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


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## HTL process

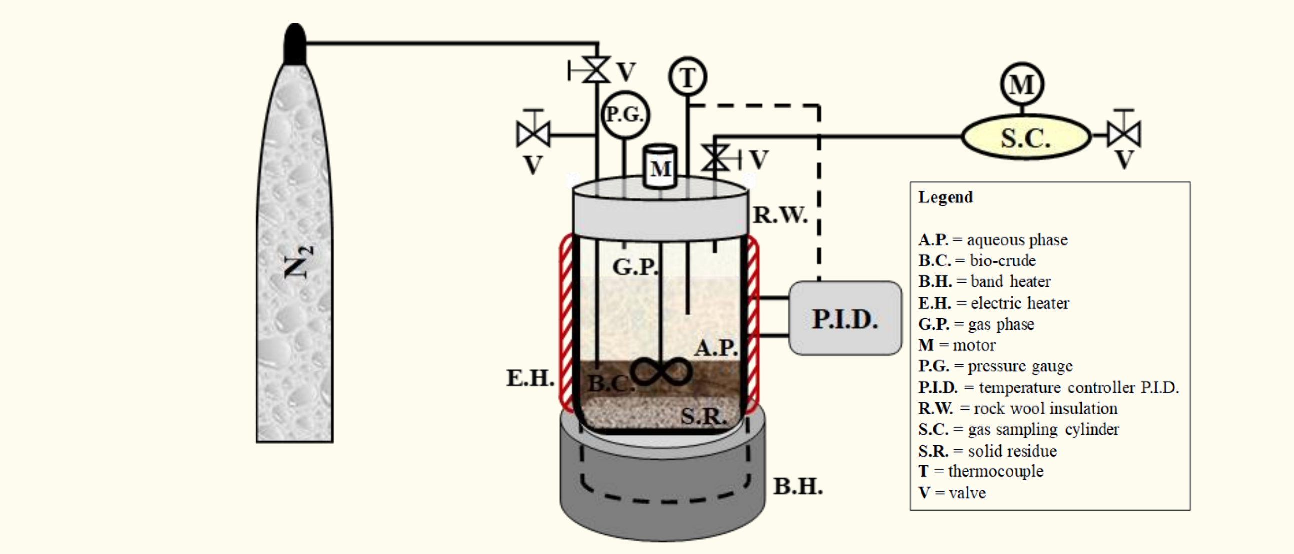
Hydrothermal liquefaction (HTL) process is a thermochemical route to obtain a liquid energy vector (bio-crude) from high-water-content waste, as sewage sludge. The aim of this work is to increase the knowledge on the possible synergistic/antagonistic effects of the biomass macro-components (i.e. carbohydrates, proteins, lipids) on the yield/quality of bio-crude, by analyzing the HTL process of real sludge and mixtures of them to different compositions.

