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Quality Enhancement of a Sewage Sludge Derived Biocrude Under Hydrothermal Conditions: an Explorative Study Using Zero-valent Metals as Hydrogen Generators

Alessandro Amadeia,\*, Riccardo Tuffib, Doina De Angelisb, Benedetta de Caprariisa, Martina Damiziaa, Paolo De Filippisa, Marco Scarsellaa

a Università di Roma La Sapienza, Via Eudossiana, 18, 00184, Roma, Italia

b Department for Sustainability, ENEA, Casaccia Research Center, Via Anguillarese 301, S. Maria di Galeria, 00123 Rome, Italy

alessandro.amadei@uniroma1.it

Hydrothermal liquefaction (HTL) is one of the most suitable processes for the thermochemical conversion of moist biomass to produce liquid biofuel precursors. Despite its potential, this technology is still not mature enough to be extensively applied, mainly due to the inadequate quality of the obtained biocrude. Its high viscosity and the excessive presence of heteroatoms as nitrogen and oxygen strongly hinders the application of HTL biocrude as drop in fuel, leading to the necessity of a downstream upgrading process. Conventional upgrading methods often require harsh conditions and significant consume of hydrogen, which reduce the overall sustainability of the process. This study aims to explore an alternative upgrading approach based on the redox potential of zero-valent metals (ZVMs) to generate hydrogen in situ under hydrothermal conditions, without external hydrogen supplies. The upgrading experiments were conducted on biocrude obtained from the HTL of digested sewage sludge, using Fe and Zn as hydrogen generators. While hydrothermal conditions alone appeared to notably reduce nitrogen and oxygen content, by 20 % and 35 % respectively, ZVMs appeared to enhance the upgraded biocrude recovery after the process. GC-MS analysis also revealed interesting results when using ZVMs, which produced a significant decrease of fatty acids concentration, increasing their corresponding reduction products, as aldehydes, alcohol and aliphatic hydrocarbons. These results indicate a potential exploitation of ZVMs conditions to improve hydrothermal upgrading processes.

* 1. Introduction

Hydrothermal liquefaction (HTL) is among the most promising thermochemical processes to produce liquid biofuel precursors from biogenic feedstocks. It operates in presence of hot pressurized water in its subcritical region, typically at temperature of 250 ÷ 374 °C and pressures up to 22 MPa (Gollakota et al., 2018), under which liquid water exhibits a reduced dielectric constant, lower viscosity and increased ionic dissociation product Kw compared to ambient conditions (Zhi et al., 2024). These characteristics produce a reducing environment with minimal mass transfer limitations, enabling the conversion of biomass into non-polar molecules, such as hydrocarbons, using water as solvent, that is unexpensive, non-toxic and highly available in nature. The possibility of using biomass moisture as a reactant in the process is a key advantage of HTL among other thermochemical processes, eliminating the need for energy-intensive dewatering pretreatments. Along with the biocrude, the valuable oily product of the HTL process, three byproducts are obtained: a gaseous phase (mainly CO2), an aqueous phase enriched with polar organic compounds, and a solid residue. Although biocrude has a moderate heating value, typically ranging between 30 and 40 MJ kg-1 (Chand et al., 2019), its high viscosity and its excessive content of heteroatoms, as nitrogen, sulfur and oxygen, render it unsuitable as drop in fuel. To meet fuel specifications, a series of upgrading operations, including hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO), is essential. These processes rely on hydrogen, supplied directly or via hydrogen donors or generators. Among other heteroatoms, nitrogen removal appears particularly challenging, as nitrogen-containing heterocyclic compounds, formed during HTL via amino acid cyclodimerization and Maillard reactions, are often recalcitrant to HDN process (Castello et al., 2024). This poses a barrier for biofuel production from protein-rich renewable biomass, such as sewage sludge and food waste, which, despite their high nitrogen content, are otherwise promising feedstock for HTL. The topic of bio-oils upgrading was extensively studied in scientific literature. Yet, the best results in the remotion of heteroatoms are still obtained via hydrotreating. Castello et al. (2024) developed a continuous catalytic hydrotreating system that managed to obtain complete removal of oxygen and a maximum nitrogen reduction of ~ 90% on a microalgae derived HTL biocrude, using relatively severe conditions (400 °C, H2 consumption of ~ 45g/kg of oil). Moderate results were also obtained by Wang et al. (2022) by combining gaseous H2 with hydrogen donor reactants in a batch catalytic hydrotreating process, resulting in maximum oxygen and nitrogen removal of 77.8% and 56.4%, respectively. Other studies explored the effects of in-situ hydrogen donors or producers during HTL, without supplying external hydrogen. For example, (Li et al., 2020) conducted batch liquefaction of macroalgae using ethanol as solvent and formic acid as in-situ hydrogen donor, achieving an increase in biocrude yield and HHV, and reductions of oxygen and nitrogen of 47% and 45%, respectively, compared to blank tests. (Tai et al., 2021) studied the effects of zero-valent iron and zinc, as in-situ hydrogen producers by their redox potential in presence of water during HTL of oakwood. They observed significant increase in biocrude yields, moderate H/C ratio improvements and reductions in O/C ratios (~ 12% for both Fe and Zn) compared to blank tests. In a follow-up study, (Hamidi et al., 2022) investigated the effects of Fe and Zn as hydrogen generators during hydrothermal upgrading of oakwood-derived HTL biocrude, using supported Ni as catalyst. While mild upgrading results are reported, with an achieved maximum reduction of O/C molar ratio of 25.7%, the study did not address nitrogen removal, due to the lignocellulosic nature of the feedstock used. The scope of this work is to extend the research of Hamidi et al. (2022) to protein-rich biomass, as municipal sewage sludge, to investigate the fate of nitrogen containing molecules, during hydrothermal upgrading in presence of zero valent Fe and Zn as in-situ hydrogen generators. This study also monitors the fate of the main detected key compounds involved in the process, trying to recognize differences that can be addressed to the use of ZVMs in the reaction medium.

