NiMo/Al₂O₃ (KF851) and CoMo/Al₂O₃ (KF1022) commercial catalysts tested at 598 K for 30 min, enhanced the quality of the synthesized biocrude by decreasing its oxygen and sulfur content. A new product phase was detected when SS were used as feedstock probably arising from microplastics trapped in the sludge. Real SS constitute a promising and costless alternative to microalgae as feedstock for the HTL processes.

INTRODUCTION

Sewage Sludge (SS) can be considered an interesting and costless renewable carbonaceous feedstocks to produce bio-fuels or value added chemicals, in substitution of agricultural and forestry wastes or microalgae [1]. Due to the growth of world population, the total amount of organic waste materials is going to increase, thus offering a costless feed for the production of biofuels [2,3]. In this context SS obtained from wastewater treatment plants (WWTPs) as residues of the primary and biological treatments are continuously generated and their disposal represents an operating cost of 80-140 €/ton [4]. Hydrothermal Liquefaction (HTL) is considered an interesting process to produce a liquid biofuel [5], termed biocrude, obtained by hydrolytic cleavage of bioconstituents of wet biomasses and by the reforming of depolymerization products to simple organic molecules. The biocrude is considered the main product of HTL and it is obtained together with an aqueous phase, a gaseous phase and a solid residue as co-products. The biocrude is typically very viscous at room temperature and is characterized by oxygen, nitrogen and sulfur contents too elevated for its direct utilization as fuel [6]. So, to make it suitable as bio-fuel it must be further upgraded by hydrodeoxygenation (HDO),

hydrodeazotation (HDN) and hydrodesulfurization (HDS) in the presence of suitable catalysts [7,8,9]. All these hydrotreating processes are more expensive the higher the average molecular weight and the heteroatom content of the biocrude [8]. We have recently performed a techno-economic analysis of a solar assisted biorefinery process for the HTL of microalgae. We found that one of the main huddles for the economic sustainability of the process was related to the high cost of the raw material [10]. So the use of SS as feedstock for the production of biocrude could be highly interesting to improve the economic profitability of the HTL process and of WWTPs [11,12]. Aim of this work was to investigate HTL processes comparing the performances of SS and *C. vulgaris* as different carbonaceous feedstocks using different types of commercial catalysts in aqueous HTL environment.

MATERIALS AND METHODS

C. vulgaris from a4f company and real SS provided by the AMAP s.p.a. waste water treatment plant in Palermo (Italy) were used as feedstock for the HTL experiments. A sample of sludge was dried for 24h at 378 K and the organic content was determined after calcination for 6 h at 823 K. Real sludge were stored at 255 K, then thawed and utilized. Cyclohexane (Sigma Aldrich, analytical grade) and acetone (VWR, $\geq 99.9\%$ technical) were used as solvents to recover the biocrude produced during the hydrothermal reactions. The commercial catalysts KF 851 quadralobe shaped pellets (NiMo/Al₂O₃) and KF 1022 cylindrical units (CoMo/Al₂O₃), both provided by Albemarle, were used as received. Trichloromethane (J.T. Beker, HPLC grade) was used to recover and isolate the additional organic phase. The HTL tests were carried out in a 31 mL home-made 316 SS batch autoclave reactor constructed from 3/4 in. Swagelok® VCR connector and caps. In each HTL experimental run an aqueous slurry (10 wt % of dry feedstock concentration) was poured into the reactor in such amount to fill 1/3 of the reactor volume. When catalysts were used, they were added with a concentration of 10 wt% with respect to the initial dry biomass. The experimental apparatus was constituted by a software controlled (Labview system design Software, National Instruments) ceramic heater (composed by two Watlow ceramic fiber semi-cylindrical units, 450 W each) equipped with a 316 stainless steel holder properly designed to place the reactor in the middle of the length of the heater. Typical heating rate was 13 K/min and the reaction time was considered to start when the set-up temperature was reached. At the end of the reaction, the reactor was extracted from the oven by a pulley-assisted lifting system and quickly cooled down with tap water shower. After cooling the reactor was connected to a previously evacuated gas expansion system to collect the produced gas phase using an Agilent Technologies 7890B GC-TCD. The effective mole percentage of each gas produced during the reaction was calculated as the ratio between the GC determined moles of each gaseous component N_i , as obtained from calibration curves, and the total moles of produced gas N_{tot} estimated by the ideal gas equation of state since final pressure in the gas expansion system was always lower than 0.2 MPa.

