Effect of Microplastics in Hydrothermal Liquefaction (HTL) of Real Municipal Sludge (RMS)

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The work herein was focused to study the effect of the microplastics on the yield and quality of biocrude (BC) produced by hydrothermal liquefaction (HTL) of real municipal sludge (RMS). HTL experiments with RMS containing 3 % w/w microplastics were conducted at 325 °C and 30 min both in the absence and in the presence of $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ and activated carbon felt (ACF) as heterogeneous catalysts. A white wax was isolated from BC with a yield of 5, 8 and 6 % w/w daf when $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ and ACF were used respectively. GC-MS analyses demonstrated that oleamide was present in the wax while FT-IR analyses showed the presence of chlorinated organic compounds, affecting negatively the BC quality. HTL experiments with mixture of microalgae and controlled amounts of polyvinylchloride, polyethylene and nylon 6,6 at 325 °C for 30 min confirmed that wax is originated from hydrothermal conversion of synthetic polymers.

1. Introduction

The applicative potentiality of a biorefinery process for waste management and valorization gained a lot of interest in recent years. Hydrothermal liquefaction (HTL) process is considered a promising route to be integrated in the biorefinery concept to allow the conversion of a wet organic matrix into a fuel precursor that is called biocrude (BC) (Dimitriadis et al., 2016). The HTL conversion route takes place using the water, contained in the raw feedstock, as solvent in sub or supercritical conditions at 300-400 °C and 10-40 MPa (Peterson et al., 2008). It is generally accepted that HTL could constitute a promising route to obtain, with high conversion efficiency, value-added compounds from a wide range of organic matrices. The most investigated bio-feedstock for HTL was represented by microalgae, however in the last years was demonstrated that their cost significantly decreases the economic sustainability of the process (Giaconia et al., 2017) In recent years increasing research interest was devoted to the utilization of RMS, as real waste bio-feedstock for HTL process, because the volume of production per year is significant, the disposal cost ranges between € 80 and € 600 per ton and they are characterized by an organic content between 40 and 90 %w/w. In this framework, HTL of RMS could be a solution providing an alternative route for their efficient disposal. Several studies were conducted to find the best operative parameters to improve the BC yield and quality approaching as much as possible that of commercialized fuels (Madsen et al., 2019; Qian et al., 2017; Shah et al., 2020; Conti et al., 2020; Prestigiacomo et al., 2021). One of the main challenges for the development of this strategy is the heterogeneous nature and wide composition variability of waste bio-feedstock. In fact, when HTL of RMS was pioneered, as an enlargement of the application of HTL to residual biomass, it was neglected that the hydrothermal conversion of its biogenic organic components (bacterial cells, polysaccharide fibres, proteins and triglycerides) can be different from that of not biogenic constituent such as plastics. It is reported by many studies that RMS are one of the main vectors of microplastics in the soil (Tagg et al., 2015). These macromolecular components come from the drain of the washing machines, toothpaste, and the degradation of car tires on the roads and they

effectively can constitute a pollutant source for the soil (Tagg et al., 2015). International legislation regulates the maximum level of heavy metal in RMS but, so far no limit on the plastic content has been proposed there are many studies in the literature on HTL of single plastics (Seshasayee and Savage, 2021; Dos Passos et al., 2020) that investigated the effects of different operative parameters like temperature, time, concentration, on the product distribution but as far as we know any study was conducted on the evolution of microplastics incorporated in RMS during HTL.

The work herein was focused to investigate the effect of the microplastics on the yield and quality of BC produced by HTL of RMS.