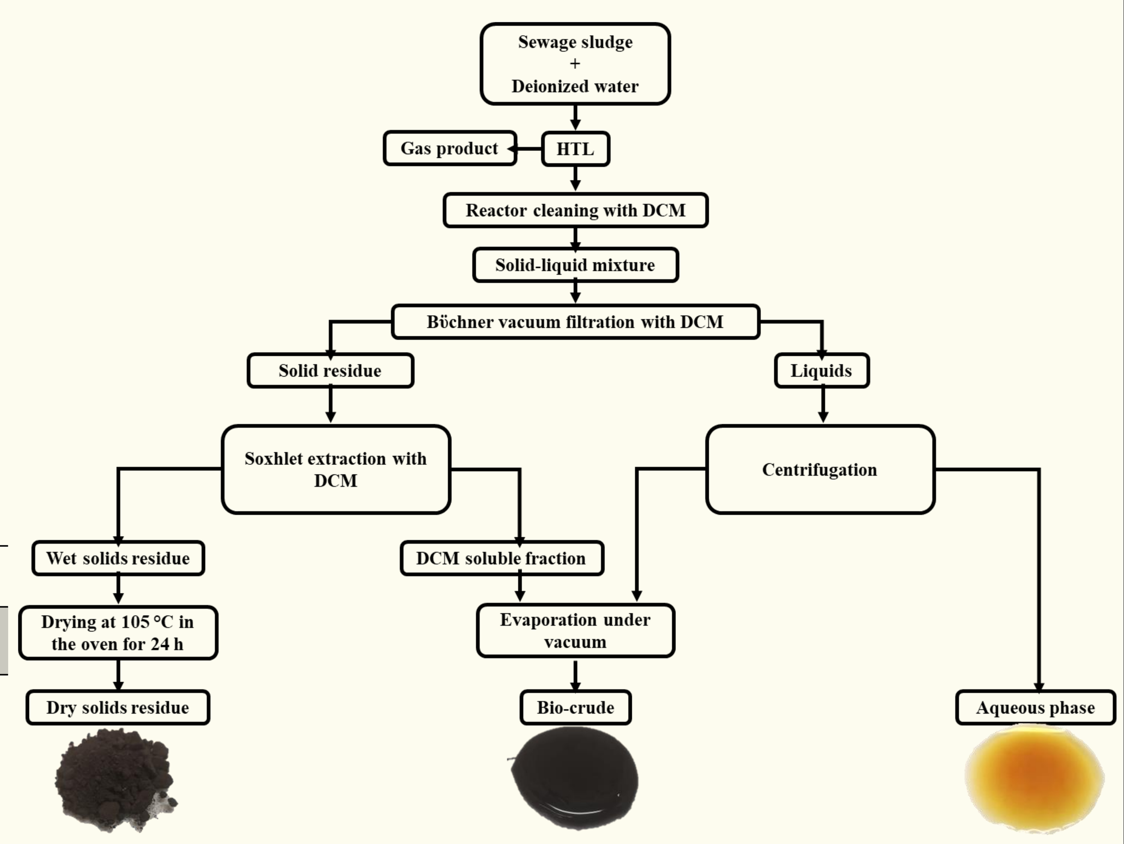

**Di Lauro et al., (2024),** "Characterization of biocrude produced by hydrothermal liquefaction of municipal sewage sludge in a 500 mL batch reactor". Industiral & Engineering Chemistry Research. 63, 955–967.
**Balsamo et al., (2024),** Unravelling the Role of Biochemical Compounds within the Hydrothermal Liquefaction Process of Real Sludge Mixtures". Sustainability. 16, 1770.


## Sludge properties and experimental apparatus

| | 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 |