$$\text{Gas concentration [mol\%]} = (N_i/N_{tot}) \times 100 \quad (1)$$

Molar fraction of produced gas compounds were determined with an average standard deviation of 2%. The procedure adopted for products separation after HTL tests with *C. vulgaris* and SS was similar to that reported by Savage et al. [13,14]. The yields of the products were expressed in dry ash free (daf) form (i.e. referred to the organic content of the feedstock) as follows:

$$\text{Yield}_{(daf)}(\text{wt\%}) = (\text{mass}_{daf} \text{ of product} / \text{mass}_{daf} \text{ of the feedstock}) \times 100 \quad (2)$$

When catalysts were used, their masses were subtracted from that of the dried solid residue and its yield was determined calcinating a sample of collected virgin solid residue (i.e. without catalyst).

All experiments were repeated twice to determine the reproducibility and reported values are mean values. CHNS elemental composition analyses were made by LNEG and the HHV of each type of biomass was estimated by the Dulong formula:

$$HHV(MJ/kg) = 0.3383 C + 1.443 (H - O/8) + 0.095 S \quad (3)$$

The yield of water soluble products (WSP) was estimated using a sample of 2 mL of recovered aqueous phase collected in a glass vial. The sample was dried overnight at 333 K and the residue was weighed. The vial containing the residue of the dried WSP was then calcinated in a furnace at 823 K for 6h to estimate the dry ash free yield. The cake formed after *vacuum* filtration of the products collected from the reactor was dried at 333 K overnight and then weighted to estimate the yield. The dried cake was scraped using a spatula and transferred into two ceramic crucibles, which were inserted into a furnace at 823 K for 6h to perform calcination of the residue and estimate the organic yield (daf wt%). Finally, the stripped and stabilized mass of biocrude was used to determine its yields (daf wt %). The biocrude HHV was estimated using Dulong formula. The yield of volatiles was obtained as complement to 100 of the sum of the yields of the four products yields. This fraction takes into account the compounds lost during the stripping of the biocrude phase, or drying of the aqueous and solids phases as well as the losses when transferring samples according to information reported in the literature [13,14]. An additional phase (ADP) was obtained when SS was used in HTL experiments. Some analyses were made to investigate its nature. Its solubility in trichloromethane was tested. The same procedure adopted for *vacuum* filtration of aqueous phase was adopted for the dewatered ADP, to separate polar from not polar compounds which form a cake on the nylon filter. FT-IR analyses (FT-IR Spectrum Two Perkin Elmer) of the polar and non-polar fractions of the ADP were performed using KBr pads (Sigma Aldrich, anhydrous, powder, 99.999% trace metals basis).

RESULTS

The reaction temperature is an important operative parameter in the HTL of microalgae. We compared the performances of HTL of *C. vulgaris* and SS at 598 and 648 K using 0 min (i.e. performing only the heating process inside the reactor) and 30 min as reaction time. Experiments were initially carried out without added catalysts.

In Table 1 the results of tests at different temperatures and reaction times using the two different biomasses are reported. The kinetic severity factor defined by Overend et al. [15] was used to analyze the collected experimental results. To estimate this parameter we have also considered the temperature profile during the heating of the reactor by numerical integration of the equation proposed by Faeth et al. [16] (Faeth et al., 2013):

$$R_0 = \int_{t_0}^{t_f} \exp\left(\frac{T_{(t)[^{\circ}C]} - 14.75}{100[^{\circ}C]}\right) dt \quad (4)$$

With both feedstocks, the highest biocrude yield was obtained at an intermediate value of the investigated kinetic severity R^0 . With *C. vulgaris* the maximum yield was 31.9 wt% and it was obtained at 598 K after 30 minutes corresponding to $\text{Log}(R^0)$ of 8.13. When SS was used the maximum yield was 35.3 wt% and was reached at 648 K stopping the reaction soon after the heating stage (0 min) corresponding to $\text{log}(R^0)$ 8.53. When higher severity factors were adopted, the reduction of biocrude yields was accompanied by higher fractions of missing compounds. In **Erreur ! Source du renvoi introuvable.** the Energy Recovery (ER) obtained in the experiments is shown, defined by the equation:

$$ER (\%) = \frac{HHV \text{ of biocrude oil} \times \text{mass yield of biocrude oil}}{HHV \text{ of feedstock}} \times 100$$

This parameter indicates how the process is effective in concentrating the energy content of the initial biomass feedstock in the obtained bio-oil. ER higher than 50% were obtained with both biomasses. In the case of *C. vulgaris*, the highest value of this parameter was obtained at the lowest adopted severity factor because of an H/C molar ratio of 1.63.