* 1. Materials and methods
     1. Materials

Anaerobically digested sewage sludge was sourced from a municipal wastewater treatment plant in central Italy and used as the feedstock for this study. Acetone (≥ 99.5%) was purchased by Honeywell Chemicals and used as received. Before processing, the sludge was oven-dried at 105 °C for 24 hours, following a widely used procedure based on ASTM D4442-07 (Chen et al., 2014), and characterized through proximate and ultimate analysis. Proximate analysis was conducted via thermogravimetric analysis (TGA) using a Mettler-Toledo TGA/DSC1, measuring the mass fraction of moisture, volatile matter, fixed carbon and ash in the dried sludge. Ultimate analysis was performed with a Eurovector EA3000 elemental analyzer, using sulphanilamide as CHNS standard. The higher heating value (HHV) was estimated from the elemental composition using Dulong’s formula (Wang et al., 2022), reported in Eq(1).

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|  | (1) |

The results of the proximate analysis are reported in Table 1, while the results of ultimate analysis and calculated HHVs are reported in Table 2.

Table 1: Proximate analysis of the dry feedstock

|  |  |  |  |
| --- | --- | --- | --- |
| Moisture (% wt.) | Volatile matter (% wt.) | Fixed carbon (% wt.) | Ashes (% wt.) |
| 0.9 ± 0.2 | 52.4 ± 0.2 | 9.9 ± 0.2 | 36.8 ± 0.3 |

Table 2: Ultimate analysis and calculated HHV of the dry feedstock

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| C (% wt.) | H (% wt.) | N (% wt.) | S (% wt.) | O\* (% wt.) | HHV (MJ kg-1) |
| 31.62 | 4.35 | 5.00 | 0.43 | 21.80 | 13.01 |

\* Calculated by difference (O % = 100 % – C % – H % – N % – S % – ashes %)

