

Catalytic hydrothermal liquefaction of municipal sludge assisted by formic acid for the production of next-generation fuels

Authors

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Nomenclature

Abbreviations

ACF	Activated carbon felt
BC	Biocrude
daf	Dry ash free
ER	Energy recovery
FA	Formic acid
HC	Hydrocarbon
HHV	High heating value
HO	Heavy Oil
HTL	Hydrothermal liquefaction
MS	Municipal sludge
SR	Solid residue
WSP	Water-soluble products
VT	Volatiles

Symbols

m_p	Mass of the product
M_{tot}^0	Total mass of organics loaded in the reactor
$N_{FA}^{t=0}$	Mols of FA initially fed to the reactor,
$N_{FA}^{t=t_r}$	Residual mols of FA
$N_{FA}^{converted}$	Converted mols of FA
X_{FA}	Conversion of formic acid
Y_p	Product yields

Abstract

Hydrothermal liquefaction (HTL) of municipal sludge (MS) was studied at 325°C and 30 min at 10 and 30% w/w concentration of MS using formic acid (FA) as a green liquid hydrogen donor both in the absence and in the presence of heterogeneous catalysts. Pellets of commercial NiMo/Al₂O₃, CoMo/Al₂O₃ and felt of activated carbon ACF 1600 were used as catalysts. The addition of FA at high MS loading allowed to increase the yields in BC from 41 to 62% and its H/C ratio from 1.80 to 2.01 leading to energy recovery (ER) higher than 100%.

When heterogeneous catalysts were used together with FA, a marked improvement of BC yields and quality was obtained at 10% MS loading. This behavior was not observed at 30% w/w concentration probably for the fouling of the catalyst surface. Experimental results obtained in this study indicates that FA can be an effective additive to improve BC yields and quality in the HTL of MS at high loading, that is a very promising result in the perspective of industrial utilization of the process.

Keywords

Hydrothermal liquefaction, biorefinery, municipal sludge, heterogeneous catalyst, formic acid, hydrogen donor

1. Introduction

In the context of waste recycling technologies, thermochemical conversion processes are considered efficient routes for the energetic valorization of waste biomass by producing crude-like oils classified as next-generation fuels [1,2]. To be competitive with fossil fuels they must have high heating value (HHV) and hydrocarbon content and low sulfur, nitrogen and oxygen levels (EN 14214:2012+A2:2019).

Hydrothermal liquefaction (HTL), performed at 300 - 400°C and at pressure in the range of 10-40 MPa [3–5], represents a promising route to transform a wet organic feedstock (bio-feedstock) into

an intermediate fuel called biocrude (BC) in the presence of a solvent, usually water [6], avoiding expensive drying steps [1,6]. Other products of the process are a solid residue (SR), an aqueous phase containing water-soluble products (WSP) and a gaseous phase (GAS) [5]. The missing fraction is defined as volatiles (VT) and its yield is calculated by difference to 100% w/w of the sum of fractional yields of collected products. HTL of microalgae, macroalgae, sewage sludge, lignocellulosic residues has been extensively studied [7,8] and techno-economic analyses were done in order to assess the feasibility of the process [9,10]. In this context, Giaconia et al. [9] estimated the minimum fuel selling price (MFSP) of BC obtained by HTL of microalgae driven by solar energy, finding that a large fraction of the index is determined by the cost of the microalgae. In this framework, the utilization of a nominal zero-cost feedstock such as sewage sludge produced by urban municipalities, termed municipal sludge (MS), could allow one to abate the operative expenses of HTL and the minimum price of the BC [9,10].

To date, it has to be considered that the quality of the BC produced by HTL, could not compete with that of fossil fuels and it must be further hydrotreated before it can be classified as next-generation fuel. The production of a BC with the lowest heteroatom content and with the highest fraction of hydrocarbons (HC), can highly improve the economic feasibility of the HTL process. Analyzing the literature on HTL one can conclude that the yield and quality of BC are mainly dependent on the feedstock composition and loading in the reactor [11–15], the work-out procedures adopted to separate the products [16–18], the reaction temperature and time [19–26], the liquefaction solvent [6]. The adoption of catalysts in HTL of wet biomass could increase the BC yield and decrease its O, N, and S concentration by in-situ upgrading but their efficacy with MS is still not clear. Qian et al. investigated at 400°C the effect of different additives, as potential homogeneous and heterogeneous catalysts in this process, finding a negligible positive effect on the BC yield. [13]. Some researchers found a positive effect on the BC quality by using activated carbon [27,28] that is known to promote deoxygenation of oleic acid in the presence of formic acid (FA) as a liquid hydrogen donor [29].

CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts are commonly used in the hydrotreating of crude oil distillates and their use in an aqueous environment does not affect the selectivity of hydrogenating reactions [31]. Commercial NiMo/Al₂O₃ was found effective in the upgrading of BC obtained by HTL of different types of feedstock, leading to fractional cuts rich in paraffinic hydrocarbons [30]. The reactions involved in the hydrotreating of a crude oil distillate can be divided in two main classes: hydrogenation of unsaturated bonds and removal of heteroatoms by hydrodenitrogenation, hydrodesulfurization and hydrodeoxygenation under the pressure of molecular hydrogen. According to the literature, the reactivity and kinetics of the transfer reactions change with the nature of the heteroatom and with the chemical structure of its bearing molecule. This behavior complicates the study of in situ hydrotreating of BC produced by HTL of MS as the organic fraction is a very complex mixture made of several types of organic compounds with broad molecular weight distribution. The main heteroatom in BC is oxygen that can be removed by two different routes: dehydration to produce H₂O and CO and decarboxylation to produce CO₂ [32, 33]. The latter is more attractive since it does not consume hydrogen thus increasing the H/C molar ratio of the BC [34].

The possibility of performing the hydrothermal deoxygenation of fatty acids to alkanes and alkenes in the absence of hydrogen donors and using cheap activated carbon as catalysts was already demonstrated. When the process was carried out with FA as a liquid hydrogen donor not only the formation of saturated hydrocarbons was promoted [29, 33, 35] but also denitrogenation was observed [36].

In the case of HTL of MS an initial pressure of H₂ decreased the temperature at which the highest yield of BC was obtained and increased the share of light compounds in the BC [22]. However, gaseous hydrogen is difficult to store and transport, dumping the economic sustainability of its use, and liquid hydrogen donors have been proposed as an alternative that can also avoid gas-liquid interfacial mass transport resistances [37]. FA is a dense liquid vector for H₂ that can be generated, together with CO₂, by its decarboxylation reaction even under mild conditions [38–43].

Furthermore, FA can be considered a green compound because its production can be achieved by electrochemical reduction of carbon dioxide in aqueous phase driven by renewable electric energy [44, 45].

Use of FA as liquid hydrogen donor in HTL processes has been already investigated with several feedstocks and reported results indicate that its effect depends on the nature of the treated biomass. Some studies showed that FA has effects similar to molecular H₂ in the HTL of several biochemical model compounds such as sunflower oil, albumin and soya protein, glucose and lignite and with some real biomasses such as microalgae, lignocellulosic biomass and cyanobacteria [46, 47]. FA was also found the most effective additive to improve the yield of the oil fraction generated by HTL of paper-mill sludge and waste newspapers [48], *Spirulina* [49] and lignin obtained from empty fruit bunch [50]. Anyway, the same effect was not observed in the HTL of several polysaccharide model compounds [51].

