Hydrothermal liquefaction of sewage sludges mixtures: Effect of the biomolecular composition on the process performance

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Keywords: sewage sludge, industrial sludge, hydrothermal liquefaction, bio-crude, biochemical compounds.
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Rapid population growth, resulting in increased production of sewage sludge, has addressed the research through the development of eco-sustainable technologies for the waste to biofuel conversion, to reduce both landfill disposal and dependence on fossil fuels. Hydrothermal liquefaction (HTL) is an emerging thermochemical process for the energy valorization of high-water-content waste, as municipal and industrial sludge (Fan et al., 2022). HTL is generally carried out using water in subcritical conditions (200–375 °C and 40–200 bar), acting as a solvent, catalyst, and thermal flywheel. HTL enables the direct conversion of the organic substances present in the sewage sludge (such as lipids, proteins, and carbohydrates) into bio-crude (or bio-oil) as target product; gas and liquid phases, and a solid residue, are produced as well. The process follows a complex reactive network accounting for hydrolysis and depolymerization of biomass, decomposition and rearrangement of reactive intermediates. To date, the interactions of biomass macro-components along the HTL process is a limitedly explored topic, and commonly analyzed through the use of model compounds (Obeid et al., 2020).

In this work, the HTL process of real sludge mixtures deriving from both municipal (MS) and tannery (TS) sewage treatment plants was carried out in a 500 mL batch reactor (Di Lauro et al., 2022). The effect of reaction time and mixture composition on the process performance was assessed at 350 °C and biomass concentration of $10\%_{wt}$ in bi-distillated water. The role of process parameters on the quality of both bio-crude and aqueous phase was unveiled via combined LC-MS and NMR analyses.

Table 1 shows the chemical and energetic properties of the starting biomasses. TS and MS sludges are characterized by similar C (33.6% vs 34.6%) and H (5.1% vs 4.9%) content; the volatile matter is slightly lower for TS (50.1% vs 56.4%). Moreover, the higher heating value (HHV) is about 16.7 and 14.9 MJ/kg for the municipal and tannery sludge, respectively. The above properties make the two biomasses promising candidates for their energetic valorization via HTL. It is highlighted that MS has a content of carbohydrates of 59%, that is almost triple the value derived for TS. On contrary, TS compared to MS has a higher lipid (5.3% vs 2.4%) and proteins (29.4% vs 25%) content.

Figure 1 shows the results of HTL tests in terms of bio-crude yield (on dry- and ash-free basis, Y^{dafb}) for sludges mixtures at different composition expressed in % by weight, MS:TS=x:(100–x) for x=100, 75, 50, 25, 0. It is highlighted that the bio-crude yield for raw MS is maximum at 10 min, around 42.5%, to decrease thereafter in time down to an asymptotical value of about 29%. In contrast, for raw TS, process time does not seem to exert a remarkable effect on the yield, and Y^{dafb} is about 28% on average. When sludges mixtures are considered, except for the test at 10 min, the bio-crude yield values are greater than those expected based on a linear combination of outcomes derived from as-received sludges. This could be linked to a synergistic effect ("activated" after 10 min) of the macro-components contained in the starting sludges. Specifically, for MS:TS=75:25, it was obtained Y^{dafb}=40.5% at 40 min. For this mixture, the protein/carbohydrate macro-component ratio was 0.5, thus suggesting the existence of an optimal value for this parameter in favoring the reactive network that leads to the formation of bio-oil. Finally, for MS:TS=75:25 tested for times of 10 and 30 min, no influence of process time on the HHV was found. HHV of bio-crude was ca. 29 MJ/kg, and about 50% of the energy content of the parent biomasses was recovered through the HTL process.

Table 1. Chemical and energetic properties of the two sludges.

	MUNICIPAL SLUDGE (MS)	TANNERY SLUDGE (TS)
	Proximate analysis [$\%_{wt}$]	
Moisture	12.68±0.01	18.46±0.31
Volatile matter	56.36±0.03	50.13±0.06
Fixed carbon	9.54±0.11	n.d.
Ash	21.43±0.18	31.41±0.43
	Ultimate analysis [$\%_{wt}$], dry basis	
C	34.55±0.32	33.61±0.14
H	4.87±0.24	5.10±0.19
N	5.90±0.07	2.44±0.05
S	0.77±0.04	4.07±0.03
Cl	0.61±0.02	0.35±0.03
	Heating value [MJ/kg], dry basis	
HHV	16.67±0.40	14.90±0.31
	Macro-components [$\%_{wt}$], dry basis	
Lipids	2.4±0.10	5.3±0.20
Proteins	25.0±0.10	29.4±0.90
Carbohydrates	59.0±0.03	21.0±0.02

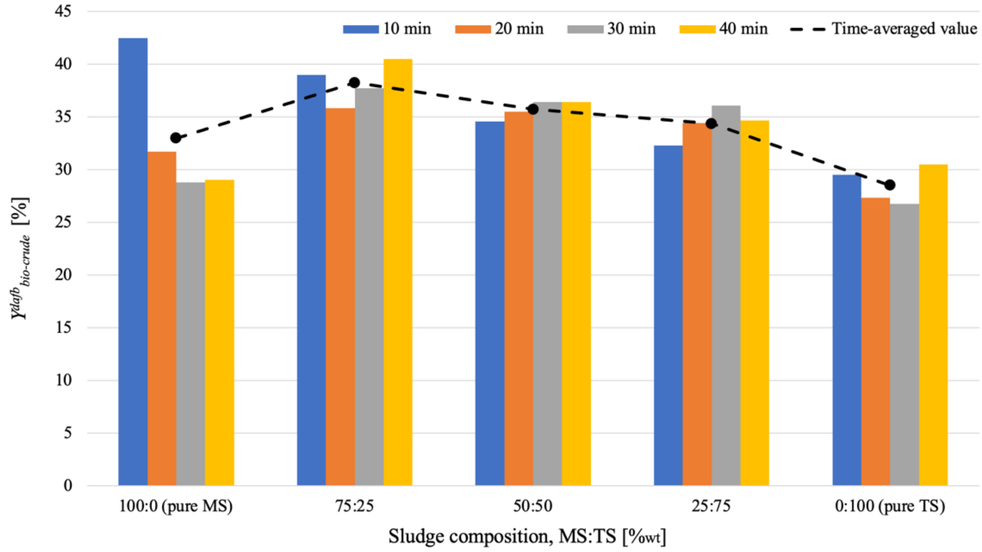

Figure 1: Yield (dry- and ash-free basis) of bio-crude obtained from HTL process of sludge mixtures of different composition; data parametric in the isothermal reaction time.

Acknowledgements

The authors acknowledge funding from: i) the project PNRR - Partenariati estesi - "NEST - Network 4 Energy Sustainable Transition" [PE0000021] and ii) Programma per il Finanziamento della Ricerca di Ateneo (FRA) 2022 of the University of Naples Federico II (Project "Eco-sustainable Production of bIofuels from the Conversion of sludges through hydrothermal liquefaction" (EPIC)).

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