* + 1. Experimental section

HTL experiments for biocrude production from sewage sludge were conducted in batch using a cylindrical stainless-steel autoclave with an internal volume of 250 mL equipped with a mechanical stirrer and an external heating resistance. The internal temperature was regulated by a PID controller connected to a thermocouple, adjusting the current in the heating resistance. This setup allowed the system to be heated with an average heating rate of ~ 5 °C/min. The autoclave was loaded with 30 g of dry sludge and 150 mL of deionized water, achieving a water-to-dry feedstock mass ratio of 5:1. The autoclave was closed without pre-pressurizing it, and the reaction was performed at a set temperature of 280 °C, the maximum allowable temperature to prevent leakage from the used autoclave, held isothermally for 30 minutes. After reaction, the autoclave cooled down at ambient temperature and the valves were opened to release the gaseous phase over 20 minutes. The aqueous phase was then separated from the water-insoluble slurry by gravitational filtration. The slurry was placed in a Soxhlet thimble, and biocrude was extracted using a Soxhlet apparatus with 150 mL of acetone. The extraction was carried out for 4 hours and the acetone was subsequently separated by vacuum evaporation, while the solid residue was oven dried. This procedure yielded approximately 5 g of biocrude for subsequent upgrading tests. Upgrading tests were conducted following the procedure of Hamidi et al. (2022). A stainless-steel autoclave with an internal volume of 10 mL was loaded with 1 g of biocrude and 5 mL of deionized water, maintaining a water-to-dry feedstock mass ratio of 5:1. Additionally, 0.5 g of zero-valent iron (Fe) or zinc (Zn) was added, achieving a ZVM-to-dry feedstock mass ratio of 1:2. Two blank tests were performed for comparison: one with 1 g of biocrude and 5 mL of water, and another with 1 g of dry sludge and 5 mL of water. After sealing, the autoclave was mounted on a mechanical stirrer and immersed in a pre-heated fluidized sand bath at 330 °C. This system enabled rapid heating (~ 110 °C/min), minimizing biocrude repolymerization to acetone-insoluble compounds, which is more pronounced at lower temperatures, due to carbonization mechanisms. The experimental setup is described with a higher level of details in our previous work (Amadei et al., 2024). The upgrading reactions were carried out at 330 °C for an isothermal holding time of 3 hours, consistent with Hamidi et al. (2022). After the reaction, the autoclave was quenched in a cold-water bath to room temperature. Product separation followed the procedure outlined in our previous work: acetone was used to extract the upgraded oil from the water-insoluble slurry, which also contained the reacted ZVMs and the repolymerized biocrude. The product yields were determined gravimetrically after their separation, while the water-soluble organic fraction in the aqueous phase was measured by evaporating a pre-weighed sample at room temperature for 24 hours and weighing the residue. Thermogravimetric analyses were performed on the solid residues to quantify their inorganic content, consisting in the reacted ZVMs after hydrothermal upgrading.

A schematic summary of the experimental procedure is provided in Figure 1.

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Figure 1: scheme of the reaction and separation operations carried out in the experimental procedure.

Elemental analysis was performed on the raw biocrude, the biocrude upgraded in the blank test, and the samples treated with 0.5 g of Fe and Zn, following the previously described method. Additionally, a semi-quantitative GC-MS analysis was conducted on the biocrudes using a Thermo Scientific Trace 1300 gas chromatograph coupled with a single quadrupole ISQ-QD mass spectrometer. The instrument was equipped with a DB5-MS capillary column (30 m × 0.25 mm) coated with a 0.25 mm 5% Diphenyl/95% Dimethylpolysiloxane thick film. The mass spectrometer operated at an electron energy of 70 eV, with the ion source and transfer line maintained at 250 °C and 280 °C, respectively. For comparison, elemental analysis was also performed on the biocrude obtained from the HTL of sewage sludge under the same reaction conditions as the upgrading tests (330 °C, 3 h).

* 1. Results and discussion

The recovery of upgraded biocrude after the upgrading reaction was not quantitative, as part of it was converted into water-soluble organics and dissolved in the aqueous phase. Additionally, a significant fraction underwent repolymerization into acetone-insoluble heavy oil, which was accounted for as solid residue after the extraction process. This result highlights one of the main limits of hydrothermal upgrading, as the quality enhancement of the final biocrude is negatively compensated by the mass losses in byproducts. The yields of the four products are plotted in Figure 2.