The effect of FA in the HTL of MS was poorly investigated. Qian et al. tested it as homogeneous catalyst at 400°C with 15% w/w MS loading. Two different FA concentration were adopted, i.e. 10 and 50% w/w with respect to the dry biomass, and a decrease of the BC yield was observed [13]. In this study, for the first time, we investigated systematically the effect of FA on the yield and quality of BC obtained by HTL of MS at a relatively mild temperature of 325°C, both in the absence and in the presence of commercial catalysts. Pellets of CoMo/Al₂O₃ and NiMo/Al₂O₃ and slices of activated carbon felt (ACF) were selected to this purpose. Collected experimental results indicate that FA, added at about 5% w/w with respect to the dry biofeedstock, can be used to convert undiluted thickened MS (30% w/w dry concentration in the aqueous slurry) in BC with high yields, energy recoveries higher than 100% and a small impact on the economic sustainability of the process.

2. Materials and Methods

2.1. Materials

MS provided by the urban wastewater treatment plant of A.M.A.P. s.p.a., Palermo, Italy were used as the feedstock of HTL experiments. The MS adopted in this study were dried at 105°C for 72 h, three samples were then calcinated at 550°C for 6h in order to determine the organic content. The proximate and elemental analysis of adopted MS are reported in Table 1.

Table 1: Proximate and elemental analyses of MS (O %w/w was determined by difference)

<i>Proximate analysis.</i>	<i>% w/w of dry matter</i>
moisture	76
organic content	80
<i>Elemental analysis</i>	<i>% w/w of dry matter</i>
C	43.39
H	6.48
N	5.04
S	0.8
HHV (MJ/kg) ^a	20
<i>Metals</i>	<i>mg/kg (dry basis)</i>
P	0.64
Cd	0.3
Hg	< 0.1
Ni	69.6
Pb	35
Cu	184
Zn	451
Cr	30
<i>Salts</i>	<i>mg/L</i>
fluorides	0.22
chlorides	44.3
sulfates	86.9

^aestimated using Dulong's formula as reported in the analytical methods section

Deionized water (laboratory utility) was used as a solvent to dilute the feedstock. Before each experiment deionized water was added to dried MS powder to reach the desired loading (dry biomass basis). Formic acid (98-100 vol%, Analytical grade, Sigma Aldrich, Italy) was used as received. Control experiments with molecular hydrogen were performed using compressed H₂ (99.999%, Alphagaz, Airliquide, Italy). CoMo/Al₂O₃ (Albemarle, KF 1022), NiMo/Al₂O₃ (Albemarle, KF 851) and activated carbon felt (ACF 1600, Ceramaterials, USA) were used as heterogeneous catalysts at 10% w/w with respect to MS. Cyclohexane and acetone (Analytical grade, Sigma Aldrich, Italy) were adopted to recover the BC according to the results of previous researches [17,27]. THF (anhydrous, +99.9% Sigma Aldrich, Italy) was used to dilute liquid samples for gas chromatography (GC) analyses. Tetradecane, 1-tetradecene, hexadecane, 1-hexadecene, octadecane and 1-octadecene (Alpha Aesar, analytical grade) were used as analytical standards. Methyl heptadecanoate (Sigma Aldrich, +99%, Italy) was added as the internal standard for GC analyses. Sulfuric Acid (Analytical grade, Sigma Aldrich, Italy) and water (HPLC grade, Honeywell, Italy) were used to prepare the mobile phase for HPLC analyses.

2.2. Experimental methods

The adopted reactor was the same used in our previous work [17]. It consists of a stirred AISI 316 high-pressure autoclave reactor with a volume of 16 mL. The suspension constituted by dry biomass in water was termed slurry. Here, 5g of slurry were treated in each experiment. In selected experiments, FA was added to the slurry to reach a concentration of 0.4 mol/L. When a heterogeneous catalyst was used it was added at 10% w/w with respect to dry feedstock. The MS loading in the slurry changed from 10 to 30 % w/w. After loading, the reactor was purged with argon and sealed with the procedures reported elsewhere [52]. Selected experiments were conducted in the presence of H₂. In this case atmospheric air was first removed by an Edwards vacuum pump. Then H₂ and nitrogen, used as inert diluent, were loaded in the reactor each at 0.2 MPa of partial pressure.

HTL experiments were carried out at 325°C for 30 min, with a stirring rate of 170 rpm. As previously reported [17], a cylindrical heater was used to heat the reactor to the reaction temperature with a heating rate of 13°C/min and the reaction time was considered as the time during which the reactor was maintained at 325°C.

In this work, we used the same optimized work-out procedures adopted in previous research to approach a quantitative closure of the mass balance [17]. Briefly, as showed in Fig. 1 after the reaction, the experimental apparatus described in detail elsewhere was used to perform the expansion of the produced gas and analyze them through GC-TCD analyses. The reactor was then opened and the produced phases were poured into a centrifuge tube. Cyclohexane was added to the centrifuge tube (1 mL) and to the reactor (10 mL) to recover the residual AP retained by the SR and BC inside the reactor. After this step, the centrifuge tube was centrifuged at 3220 rpm for 20 min and the reactor filled with cyclohexane was placed inside a laboratory stirred oscillator for 3h. A glass Pasteur was employed to separate cyclohexane and AP from the centrifuge tube and from the reactor. The AP were recovered and stored in a glass vial for further gravimetric analyses to determine the mass of produced WSP. The cyclohexane soluble products were stored in a rounded bottom flask. After the recovery of AP, acetone was used to recover the residual BC retained from the SR inside the reactor and inside the centrifuge tube. Acetone solutions were poured inside the same aforementioned rounded bottom flask full of cyclohexane solution. A spatula was used to scrape the SR from the centrifuge tube and from the reactor and it was also added to the rounded bottom flask. Vacuum filtration was then performed using Büchner filtration apparatus joined with a dry and pre-weighted nylon filter 47 mm, 0.2µm pores diameter and an Edwards vacuum pump. The SR on the filter was washed with acetone and dried at 60°C to determine its mass. The rounded bottom flask, containing the filtered liquid phase, was joined to the apparatus described in detail elsewhere that allowed us to perform a controlled stripping of the solvents from the BC at 50°C. The residual product in the flask after evaporation constitutes an heavy oil fraction (HO) while

stripped vapors were collected in a cold trap at -10°C and analyzed through GC-FID analyses to quantify the hydrocarbon fraction (HC) C14-C18 that was stripped with the solvents.