Chemical and energetic properties of two kind of sludge. *HHV* = higher heating value; *LHV* = lower heating value.




| Biomass composition | t [min] | T [°C] |
|---|---|---|
| MS, MS:TS= 75:25, MS:TS=50:50, MS:TS=25:75, TS | 10, 20, 30, 40 | 350 |

Operating conditions of HTL test of parent sludge and their mixtures during the isothermal stage.

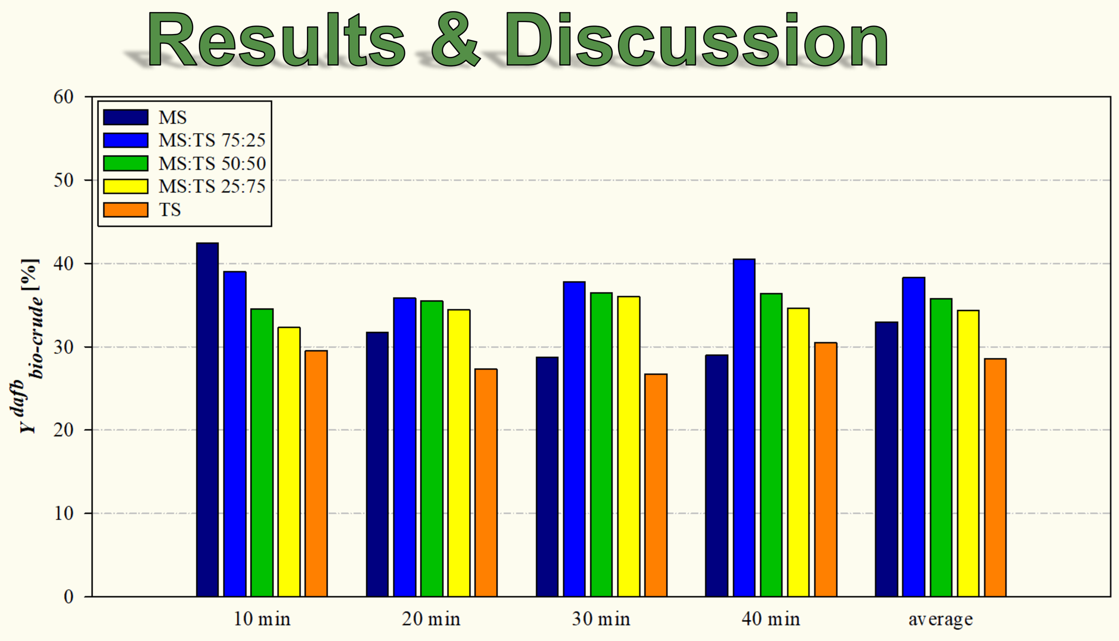
$$Y^{dafb}_{bio-crude} = \frac{m_{bio-crude}}{m_{biomass,dafb}} \cdot 100 \qquad ER = \frac{HHV_{bio-crude}}{HHV_{biomass}} \cdot Y^{db}_{bio-crude}$$