Figure 2: Dry based yields obtained from the conversion of 1 g of biocrude without and in presence of ZVMs as hydrogen generators. d.b. = on dry basis.

The upgraded biocrude yield without hydrogen generators was 60 %, while approximately 24 % of the initial biocrude repolymerized into acetone-insoluble heavy oil. The addition of Fe significantly enhanced the biocrude recovery, increasing it to 72 %, whereas Zn led to a more moderate improvement, reaching 67 %. These results align with those reported by Hamidi et al. (2022), who observed similar trends when using Fe and Zn.

According to the work of Tai et al. (2021), Fe and Zn undergo oxidation reacting with water under hydrothermal conditions, generating hydrogen while forming Fe3O4 and ZnO respectively, as described by the simplified reactions in Eq(2) and Eq(3).

|  |  |
| --- | --- |
|  | (2) |
|  | (3) |

The repolymerized biocrude, accounted for as organic solid residue, was quantified by subtracting the ash content, comprising oxidized metals, from the total solid residue weight, using thermogravimetric analysis data. After this correction, it was possible to observe that the presence of ZVMs significantly reduced organic solid residue when Fe was used (4.5 %), whereas Zn resulted in a residue amount similar to the blank test (21.9 %). This difference aligns with what was observed by Tai et al. (2021) and was attributed to the different oxidation mechanisms for the two metals. Iron particles undergo slower oxidation compared to zinc, forming incoherent layers of iron oxide that detach from the zero valent core, that continue to react and generate active hydrogen that stabilize the biocrude, preventing its repolymerization. Zinc, on the other hand, rapidly undergoes complete oxidation and generates hydrogen for a shorter period, that is not sufficient to prevent repolymerization mechanisms. Both Fe and Zn led to a slight increase in gaseous phase production, rising from 5.7 % to 9.6 % and 10.4 %, respectively, suggesting an enhancement of decarboxylation mechanisms. Additionally, Fe slightly enhanced the yields in water-soluble organics compared to the other tests, suggesting a higher production of light polar components. These results demonstrate a primary positive effect of the use of ZVMs in hydrothermal upgrading, resulting in an enhanced recovery of upgraded oil. Iron appeared more suitable than zinc for this purpose, as it significantly reduced repolymerization phenomena and maximized the yield of upgraded biocrude.

The elemental composition of the biocrudes and their calculated HHVs are summarized in Table 3. These results highlight a significant increase in carbon content and HHV, along with a reduction in heteroatom content of the hydrothermally upgraded biocrude, compared with the raw biocrude. The analysis of the raw biocrude obtained from the HTL of sewage sludge under the same operative condition used in upgrading tests, reported in Table 3 as “Raw 330 °C, 3 h”, served as comparison to correctly address these quality enhancements to the hydrothermal upgrading, rather than the higher severity.

Table 3: Elemental weight percentages and calculated HHVs of the raw and upgraded biocrudes

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | C % | H % | N % | S % | O\* % | HHV (MJ kg-1) |
| Raw 280 °C, 30 min | 69.28 | 7.27 | 4.08 | N.D. | 19.36 | 30.34 |
| Raw 330 °C, 3 h | 73.14 | 7.67 | 5.96 | N.D. | 13.23 | 33.31 |
| Upgraded blank | 76.41 | 7.74 | 3.28 | N.D. | 12.57 | 34.64 |
| Upgraded 0.5 g of Fe | 75.31 | 7.67 | 3.27 | N.D. | 13.75 | 33.95 |
| Upgraded 0.5 g of Zn | 76.67 | 7.87 | 3.51 | N.D. | 11.95 | 35.02 |

\* Calculated by difference (O % = 100 % – C % – H % – N % – S % – ashes %). N.D. = not detected