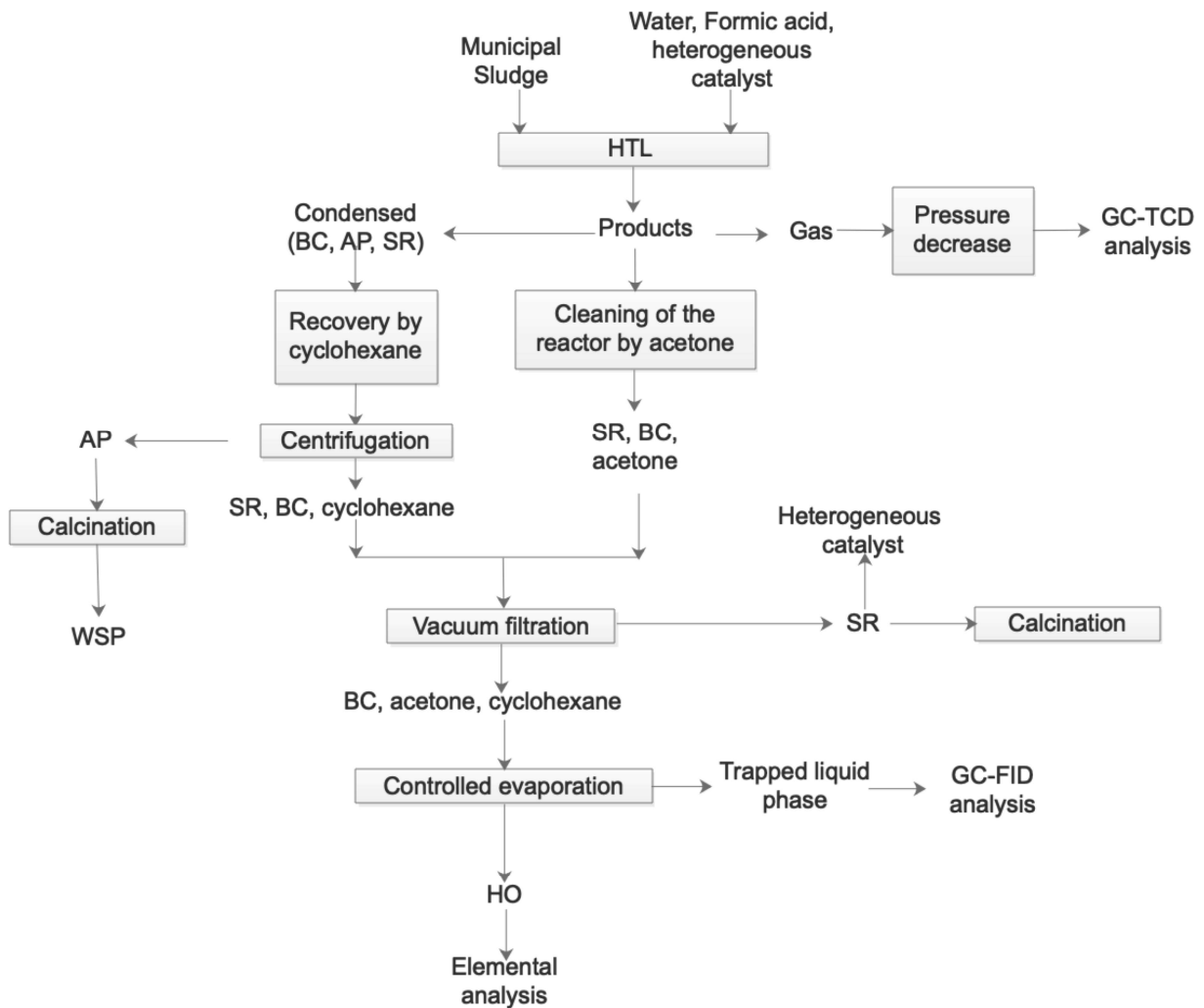


Figure 1: Schematic description of experimental procedure adopted to separate products after HTL of MS.

2.3. Analytical methods

The yields of products Y_p were calculated by the equation (1) in the dry ash free form (daf):

$$Y_p(\% w/w) = m_p / M_{tot}^0 \times 100 \quad (1)$$

$$M_{tot}^0 = m_{MS}^0 + m_{FA}^0 \quad (2)$$

where m_p is the mass of the product and M_{tot}^0 is the total mass of organics initially loaded in the reactor in the daf form, given by the sum of the initial mass of MS m_{MS}^0 and of FA m_{FA}^0 (eq. 2).

The dry ash free mass of WSP and of SR was determined by calcination at 550°C for 6h. The yield of HC was determined using equation (1). It must be considered that the effective mass of BC is the sum of the relative mass of HO and HC fractions.

The yield of BC was calculated as in eq. 3:

$$Y_{BC} (\% w/w) = Y_{HO} (\% w/w) + Y_{HC} (\% w/w) \quad (3)$$

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 yield of produced gaseous compounds was determined following eq. (1), using the equation of state for ideal gases to determine the moles of produced gases. Selected HC compounds in liquid solutions were identified and quantified, using high purity standards, by gas chromatographic analyses performed using an Autosystem XL Perkin Elmer GC equipped with a ZB-FFAP capillary column (30m*0.25mm*0.25 μ m) and a FID detector with Helium (99.999%, Air Liquide, Italy) as the carrier gas as reported elsewhere [17,27]. The following temperature profile was adopted to perform GC runs: oven holding at 40°C for 3 min followed by an heating ramp at 8°C/min up to 244°C with an holding time of 0 min. Injector and detector were heated at 250°C. Adopted injection volume was 0.4 μ L, He flow-rate in the column was set to 2.4 mL/min with 15/1 split ratio. Methyl heptadecanoate was used as the internal standard, tetradecane, 1-tetradecene, hexadecane, 1-hexadecene, octadecane and 1-octadecene (Alpha Aesar, analytical grade) were used as reference standards to identify peaks and prepare linear calibrations. Peak assignments in the GC chromatograms were made by direct addition of small amounts of the standards to the liquid phases collected from HTL experiments. THF was used as dilution solvent to prepare the samples. GC-MS analyses of samples of the liquid solution were conducted using a TRACE GC 2000 with a TRACE

MS plus spectrometry detector equipped with a MEGA-5 (30m*0.32 mm*0.25 μm) capillary column. The following temperature profile was adopted to perform GC-MS runs: oven holding at 40°C for 10 min followed by an heating ramp at 5°C/min up to 250°C with an holding time of 10 min, then an heating ramp at 10°C up to 310°C with an holding time of 10 min. Source temperature 230°C. Transfer line at 250°C. Adopted injection volume was 1 μL, 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 %.

The residual concentration of FA in water, after the experiments conducted to study its thermal decomposition, was detected through liquid chromatography using an Agilent HP 1100 HPLC joined with a Rezex ROA-Organic Acid H+ (8%) column (Phenomenex) heated at 55°C and a UV detector working at 210 nm. Formic Acid (98-100 %, analytical grade, Sigma Aldrich, Italy) was employed to build proper calibration lines, using 0.005 mol/L H₂SO₄ water solution at pH= 2.5 as mobile phase eluted at 0.6 mL/min.

Elemental analyses to determine carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content in HO were performed by Perkin Elmer 2400 Series II elemental analyzer and O (% w/w) was determined by eq. (4):

$$O = 100 - C - H - N - S - \text{ashes} \quad (4)$$

Where C, H, N, S are the % w/w detected by the elemental analyzer and the ashes are the ash average percentage determined after calcination of the samples at 550°C, for 6h.

The ash content in the SR was determined after calcination of a dry sample at 550°C and 6h. The High Heating Values (HHV) were estimated by the Dulong formula [53] expressed through the equation (5):

$$HHV_{products} (MJ/kg) = 0.338 C + 1.44 (H - O/8) + 0.094 S \quad (5)$$

The energy recovery (ER) was used as figure of merit to evaluate the practical feasibility of the HTL of MS under the investigated operative conditions.