2. Materials and methods

2.1 Materials

RMS adopted in the work herein were provided by the WWTP in Palermo (A.M.A.P. s.p.a.) with an initial moisture content of 76 % w/w (dry mass) and organic content of 80 % w/w. A method reported in the literature by Tagg et al., 2015 was used to isolate and determine the microplastic fraction (MF) in the RMS, that was 3±1 %w/w. NiMo/Al$_2$O$_3$ (KF 851, quadralobe units, Albemarle), CoMo/Al$_2$O$_3$ (KF 1022, cylindrical units, Albemarle) and activated carbon felt 1600 supplied by Ceramaterials were used as catalysts. *Chlorella v.* provided by algae4future (a4f), Lisbon, Portugal is used as a model of biogenic matter to perform selected experiments. Hydrogen peroxide (30 vol %, Sigma Aldrich) was used to identify microplastic content in RMS. Poly(vinyl chloride) (high molecular weight, M$_n$ 565 kg/mol, Sigma Aldrich), extruded films of polyethylene and nylon 6,6 were cut to obtain particle size distribution between 0.5-1.0 mm and used as microplastic models. Deionized water, available as a laboratory utility, was employed as a solvent for microplastic identification in RMS and for HTL experiments. Trichloromethane (≥99.8 %, J.T. Baker®, Avantor) was used as a solvent to recover the BC. Acetone (HPLC grade, Sigma Aldrich) was used to clean the reactor and collect the additional phase (ADP). KBr was used as a sample carrier for FT-IR analyses (99+ %, FT-IR grade, Sigma Aldrich).

2.2 Experimental methods

HTL of RMS was carried out using the experimental system elsewhere described (Prestigiacomo et al., 2020). The AISI 316 assembled reactor, internal volume of 16 mL, was loaded with 5 g of aqueous slurry characterized by a RMS concentration of 10 % w/w. When catalyst was used, it was added with a concentration of 10 % w/w with respect to the initial dry mass of RMS. The reactor was then sealed and purged with argon (Air Liquide 99.999 % purity), a residual pressure of 2 bar of argon has been left in the reactor. The reactor heating system was described in detail in a previous work (Prestigiacomo et al., 2020) and it included an assembled ceramic heater controlled by LabVIEW Software, National Instruments. It allowed heating the reactor to 325 °C for 30 min with a heating rate of 13 °C/min. A water bath was used to quench the reactor at the end of the reaction. After 1 h from the quench the reactor was connected to a gas expansion system already described (Prestigiacomo et al., 2020a, 2021b) and three samples of gaseous phases were collected and analyzed. Later on, the reactor was opened and the content was poured into a glass centrifuge tube. Then the tube was centrifuged at 3220 rpm for 20 min, the aqueous phase was recovered and stored in a glass vial. In the work herein 5 mL of trichloromethane was used as solvent to recover BC from the bottom part of the reactor and added in the same centrifuge tube used to collect the products. 6 mL of acetone was used to clean the upper part of the reactor, in which a white wax, called "additional phase" (ADP), was detected. The recovered solid residues (SR), BC and trichloromethane suspension were stored in the aforementioned glass centrifuge tube to collect the SR and the BC entrained in the tube after the aqueous phase withdrawal. At this point a supernatant wax phase, if present was collected with a spatula and stored separately. Vacuum filtration apparatus assembled with a pre weighted polytetrafluoroethylene filter (47 mm, 0.2 hole diameter) was used to separate SR from the liquid phase composed of BC and trichloromethane. The ADP, the filter with SR cake and three samples of liquid trichloromethane solution were left for 24 h inside a vacuum desiccator to determine their dry mass. A sample of aqueous phase was dried at 60 °C over night to determine the dry mass of water soluble products (WSP). Then samples of WSP and SR were calcinated at 550 °C for 6 h in order to estimate the mass of products in the dry ash free form. Through preliminary calcinations, no detectable (ND) amount of ashes in the ADP and in the BC were found.

2.3 Analytical methods

The yields of the products (Y$_P$) dry ash free (daf) percentage were determined following the eq. (1):

$$Y_P \% w/w_{(daf)} = m^P_{(daf)} / m^{RMS}_{(daf)} \times 100 \tag{1}$$

Where $m_{(daf)}^P$ and $m_{(daf)}^{RMS}$ are the mass of the product and the RMS loaded in the reactor in the dry ash free form respectively.

The total mass of isolated ADP (m_{ADP}^{tot}) was calculated as in the eq. (2), as sum of the mass in the acetone phase ($m_{ADP}^{acetone}$) and mass recovered as wax from trichloromethane solution (m_{ADP}^{wax}):

$$m_{ADP}^{tot} = m_{ADP}^{acetone} + m_{ADP}^{wax} \tag{2}$$

The characterization of the gas phase was obtained through gas chromatographic analysis performed using an Agilent 7809 GC equipped with a Supelco Carboxen 60/80 column and a thermal conductivity detector using Helium (99.999 %, Air Liquide, Italy) as the carrier gas. The equation of state for ideal gases was used to determine the moles of produced gases.