Table 1: Comparison of products yields (dry ash free daf wt %) and elemental analyses of biocrude obtained from HTL experiments of *C. vulgaris* and SS (10 wt% dry feedstock).

| Feed | T (K) | t (min) | Log (R ₀) | Products yields (daf wt%) | | | | H/C | O/C | N/C | HHV (MJ/kg) | ER (%) |
|--------------------|-------|---------|-----------------------|---------------------------|------|------|------|------|------|------|-------------|--------|
| | | | | BC | Gas | WSP | SR | | | | | |
| <i>C. vulgaris</i> | 598 | 0 | 6.95 | 28 | 2.6 | 24.9 | 13 | 1.63 | 0.18 | 0.03 | 34.73 | 55.8 |
| | 598 | 30 | 8.13 | 31.9 | 7.3 | 16.2 | 2.6 | 1.85 | 0.42 | 0.02 | 26.52 | 48.6 |
| | 648 | 0 | 8.37 | 24.7 | 9 | 16.8 | 2.6 | 1.35 | 0.18 | 0.02 | 33.03 | 46.7 |
| | 648 | 30 | 9.60 | 23.5 | 17.6 | 7.2 | 1.5 | 1.40 | 0.20 | 0.02 | 32.38 | 43.6 |
| SS | 598 | 0 | 6.89 | 26.3 | 4.9 | 3.3 | 18.8 | 1.52 | 0.34 | 0.00 | 27.73 | 41.8 |
| | 598 | 30 | 8.06 | 27.0 | 11.8 | 14.0 | 15.1 | 1.43 | 0.16 | 0.02 | 34.58 | 34.6 |
| | 648 | 0 | 8.53 | 35.3 | 9.8 | 8.7 | 12.3 | 1.39 | 0.21 | 0.00 | 32.23 | 65.2 |
| | 648 | 30 | 9.64 | 22.6 | 9.7 | 2.8 | 10.3 | 1.35 | 0.12 | 0.04 | 35.23 | 45.7 |

BC: biocrude; WSP: Water Soluble Products; SR: solid residue

When SS were used, the highest ER was obtained when the highest biocrude yield was achieved even if the H/C ratio decreased to 1.39. Indeed, from elemental analysis we found that H/C molar ratio in the biocrude synthesized from SS decreased monotonically with the global severity. Composition of gaseous products collected in all experiments are mainly constituted by CO₂. In the case of gas phase obtained from HTL of *C. vulgaris*, especially when liquefaction was carried out at 598 K, molecular nitrogen was clearly detected in the gas phase that must be ascribed to denitrification of biomass since purging of the reactor and of the gas sampling valves was performed using Ar as inert gas. Nitrogen was not detected or was present in very small amount in gaseous mixtures generated during the HTL of SS probably because of the different nature of proteins incorporated in the biomass. The main result of this set of experiments is that similar biocrude yields and quality in term of elemental analysis and HHV can be obtained with both biomasses thus confirming that sewage sludge are a viable and costless alternative to microalgae as feed for HTL processes.

The biocrude obtained from HTL of both *C. vulgaris* and SS is characterized by an high oxygen content that make it unsuitable as a fuel unless it is upgraded by hydroprocessing (Tab. 1). To make less expensive the upgrading process it would be useful to synthesize a biocrude characterized by high H/C and low O/C molar ratios. To pursue this result we studied the effect of two commercial

catalysts on the performances of the HTL of *C. vulgaris*. and SS and on the composition of the corresponding biocrude.

When CoMo and NiMo based catalysts were used in the HTL of *C. vulgaris* we observed a marked change of the oxygen content of the biocrude highlighted by the reduction of the O/C mole ratio from 0.42 in the catalyst-free test to 0.21 and 0.19 with KF 851 and KF 1022 catalysts respectively (Table 2).