The ER of each collected product (ER_p) was estimated by the equation (6):

$$ER_p(\%) = M_{tot}^0 \times Y_p HHV_p / (m_{MS}^0 HHV_{MS} \times (1 + (m_{FA}^0 HHV_{FA} / m_{MS}^0 HHV_{MS})) \times 100 \quad (6)$$

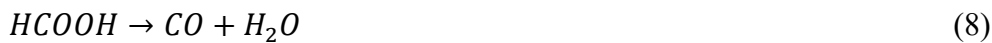
Where M_{tot}^0 is the total mass defined by eq. (2), Y_p is the product yield defined in eq. (1), m_{MS}^0 and m_{FA}^0 are the initial mass of MS and of FA, HHV_{MS} and HHV_{FA} are the high heating value of MS and FA respectively. HHV_{FA} was calculated with equation (5) knowing that the elemental composition of pure FA is 26.1 % of C, 4.38 % of H and 46.02 % of O.

The catalysts were recovered after vacuum filtration and they were cleaned following a similar procedure described by Egesa et al. [54] using acetone (HPLC grade) as cleaning solvent. Briefly, the pellets of catalysts were placed in a glass tube. Than 10 mL of acetone were added and the tube was sonicated for 30 min. Samples of recovered catalysts were analyzed by Scanning Electron Microscope (FEI Quanta 200 FEG) and energy dispersive X-ray analyses (EDAX) operating at 30 kV using low-vacuum conditions.

3. Results and discussion

3.1. Thermal degradation of FA in water

To assess the role of FA as a hydrogen vector in the hydrothermal environment we studied its decomposition in hot liquid water. FA can be degraded in water through decarboxylation (eq. 7) or decarbonylation (eq. 8) [40,43,55] and the first reaction prevails above 320°C with a rate of consumption following first order kinetics [43]



Yasaka et al. [40] studied the effect of pH on the parallel competition described by eq. 7 and 8, finding that decarboxylation is faster at basic pH. Moreover, if decarbonylation prevails, carbon monoxide from FA could be consumed by the water-gas shift reaction (WGSR) (eq. 9):



Thermal degradation of FA in water solutions was studied at the same operative condition of HTL of MS, i.e. at 325°C and 30 min as reaction time also in the presence of different heterogeneous catalysts.

FA conversion (X_{FA}) was calculated as in eq. (10):

$$X_{FA}(\%) = (N_{FA}^{t=0} - N_{FA}^{t=t_r})/N_{FA}^{t=0} \times 100 = (N_{FA}^{converted})/N_{FA}^{t=0} \times 100 \quad (10)$$

where $N_{FA}^{t=0}$ are the mols of FA initially fed to the reactor, $N_{FA}^{t=t_r}$ represent the residual mols of FA in water detected through HPLC analyses after the reaction time $t_r = 30$ min has passed and

$N_{FA}^{converted}$ are the mols of FA converted by reactions (7) and (8). Considering that reaction (9) is consecutive to FA decarbonylation (eq. 8) cumulative mols of produced CO_2 and CO detected by GC-TCD analyses can be used to estimate the molar amount $N_{FA}^{converted}$ of converted FA, in the eq. (10). Then the FA conversion X_{FA} was calculated as:

$$X_{FA}(\%) = (N_{CO}^{prod} + N_{CO_2}^{prod})/N_{FA}^{t=0} \times 100 = N_{H_2}^{prod}/N_{FA}^{t=0} \times 100 \quad (11)$$

Table 2: Composition of the gas phase (% mol/mol) produced by FA decomposition in water. Experiments were conducted at 325°C for 30 min, with 0.4 mol/L of FA with different catalysts. The standard deviation of the % mol of gas phase composition was ± 9 .

Catalyst	Composition of the gas phase (% mol/mol)			FA conversion (%)
	H ₂	CO ₂	CO	
–	48	40	12	15
CoMo/Al ₂ O ₃	53	44	3	22
NiMo/Al ₂ O ₃	58	40	2	19
ACF 1600	36	63	1	26

ACF: activated carbon felt; FA: formic acid.

The gas phase obtained from experiments was mainly composed of H₂ and CO₂ in almost equivalent quantity, indicating that the decarboxylation route prevails under adopted conditions (Table 2). FA conversion of 15 % was obtained in the absence of catalysts and increased to 22, 19 and 26% when CoMo, NiMo and activated carbon felt ACF 1600 were used, thus suggesting that the catalysts can promote the decarboxylation.

3.2. Effect of FA as liquid vector of hydrogen in the HTL of MS

In literature, it was reported that the presence of hydrogen donors promotes the hydrogenation of the organic fragments generated from the hydrothermal degradation of the feedstock initially loaded in the reactor. On the other hand, the local concentration of hydrogen in hot liquid water is limited by its low solubility [56].

For this reason, we used FA that can act as a liquid vector of hydrogen and acid catalyst of hydrolytic depolymerization of biomacromolecules in the HTL of MS at 325°C for 30 min.

Experiments were conducted using stirred regime to minimize the mass transport resistance.

Looking at the product yields in Fig. 2 one can observe that the addition of hydrogen with an initial pressure of 0.2 MPa affected marginally both the HO and SR yields that changed from 37 to 39% and from 23 to 24% respectively, while it increased significantly the amount of the isolated HC fraction whose yield increased from 2 to 7% highlighting the higher rate of decarboxylation reactions. Among detectable hydrocarbons, the main components of this fraction are C14 and C16 unsaturated compounds, but we must underline that the adopted GC method can only detect the presence of hydrocarbons with more than 12 carbon atoms as lower molecular weight compounds are not separated from the solvent.

When the HTL was carried out under hydrogen pressure, the H/C ratio of the produced BC increased from 1.80 to 1.95 while O/C and N/C molar ratios were only slightly modified (Table 3). FA concentration was selected to generate by decomposition according to eq. 6, an amount of hydrogen similar to that of exp. 2. The addition of FA in the HTL of MS induced an increase of the concentration of hydrogen in the gaseous products from 2 to 10 % mol/mol with respect to the blank experiment (i.e. the HTL of MS without added FA) confirming the role as hydrogen vector of the carboxylic acid. With this dosage, we found a significant reduction of both HO and SR yields from 37 to 29% and from 23 to 16% respectively, in agreement with results obtained in fast HTL of sewage sludge in the presence of FA [13]. These reductions were accompanied by a slight increase of the HC yield (from 2 to 4%) and by a marked enhancement of VT yields that changed from 11 to

24% (Fig. 2). We made the hypothesis that the observed reduction in yields of HO and SR can be attributed to formation of low volatile compounds, not detected by the adopted GC method, that fictitiously increased the VT yields. To investigate this possibility we performed GC-MS analyses of the condensate phases and we detected the presence of many compounds, different from hydrocarbons, whose number increases in the presence of FA (Fig. 3b and 3d).

Using FA, H/C ratio of the BC of 1.96, similar to that obtained under hydrogen pressure, was measured, while the O/C ratio remained close to 0.1, leading to a HHV value of 40 MJ/kg.

In the perspective of industrial application of HTL, it would be interesting to use a high biomass loading avoiding dilution of thickened MS whose water content ranges between 70 and 80%.