A moderately higher biocrude quality was observed in this case, with higher HHV and carbon and hydrogen percentages, although slightly lower compared with other upgrading tests. However, that test gave the highest nitrogen content compared to the others, attributed to the transfer of nitrogen-containing compounds from the aqueous phase to the biocrude at elevated temperatures and prolonged reaction times. This result indicates that a second hydrothermal step is more effective on biocrude quality respect to a prolonged HTL directly from sewage sludge. In all biocrude samples, sulfur content was below the detection limit of the instrument. Regarding the upgraded biocrudes, the addition of ZVMs did not induce significant changes in elemental composition compared to the blank test. For all the upgrading tests, carbon content increased by 9 ÷ 10 %, hydrogen content by 5 ÷ 8 %, while nitrogen and oxygen content decreased by 14 ÷ 20 % and 29 ÷ 38 %, respectively. These findings suggest that the effect of ZVMs in hydrothermal upgrading is limited to enhanced biocrude recovery, rather than substantial changes in biocrude elemental composition. However, GC-MS analysis provided valuable insights into the chemical transformations occurring during hydrothermal upgrading. The detected compounds were categorized based on their functional groups, and their relative signal area (%) were recorded. Figure 3 summarizes the most relevant variations among key compound classes under different upgrading conditions.

Figure 3: Area % of the most relevant classes of compounds detected by GC-MS analysis of the biocrudes, with their variations for different upgrading conditions.

A significant increase in fatty acids, such as hexadecenoic and octadecenoic acid, was observed in the blank test, likely due to the completion of the hydrolysis of the glycerides, which are typically difficult to detect via GC-MS analysis. This increase was not observed in the presence of Fe and Zn, where fatty acid concentrations were lower than in the raw biocrude. This detail suggests that ZVMs also significantly affects the composition of the biocrude, during hydrothermal upgrading. The amide class, which was among the dominant compound classes in the raw biocrude, including fatty acid derived amides such as hexadecanamide and octadecenamide, showed a significant reduction in the upgraded samples. This reduction may explain the observed decrease in nitrogen content, suggesting nitrogen migration to the aqueous phase. Finally, biocrudes upgraded with ZVMs exhibited an increased concentration of alcohols and aldehydes, identified as reduction products of fatty acids (e.g. 1-hexadecanol and 17-Octadecenal, respectively), as well as aliphatic hydrocarbons, which were recognised as decarboxylation products from fatty acids (e.g. pentadecane and 3-Heptadecene, (Z)-). The relative increase in aliphatic hydrocarbons was quantified at + 480 % for Fe and + 520 % for Zn, compared to the not upgraded biocrude. These last results are particularly noteworthy, as they demonstrate the effectiveness, although limited, of ZVMs to reduce oxygenated compounds as fatty acids to “diesel-like” compounds such as C15 - C17 linear hydrocarbons. This opens interesting perspectives in combining ZVMs with hydrogenation catalysts, to enhance their effectiveness and maximize the conversion of these upgrading mechanisms, in order to gradually fill the gap between HTL biocrude and commercial liquid fuels.

* 1. Conclusions

This exploratory study provides valuable insights into the hydrothermal upgrading of HTL biocrude assisted by zero-valent metals as in-situ hydrogen generators. The effects of zero-valent Fe and Zn on biocrude derived from digested sewage sludge were investigated in terms of upgraded biocrude recovery and composition, including elemental analysis and GC-MS characterization. All the upgrading tests revealed a relative increase in biocrude quality, with maximum enhancements reaching a 10.7 % increase in carbon content and 38.3 % decrease in oxygen content, leading to a corresponding relative increase of HHV up to 15.4 %. Compared to the blank test, the primary impact of ZVMs was an increase in upgraded biocrude recovery, rising from 60% in the blank test to 72 % with Fe and 67 % with Zn. This improvement was attributed to the stabilization of the oil-like molecules in the presence of active hydrogen generated by the oxidation of metals in water, with Fe exhibiting a particularly pronounced effect. Although no significant changes in the elemental composition of the upgraded biocrude were observed compared with the blank test, GC-MS analysis revealed several reduction products in samples treated with ZVMs. Notably, fatty acid concentrations decreased, while aliphatic hydrocarbons, identified as decarboxylation products of fatty acids, increased by a factor of five compared with the non-upgraded biocrude. These preliminary findings suggest that further research should explore the effects of the use of ZVMs under hydrothermal conditions in combination with hydrogenation catalysts, aiming to develop sustainable biobased fuel upgrading strategies that minimize hydrogen consumption.

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