Table 2: Comparison of products yields (dry ash free daf wt %) and elemental analyses of biocrude obtained from HTL experiments of *C. vulgaris* and SS. Reaction conditions: T=598 K and 30 min as reaction time. Biomass 10 wt% concentration in the slurry, catalyst 10 wt% with respect to biomass.

| Feed | Catalyst | Dry ash free (wt %) | | | | H/C | O/C | N/C | S/C | HHV (MJ/kg) | ER (%) |
|--------------------|----------|---------------------|------|------|------|------|------|------|--------|----------------|--------|
| | | BC | Gas | WSP | SR | | | | | | |
| <i>C. vulgaris</i> | none | 31.9 | 7.3 | 16.2 | 2.6 | 1.85 | 0.42 | 0.02 | 0.0012 | 26.52 | 48.6 |
| | KF 851 | 29.3 | 8.6 | 13.0 | 9.8 | 1.33 | 0.21 | 0.06 | ND | 30.61 | 46.4 |
| | KF 1022 | 35.3 | 10.2 | 14.3 | 5.2 | 1.32 | 0.19 | 0.06 | ND | 31.50 | 57.5 |
| SS | none | 27.0 | 11.8 | 14.0 | 15.1 | 1.43 | 0.16 | 0.02 | 0.0052 | 34.58 | 34.6 |
| | KF 851 | 23.9 | 9.0 | 6.4 | 19.3 | 1.40 | 0.11 | 0.02 | 0.0042 | 37.34 | 37.3 |
| | KF 1022 | 20.8 | 8.6 | 7.6 | 18.0 | 1.38 | 0.12 | 0.04 | 0.0047 | 35.56 | 35.6 |

BC: biocrude; WSP: Water Soluble Products; SR: solid residue. ND=not detectable

This effect was accompanied by removal of S at levels below the detection threshold of the elemental analyzer (Table 2). For what concern the biocrude yields while KF 851 catalyst gave average yields of 29.3 wt% quite close to that obtained in the absence of catalyst (31.9 wt%), a significant increase in the value of this parameter was obtained with KF 1022 catalysts that gave 35.3 wt% average biocrude yields.

The same catalysts were tested with SS at the same operative conditions. In this set of experiments all catalysts gave similar results for oxygen removal leading to a biocrude with O/C 0.11 -0.12 instead of the 0.16 obtained in the pure thermal process. When SS was used, CoMo and NiMo based catalysts were not effective in S removal and biocrude yields decreased with respect to the not catalyzed test. HTL of SS was performed using the same procedure of product separation of the microalgae. However, when catalysts were used in the HTL of SS, a new product denoted by the acronym ADP, in addition to biocrude, aqueous phase, solid residue and gas, was collected from the reactor even if in amounts lower than 5 wt% with respect to the dry mass of SS. This product, that seemed heterogeneous, was found to be soluble in acetone like biocrude but insoluble in trichloromethane. Indeed by drying a sample at 378 K overnight, we estimated a moisture content of 75 wt%. To better understand the nature of ADP its *vacuum* filtration was performed with a procedure similar to that adopted to separate solid residue from other liquid products of the HTL process. After filtration two different phases were obtained: a solid wax retained by the filter and a colorless and viscous liquid phase. FT-IR analyses were made on the solid wax and on initial product (previous drying and after drying process). From these analyses we found that poly(vinylchloride) derivative could be a component of this new product.

Mahon et al. reported that up to 30 wt% of the organic content of the mixed sludge could be constituted by microplastics. Their presence is considered a technological problem for the WWTPs

because they are made of cloth fibers, polyamides and polyesters, polyvinylchloride lost during cleaning process, plastics contained in scrubs soap or toothpastes and they end up in the sewers. For these reasons, we hypothesized that the new product phase derives from microplastics trapped in SS.

CONCLUSION

This experimental work was useful to explore the potential that HTL of SS could have. However the HTL conversion of SS needs more investigation. We found that SS are very challenging for their treatment also because of the presence of microplastics whose effect on the biocrude quality is still unclear. These results will be object of further investigation because if the hydrothermal treatment could convert or segregate microplastics in a different phase preventing them to reach the environment it would increase its utility. The catalytic process is one of the major challenges in HTL process of biomasses, in this study we found that the commercial Albemarle catalysts (KF 851 and KF 1022), commonly used in hydrotreating of kerosene and diesel, showed good activity in removing S and O from the biocrude.

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