Previous studies on the HTL of microalgae have shown that higher biomass loading decreases the BC yield. However, to the best of our knowledge, only Qian et al. [13] studied the isothermal HTL of sewage sludge changing the moisture content. These researchers found that the BC yields increased up to a maximum and then decreased when the biomass loading was higher than 20% w/w even if reported values of yield moves inside a relatively narrow range (22.5% to 27.5%).

When we performed the HTL of MS at 30% w/w loading we obtained a BC yield of 38%, quite similar to that obtained at 10% w/w loading (BC yield 37%), accompanied by an increase in the SR yield from 23 to 28%. This result is comparable with that reported by Ali Shah et al. [14] studying the HTL of concentrated sewage sludge. When the same experiment was repeated in the presence of FA, we found a marked enhancement of the HO and HC yields that changed from 38 to 55% and from 3 to 7% respectively. Moreover, the H/C ratio of BC increased from 1.85 to 2.00 while O/C still remained close to 0.1 (Table 3). In these conditions, the ER of HO, generally close to 70%, reached a value of 108% (Exp. 5 Tab. 3) that is a clear indication that the HTL of MS with this additive makes possible to store thermal energy in the biofuel.

In the presence of FA the yield in SR decreased from 30 to 20% (Fig. 2) that is an interesting result as a lower mass of solids has to be disposed of or devoted to other kinds of energetic valorization as

solid recovered fuels. According to collected results, FA candidates as a very interesting additive to perform HTL of MS in their native form without need of dilution or pretreatments.

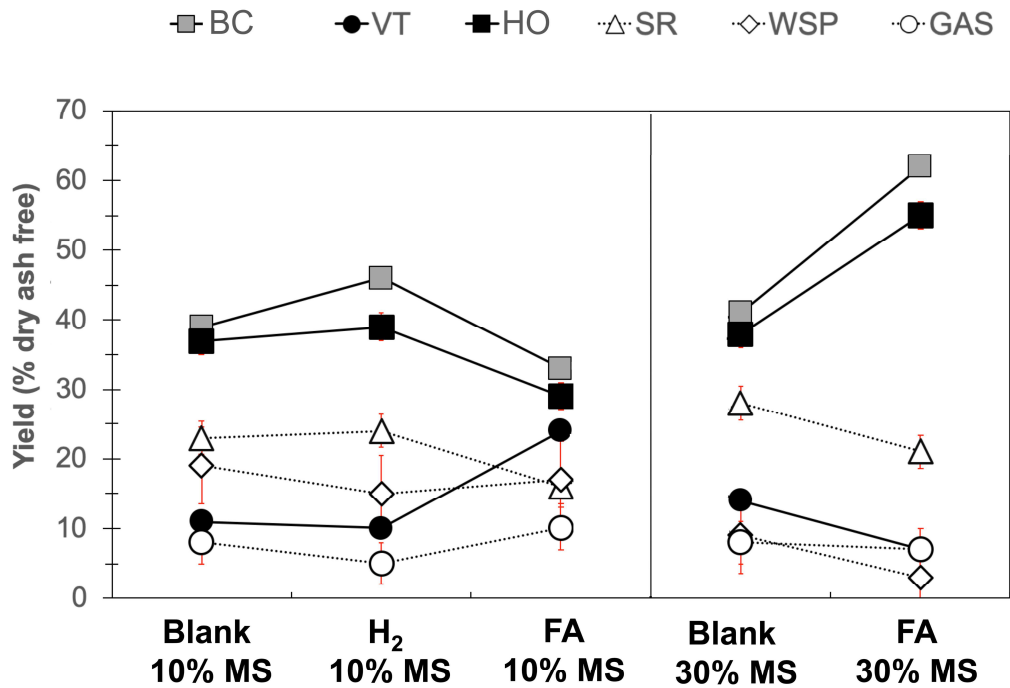


Figure 2: Product yields obtained from HTL experiments conducted at 325°C as reaction temperature, 30 min as reaction time, 10% - 30 % w/w of dry MS loading in water, 0.2 MPa of H₂ or 0.4 M of FA. MS: municipal sludge; daf: dry ash free; HO: heavy oil; HC: hydrocarbon fraction; BC: cumulative amount of HO and HC; SR: solid residues; WSP: water soluble products; VT: volatiles; HHV: high heating value; ER: energy recovery.

Table 3: Elemental molar ratios of the BC produced from HTL experiments at 325°C 30 min of reaction time, 0.2 MPa of H₂ or 0.4 M of FA.

Exp.	MS loading (% w/w)	Reducing agent	H/C ^a	O/C ^a	N/C ^a	HHV ^b	ER	
							ER% HO	ER% HC
1	10	—	1.80	0.12	0.04	39	71	5
2	10	H ₂	1.95	0.10	0.05	39	73	18
3	10	FA	1.95	0.08	0.04	42	68	11
4	30	—	1.85	0.10	0.06	39	74	8
5	30	FA	2.00	0.12	0.07	39	108	19

^a molar ratio

^b(MJ/kg).

Exp: experiment; MS: municipal sludge; HHV: high heating value; ER: energy recovery; FA formic acid; HO: heavy oil; HC: hydrocarbon fraction.