Yield on dry and ash-free basis and energy recovery of bio-crude.

## Results & Discussion

| Biomass composition | Lipids (L) [$\%_{wt}$] | Proteins (P) [$\%_{wt}$] | Carbohydrates (C) [$\%_{wt}$] | L:P:C |
|---|---|---|---|---|
| MS | 2.4 | 25.0 | 59.0 | 1:10.4:24.6 |
| MS:TS 75:25 | 3.1 | 26.1 | 49.5 | 1:8.4:16.0 |
| MS:TS 50:50 | 3.8 | 27.2 | 40.0 | 1:7.2:10.5 |
| MS:TS 25:75 | 4.6 | 28.3 | 30.5 | 1:6.2:6.6 |
| TS | 5.3 | 29.4 | 21.0 | 1:5.6:4.0 |

Lipids, proteins and carbohydrates content, expressed in dry basis, for the 5 cases investigated.

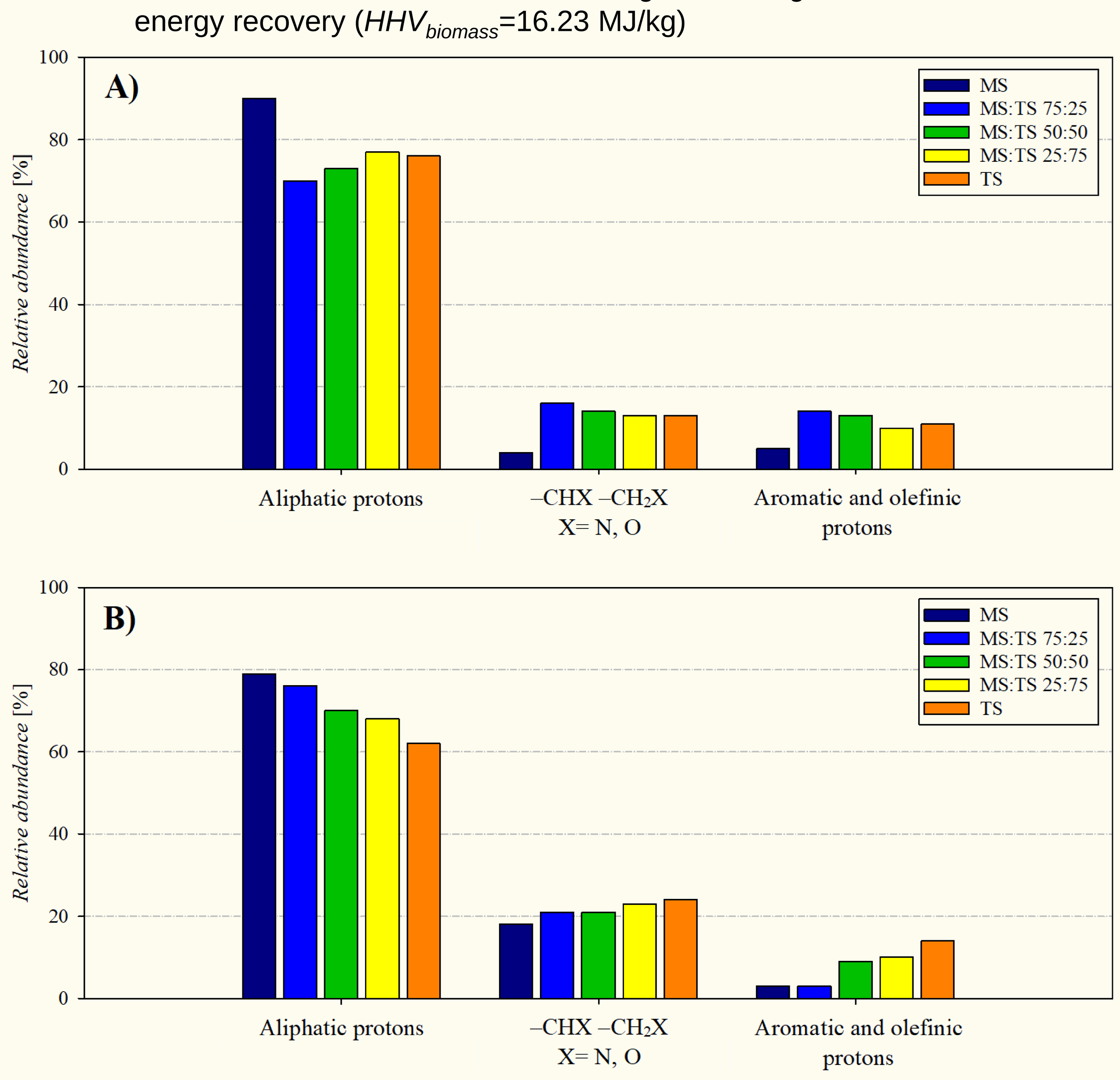