Elemental analyses (CHNS) of the ADP, of the wax and the BC were performed by a Perkin Elmer Elemental Analyzer 2400 Series II. The % w/w of other atoms incorporated in analyzed compounds could be estimated as in eq. (3):

$$others_\% = 100 - C_\% - H_\% - N_\% - S_\% - ashes_\% \tag{3}$$

Fourier- Transform Infra-Red (FT-IR) analyses of the wax, of the ADP and of the SR were performed using a Perkin-Elmer Spectrum One spectrometer. Spectra were recorded with 8 scans at a resolution of 4 cm^{-1}. Weighted amounts of samples were mixed with KBr and 13 mm pellets were prepared used an evacuable KBr die and a Specac hydraulic press using 10 metric ton of pressure. All the analyses were repeated at least twice for reproducibility. GC-MS analyses of samples of the ADP diluted in acetone were conducted using a TRACE GC 2000 with a TRACE MS plus spectrometry detector equipped with a MEGA-5 (30 m*0.32 mm*0.25 mm) capillary column. The following temperature profile was adopted to perform GC-MS runs: oven holding at 40 °C for 10 min followed by a heating ramp at 5 °C/min up to 250 °C with a holding time of 10 min, then a heating ramp at 10 °C/min up to 310 °C with a holding time of 10 min. Source temperature 230 °C. Transfer line at 250 °C. The adopted injection volume was 1 mL, He flow-rate in the column was set to 1 mL/min. The compounds were identified using a NIST/EPA/NIH mass spectral library version 2.0 d, considering molecules with a match quality above 80 %.

3. Results and discussions

Experiments of HTL of RMS were performed at 325 °C and 30 min in the absence and in the presence of $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ and activated carbon felt (ACF). Product yields suggested that ADP was produced only in the presence of the heterogeneous catalysts and its yield was always lower than 10 % (Figure 1). Furthermore, it was noticed that the ADP is different from the BC because it was not soluble in the solvents commonly used to recover the BC. The produced ADP (the white fraction in Figure 2) was quite soluble in acetone but insoluble in water or trichloromethane. Hence, trichloromethane was used to separate BC from ADP after HTL experiment. ADP was then collected, quantified and analyzed. Calcination trials at 550 °C for 6 h of ADP samples gave undetectable ash content thus indicating that is an organic matrix. Interesting evidence were collected from the comparison of the elemental analyses of the BC, the collected ADP and the SR. In the literature on the HTL of biofeedstocks, the main elements in the BC are C, H, N, S and O whose percentage is generally estimated by difference to 100 %. In the study conducted herein, the latter assumption is not possible, since, cannot be neglected the presence of other heteroatoms such as Cl. In fact, in Table 1, it is possible to observe that the produced ADP (Table 1 b) were different with respect to the BC (Table 1 a) and the SR (Table 1 c) even if the H/C ratio is always in the same range. Quite interestingly, the amount of "other elemental compounds" not detected by the CHNS elemental analyzer for ADP was always double compared to those of the BC. Given the above evidence, GC-MS and FT-IR analyses of ADP samples were performed. GC-MS analyses clearly indicated the presence of oleamide ($C_{18}H_{35}NO$) which can be already present in the RMS because it is used as industrial slip agent and lubricant for plastics or it can be generated during HTL from the decomposition of Nylon 6,6 microplastics. Furthermore, FT-IR spectra of dried ADP (Figure 3) was characterized by the presence of resonance bands between 600 and 700 cm^{-1} attributable to the stretching vibrations of C-Cl bond (Lu et al., 2002) suggesting the presence of poly(vinyl chloride) (PVC) in this product. These bands were also detected in FT-IR spectra of the raw RMS, of the isolated MF and of the SR. To validate this hypothesis we studied the degradation of PVC in water at 325 °C and 30 min, with and without $CoMo/Al_2O_3$. After the hydrothermal treatment, we obtained a solid residue, whose mass was only 50 % of the initial mass of PVC, and an acid aqueous solution (pH = 2.6).