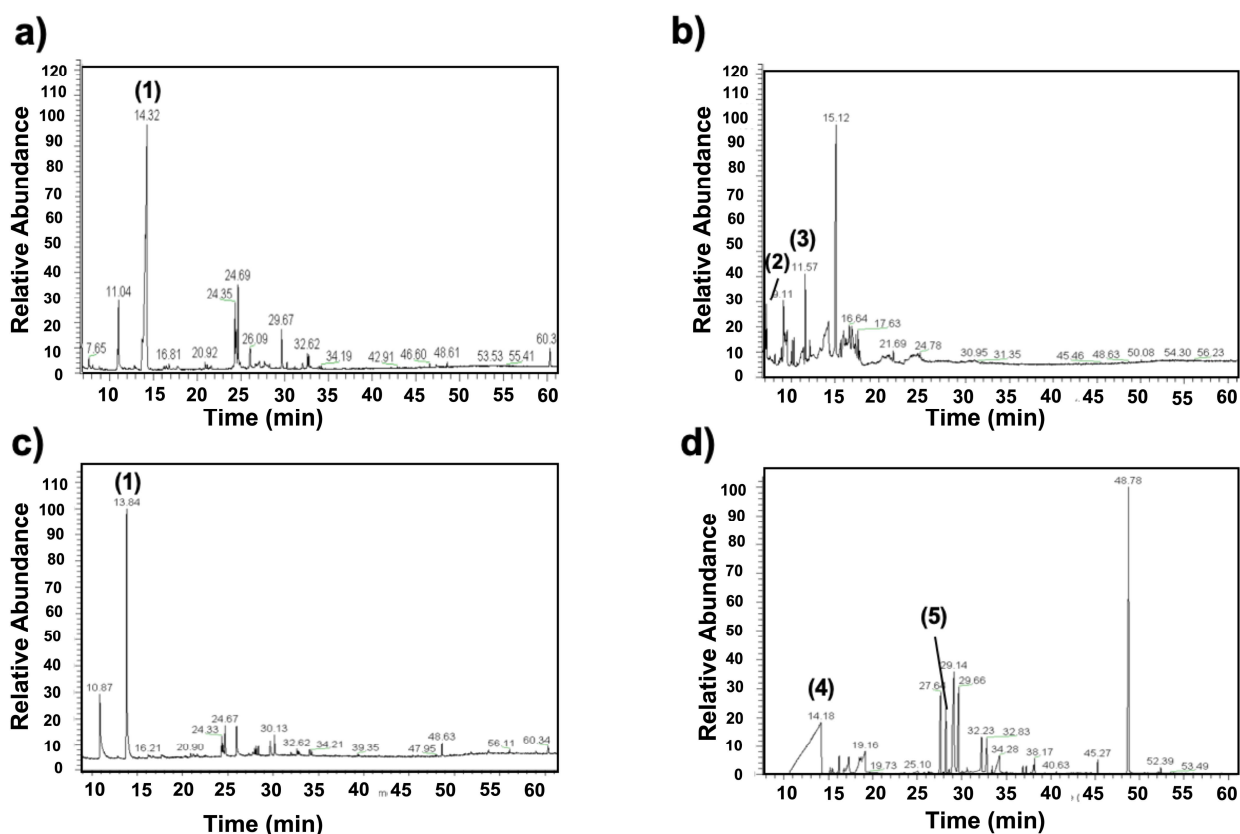


Figure 3: GC-MS total ion chromatogram of the trapped liquid phase, diluted in acetone, collected from HTL experiments at 325°C, 30 min of a) municipal sludge (MS) 10% w/w in water; b) municipal sludge (MS) 10% w/w in water, formic acid 0.4 M; c) municipal sludge (MS) 30% w/w in water; d) municipal sludge (MS) 30% w/w in water, formic acid 0.4 M; The main peaks identified are: (1) 2-Pentanone, 4-hydroxy-4-methyl-; (2)furan, tetrahydro (C_4H_8O); (3) toluene (C_7H_8); (4) 2-furanol, tetrahydro ($C_4H_8O_2$); (5) 2,3'-Bifuran, octahydro ($C_8H_{14}O_2$).

3.3. Combined effect of FA and of heterogeneous catalysts in the HTL of MS

The possibility of using heterogeneous catalysts to promote the performances of HTL of MS is challenged by the complex and wide nature of the feedstock that also contains not biogenic components such as heavy metals, microplastics and inorganic salts.

Interesting results obtained using FA prompted us to postulate a process architecture in which the HTL step is followed by separation of the SR and of the gaseous products while the BC/AP

mixture, still containing unreacted FA, that is a much less demanding environment for heterogeneous catalysts, is addressed to catalytic up-grading being.

In the perspective of this strategy, we investigated the behavior of commercial catalysts in the HTL of MS in stirred reactors in the absence and in the presence of FA adding them at 10% w/w concentration with respect to loaded MS. In some of these experiments, significant amounts of HC fraction were detected whose yield and composition must be cumulated with those of HO to estimate the real outcome of the experiment.

In the absence of FA, at 10% w/w MS loading, CoMo/Al₂O₃ strongly increased the yield in BC that reached 61% compared with 39% obtained in the pure thermal experiment (Fig. 4a). This enhancement was mainly due to the production of a significant amount of HC fraction and was accompanied by a marked decrease of WSP (from 19 to 6%) and VT (from 11 to 3%). With NiMo/Al₂O₃ and ACF catalysts, the isolated HC fraction was much less relevant and the BC yields were estimated to 42% and 37% respectively together with quite high VT yields of 18 and 22% that could be due to the production of VT compounds not detected by the adopted separation procedures.

As HTL is carried out at high pressure, compact reactors with a high production rates would be the best option for industrial production of the BC. To obtain the highest possible biomass loading in these apparatuses it should be avoided any dilution of thickened MS. For these reasons, we performed some experiments with native MS in which biomass loading increased to 30%w/w.

In a pure thermal experiment (termed blank in Fig. 4c), the higher biomass loading did not change HO and HC yield. When heterogeneous catalysts were added, the highest BC yields were obtained with NiMo/Al₂O₃ and ACF, with values of 53 and 51% respectively, with an almost quantitative closure of the global mass balance. As already reported, when FA was added alone it strongly enhanced the BC yields at 30% MS loading (Fig. 4d). When both FA and catalysts were added, BC yields increased with respect to pure thermal HTL at both investigated MS loadings (Fig. 4b and 4d). At 10% w/w MS, in the presence of catalysts, the VT yields were depressed. The opposite

behavior was observed at 30% MS loading. HC fraction detected in experiments with heterogeneous catalysts were mainly constituted by n-C16 saturated hydrocarbons.

In Fig. 5 are reported the Van Krevelen diagrams of BC obtained at the two different biomass loadings together with the initial composition of adopted MS as a reference. In the most diluted system, the elemental composition of BC was enriched in H and depleted in O coherently with the hypothesis that decarboxylation reactions are prevalent. At 30% MS loading, only the H/C ratio was improved by the catalysts while a clear reduction of O content was not detected probably owing to the inhibition of decarboxylation reactions due to catalyst deactivation.