Bio-crude yield (on dry and ash-free basis) as a function of HTL time and initial biomass, and t-averaged values.

The average yields of bio-crude on dry and ash-free basis show a synergistic effect for the mixtures compared to single sludges.
Carbohydrate-to-protein mass ratio 2:1 (i.e. mixture MS:TS 75:25) enhances the bio-crude yield, likely by promoting the reactive networks as Maillard reactions.

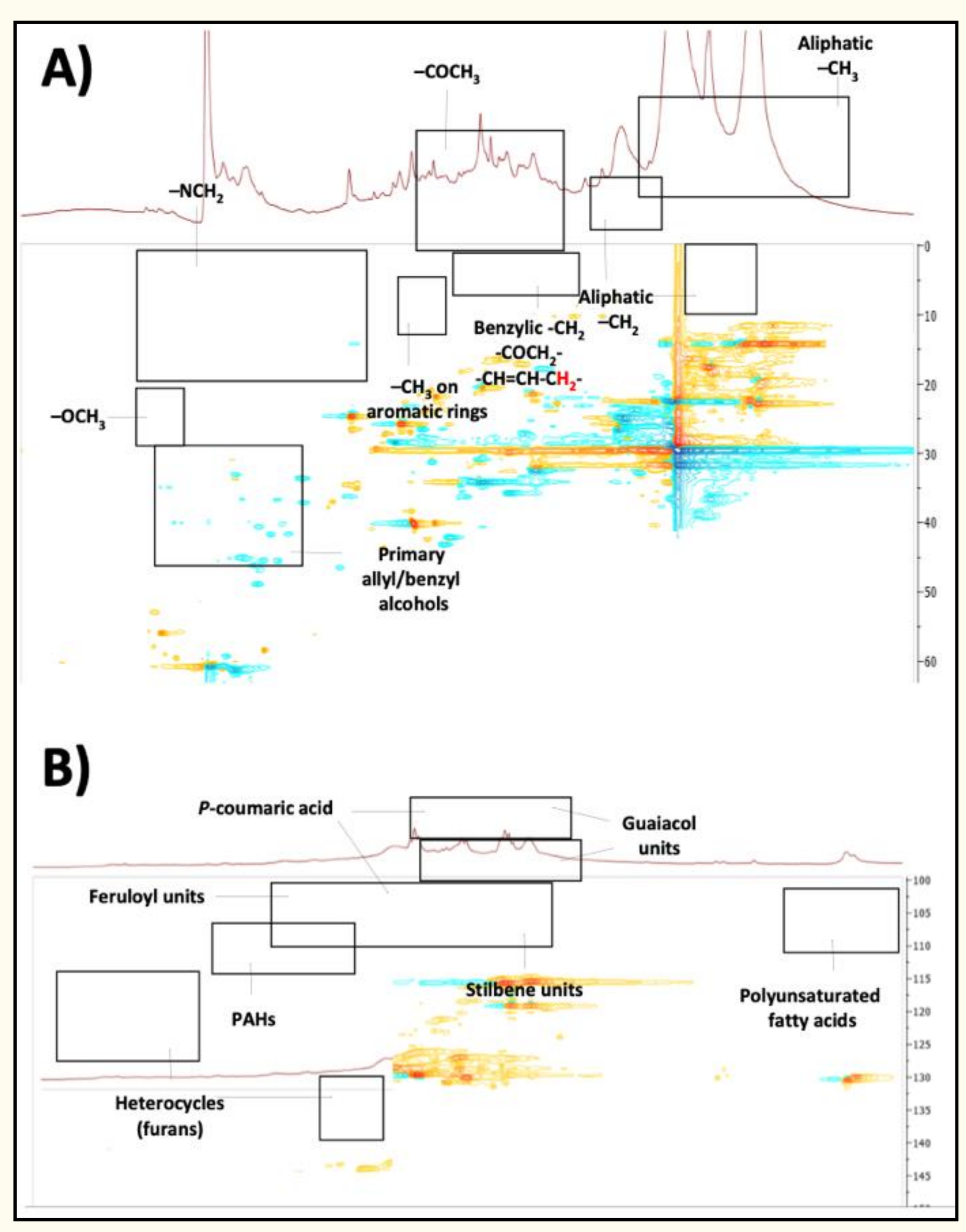
| Biomass composition | $Y^{dafb}_{bio-crude}$ [%] | $HHV_{bio-crude}$ [MJ/kg] | *ER* [%] |
|---|---|---|---|
| MS:TS 75:25 (t=10 min) | 39.15 | 29.42 | 50.83 |
| MS:TS 75:25 (t=30 min) | 37.92 | 28.57 | 47.81 |