To validate the hypothesis of a possible correlation between the ADP and the presence of MF in the initial matrix, HTL of RMS was then compared to HTL of the microalga *C. vulgaris*, used as model plastic free biofeedstock. The collected outcomes suggested that, when catalytic HTL of *C. vulgaris* was conducted without plastic

addition, ADP production does not occur. While, when 3 % of PVC, 3 % of PET and 3 % of Nylon 6,6 (dry biomass basis), were added as models of plastic 4 % of ADP yield was obtained.
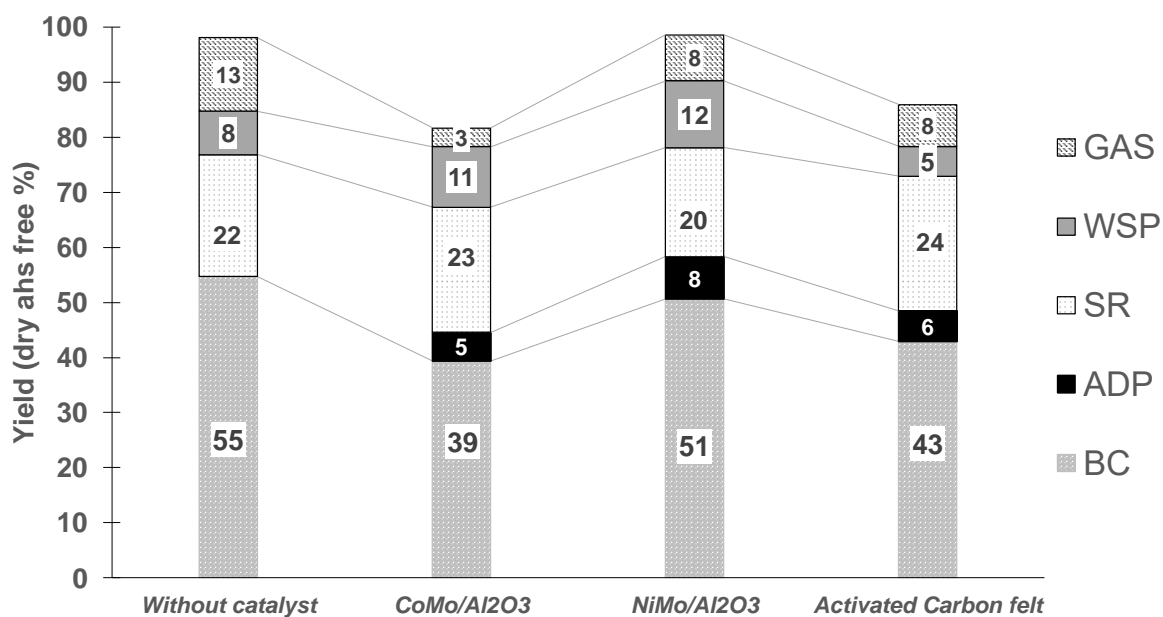

Figure 1: Product yields of HTL experiments performed at 325 °C and 30 min as reaction temperature and time and 10 % w/w of RMS concentration.

Figure 2: Picture of the typical product behavior after HTL of RMS in the presence of CoMo/Al$_2$O$_3$ once the reactor was opened.

Table 1: Elemental analyses of the a) biocrude (BC); of the b) additional phase (ADP) and c) solid residues (SR) obtained from experiment of HTL of RMS at 325 °C, 30 min, without catalyst addition and in the presence of CoMo/Al2O3, NiMo/Al2O3 and ACF. C, H, N, S are mass fractions. "Others" percentage was determined by the difference from 100 % and the sum of C, H, N, S % as in equation (3)