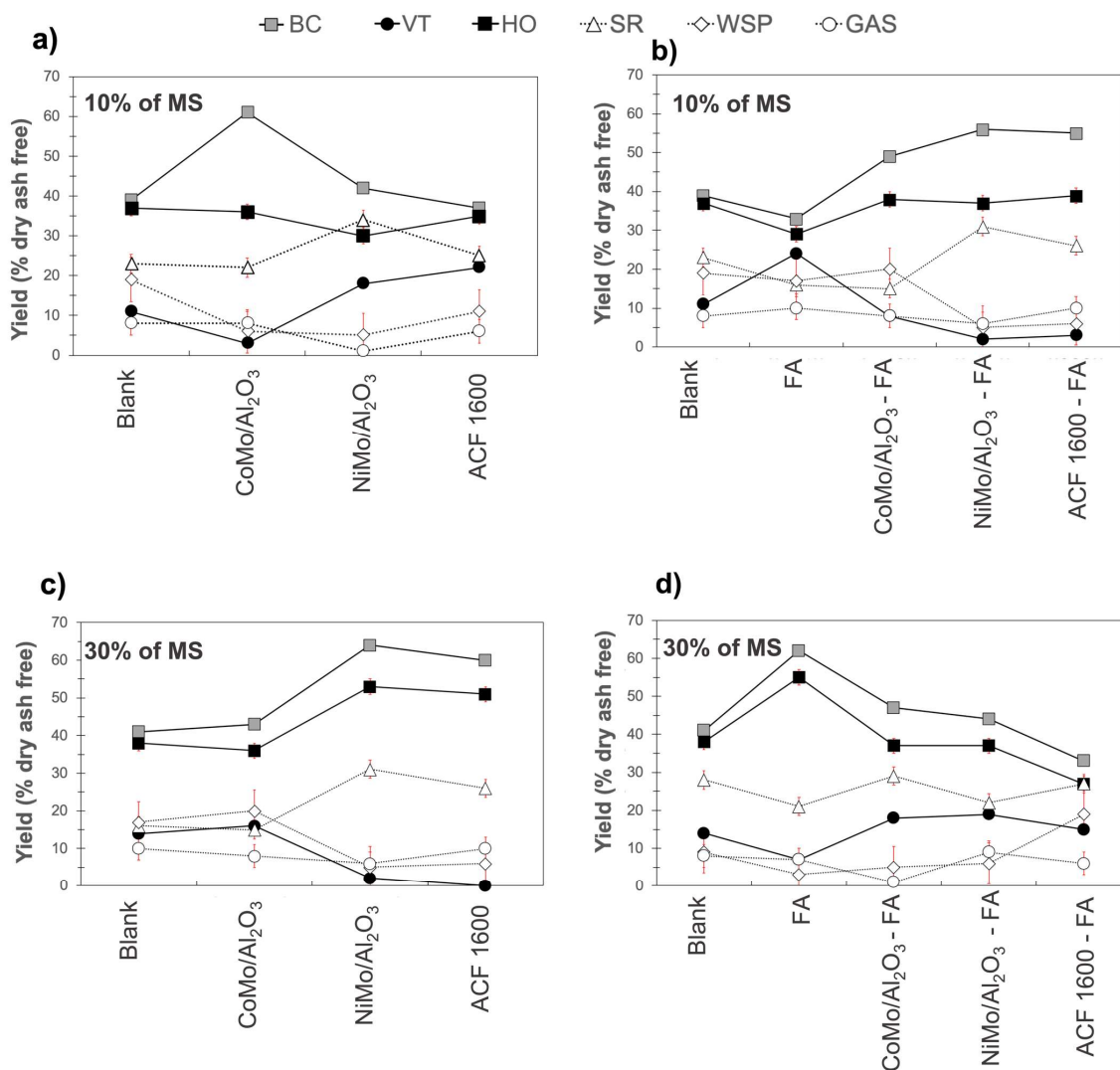
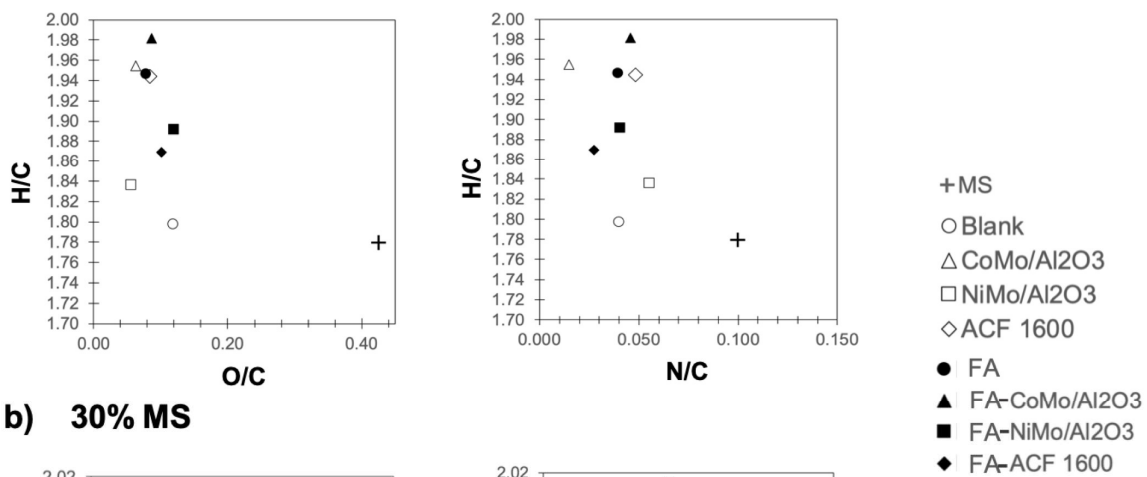


Figure 4: Product yields obtained from catalyzed HTL experiments conducted with a MS loading of 10% and 30% w/w at 325°C and 30 min as reaction temperature and time. CoMo/Al₂O₃, NiMo/Al₂O₃, ACF 1600 were used as catalysts, FA was added as liquid hydrogen donor.

Heterogeneous catalysts loading was 10% w/w with respect to mass of municipal sludge. MS: municipal sludge; daf: dry ash free; HO: heavy oil; HC: hydrocarbon fraction; BC: cumulative amount of HO and HC; SR: solid residues; WSP: water soluble products; VT: volatiles; HHV: high heating value; ER: energy recovery; CoMo/Al₂O₃: KF 1022; NiMo/Al₂O₃: KF 851; ACF: activated carbon felt.

a) 10% MS



b) 30% MS

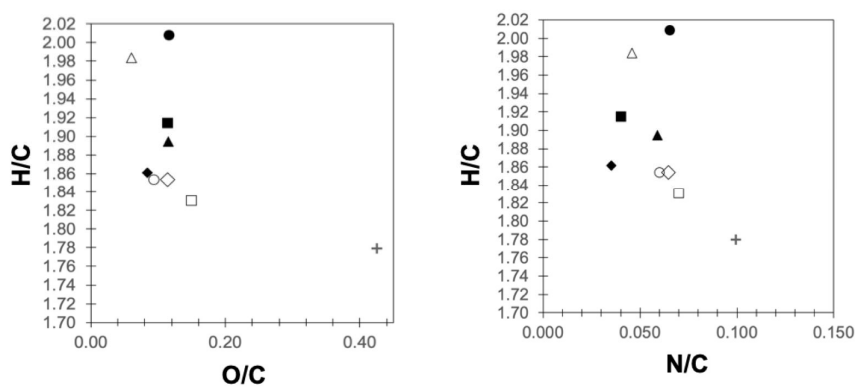


Figure 5: Elemental molar ratio diagram for the BC obtained from the experiments with a MS loading of a) 10% and b) 30% w/w at 325°C, 30 min as reaction temperature and time. CoMo/Al₂O₃, NiMo/Al₂O₃, ACF 1600 were used as catalysts at 10% loading with respect to biomass, FA was added as liquid hydrogen donor.