Evaluation, for cases of interest, of higher heating value and energy recovery ($HHV_{biomass}$=16.23 MJ/kg)

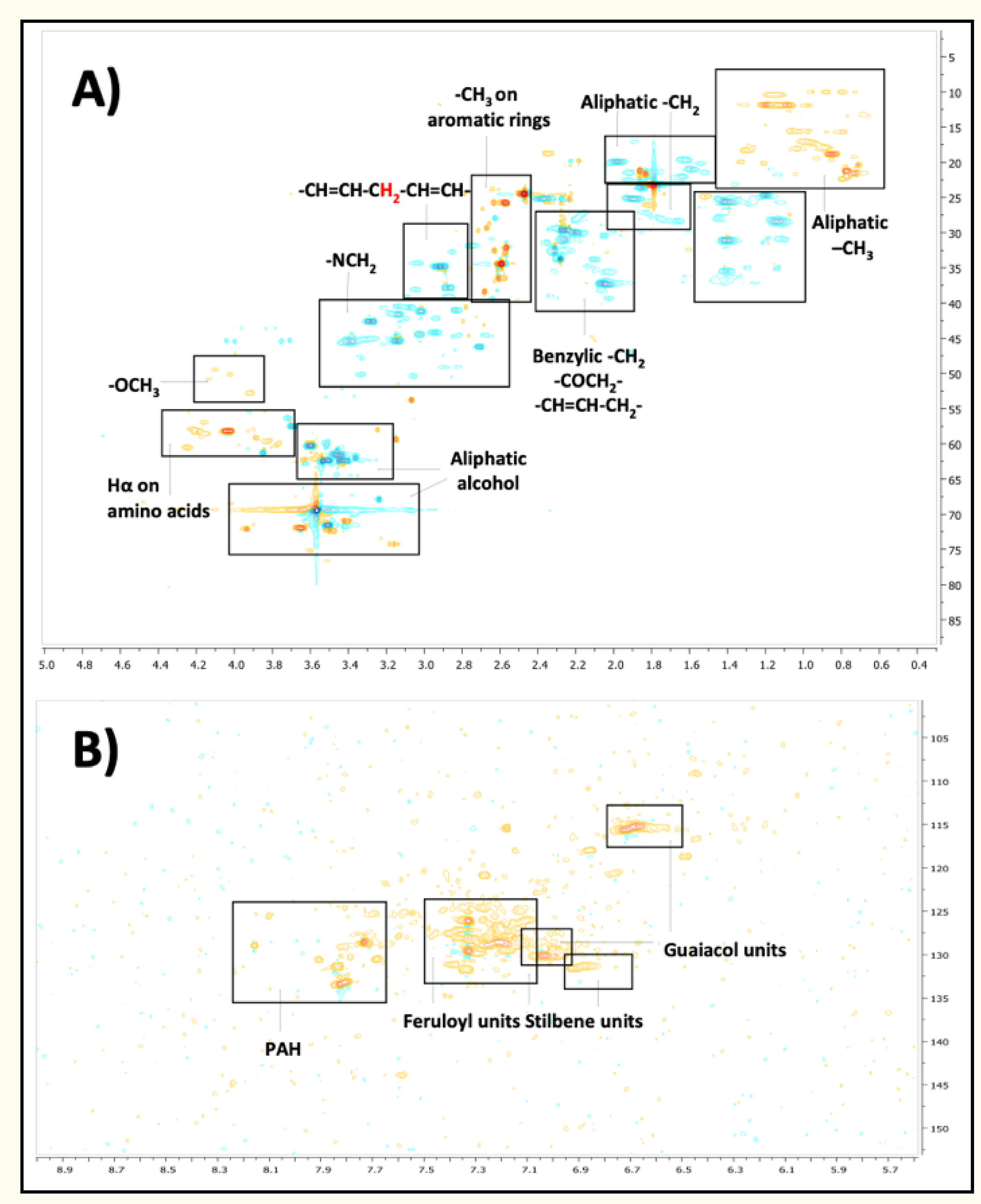



Relative abundance of the aliphatic compounds, alcohols, amines, olefins and aromatic compounds in the **bio-crude** (A) and **water fraction** (B) for MS, TS and mixed sludges. The relative abundances have been calculated by integration of the $^1$H-NMR spectra in the 0–3 ppm range for aliphatic protons, 3–5 ppm range for alcohols and amines protons, 9–5 ppm range for olefins and aromatic compounds.

In sludge mixtures, a higher content of TS leads to the formation of greater quantities of alcohols, amines, olefins and aromatic compounds than aliphatic compounds.




$^1$H,$^{13}$C-HSQC DEPT spectrum (DMSO-$d_6$) of the bio-crude fractions obtained at 350 °C and 10 min for MS:TS 75:25. Aliphatic proton/carbon region (A) and olefin/aromatic proton/carbon region (B).




$^1$H,$^{13}$C-HSQC DEPT spectrum ($D_2O$) of the aqueous fractions obtained at 350 °C and 10 min for MS:TS 75:25. Aliphatic proton/carbon region (A) and olefin/aromatic proton/carbon region (B).

In the spectra of the mixed sludge a high number of signals due to amines, PAHs and heterocycles (i.e furans and pyridines) are detected. The bio-crude fractions exhibit the signals of olefinic protons of polyunsaturated fatty acids (5.3/130 ppm) and of aliphatic -$CH_2$ and -$CH_3$ protons in the 0.5–2.5/10–40 ppm region, whereas the aqueous phases exhibit a higher number of signals due to protons of amines (2.6–3.5/40–50 ppm), alcohols (3.0–4.1/55–75 ppm) and Hα of amino acids (3.7–4.2/55–60 ppm).

## Conclusion

In this work, the role of the possible synergistic/antagonistic effects of lipids, proteins and carbohydrates, during the hydrothermal liquefaction process applied to realistic matrices, was examined. For bio-crude yield obtained from tannery and municipal sludges mixtures, there is an optimal value of the carbohydrate-to-protein mass ratio (2:1, as in the case of MS:TS 75:25) which favours the reactive network towards the formation of bio-oil. The reaction mechanisms that lead to the formation of bio-crude from mixtures of carbohydrate and protein derivatives could be traced back to Maillard reactions. Indeed, reactions involving the solubilisation of carbohydrates to form soluble products in the aqueous phase, such as hydrolysis and retro-aldol condensation, are favoured for short reaction times at the operating temperature (350 ° C) used in the present work.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