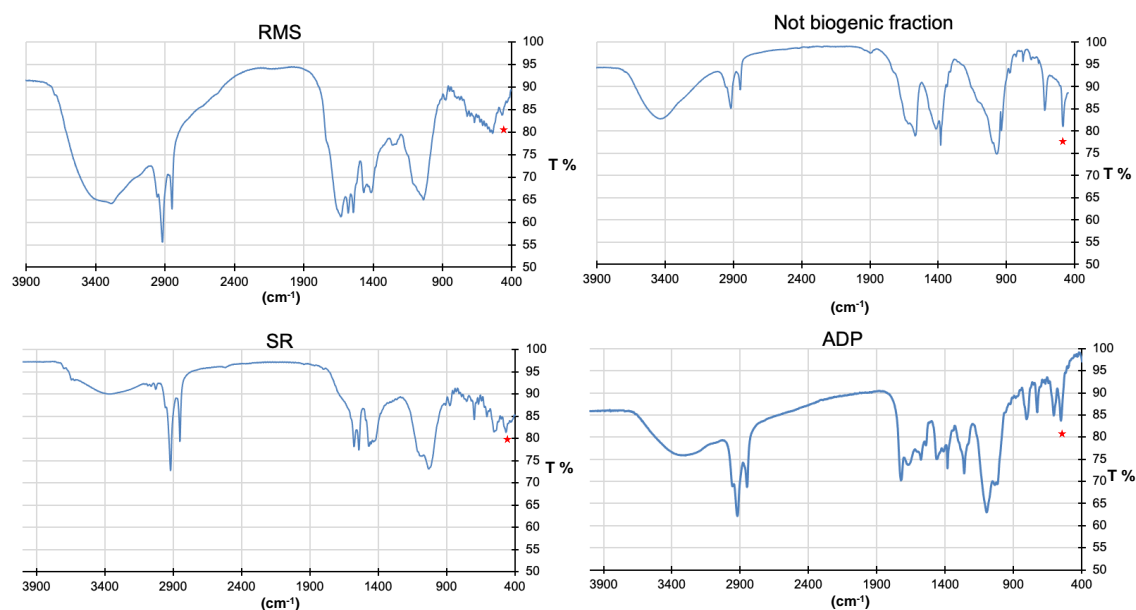| a) BC								
Catalyst	C	H	N	S	others	H/C	N/C	S/C
_	73.28	10.81	5.73	1.96	8.22	1.76	0.07	0.010
CoMo/Al2O3	76.74	11.35	3.92	1.77	6.24	1.76	0.04	0.009
NiMo/Al2O3	71.70	10.95	4.37	1.58	11.41	1.82	0.05	0.008
ACF	71.64	10.40	4.16	2.19	11.62	1.73	0.05	0.012
b) ADP								
Catalyst	C	H	N	S	others	H/C	N/C	S/C
_								
CoMo/Al2O3	47.68	7.48	4.31	1.45	39.08	1.87	0.08	0.011
NiMo/Al2O3	49.44	5.96	2.53	1.26	40.82	1.44	0.04	0.010
ACF	39.33	5.80	7.90	1.66	45.31	1.76	0.17	0.016
c) SR								
Catalyst	C	H	N	S	others	H/C	N/C	S/C
_	24.85	3.55	1.45	1.08	11.07	1.70	0.05	0.016
CoMo/Al2O3	28.43	3.80	1.37	1.14	11.27	1.59	0.04	0.015
NiMo/Al2O3	26.45	3.95	1.45	1.35	10.80	1.78	0.05	0.019
ACF	27.71	3.89	1.29	1.17	15.94	1.67	0.04	0.016

Figure 3: FT-IR analyses performed on samples of RMS, of the isolated not biogenic organic matter (i.e. isolated microplastics of RMS), of the SR and the ADP.

4. Conclusions

It was observed that the complexity of the feedstock affects the phase behaviour of the product obtained from the HTL of RMS. In particular, the production of anew additional phase (ADP) was observed in the presence catalyst. Even if the ADP yield was quite limited, never exceeding 10 % w/w, its formation must be carefully considered because N and Cl were detected in its composition and their presence can adversely affect the quality of BC and the economic sustainability of the upgrading steps.

Nomenclature

ADP – additional phase
ACF – activated carbon felt
BC - biocrude
daf – dry ash free
HTL – hydrothermal liquefaction
$m_{(daf)}^{P}$ – mass of product
$m_{(daf)}^{RMS}$ – initial mass of RMS
m_{ADP}^{tot} - total mass of isolated ADP

$m_{ADP}^{acetone}$ – mass of ADP in the acetone phase
m_{ADP}^{wax} – mass of ADP recovered as wax from tri-chloroethane phase
MF – Microplastic fraction
ND – not detectable
RMS – real municipal sludge
SR – solid residues
WWTP – wastewater treatment plant
Y_p – product yield

Acknowledgments

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