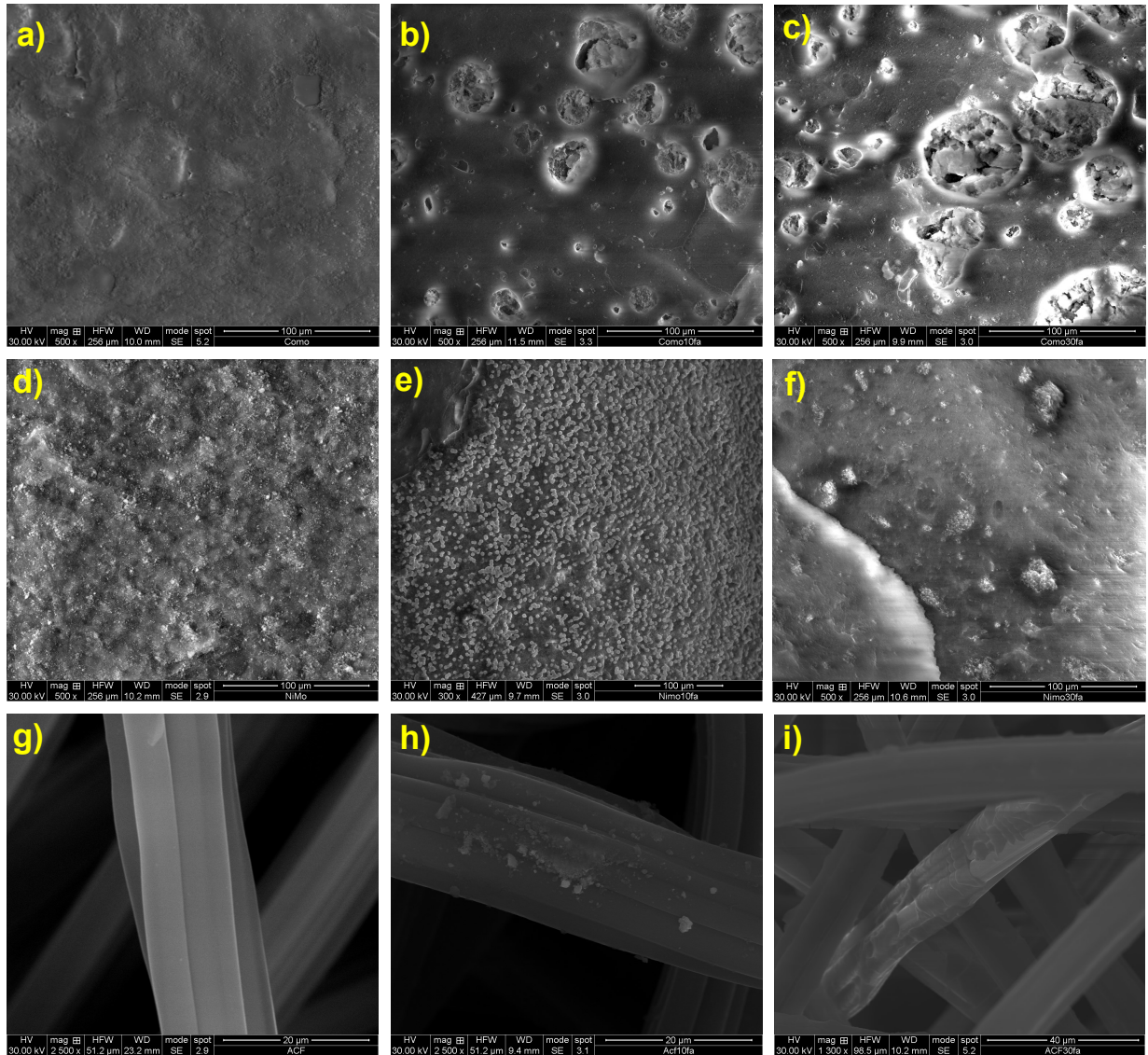


Figure 6: SEM analyses of a) CoMo/Al₂O₃ before HTL; b) CoMo/Al₂O₃ recovered after HTL of MS at 10 % of concentration in the presence of FA; c) CoMo/Al₂O₃ recovered after HTL of MS at 30 % of concentration in the presence of FA; d) NiMo/Al₂O₃ before HTL; e) NiMo/Al₂O₃ recovered after HTL of MS at 10 % of concentration in the presence of FA; f) NiMo/Al₂O₃ recovered after HTL of MS at 30 % of concentration in the presence of FA; g) ACF before HTL; h) ACF recovered after HTL of MS at 10 % of concentration in the presence of FA; i) ACF recovered after HTL of MS at 30 % of concentration in the presence of FA.

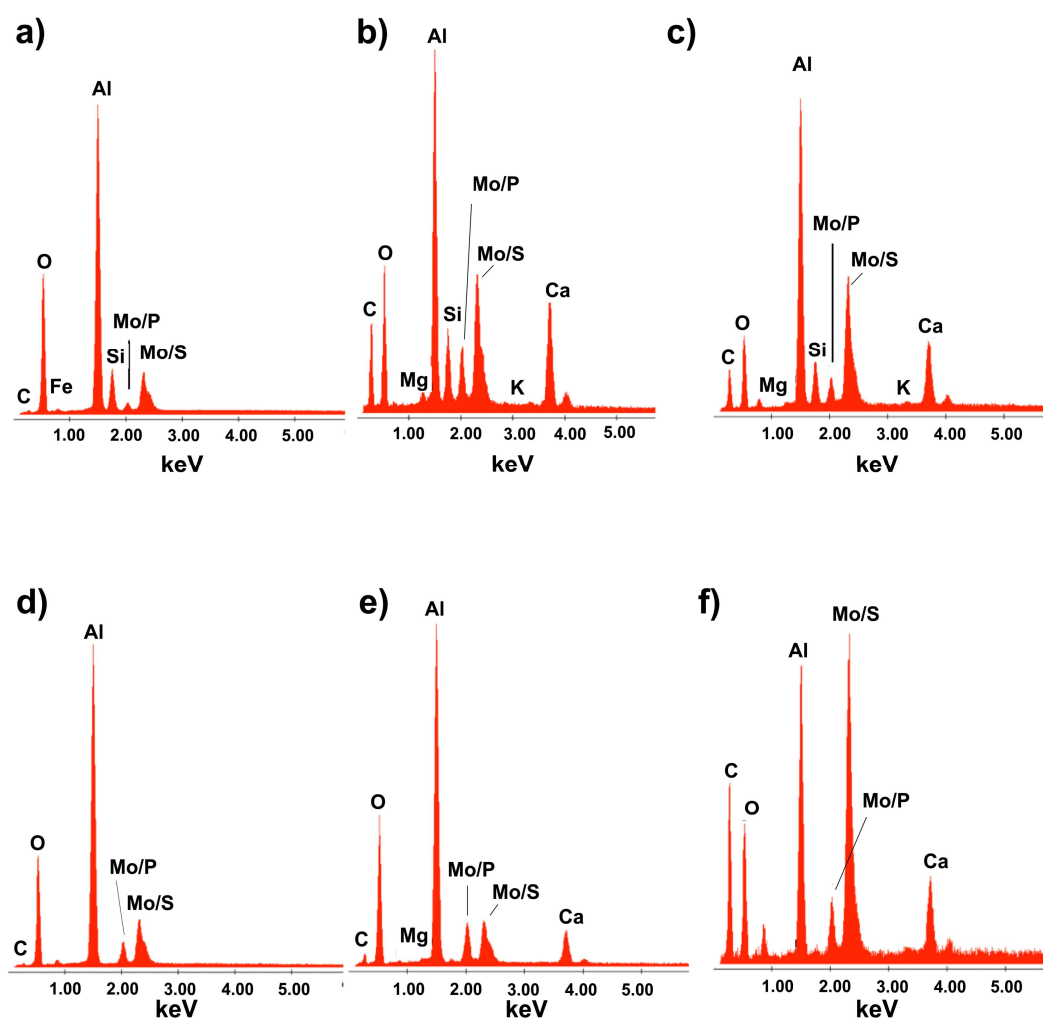


Figure 7: EDAX of a) CoMo/Al₂O₃ before HTL; b) CoMo/Al₂O₃ recovered after HTL of MS at 10 % of concentration in the presence of FA; c) CoMo/Al₂O₃ recovered after HTL of MS at 30 % of concentration in the presence of FA; d) NiMo/Al₂O₃ before HTL; e) NiMo/Al₂O₃ recovered after HTL of MS at 10 % of concentration in the presence of FA; f) NiMo/Al₂O₃ recovered after HTL of MS at 30 % of concentration in the presence of FA.

To investigate this possibility we analyzed samples of used catalysts by SEM and EDAX (Fig. 6-7). Before SEM/EDAX the samples were sonicated in acetone for 30 min to dissolve any residual BC. In these samples it was possible to detect the deposition of particulate matters whose amounts significantly increased at the highest investigated MS loading where most of the visible surface was found covered. EDAX analyses of materials deposited on CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts, carbon free in their native form, indicated the presence of significant amount of C on their surface.

These results support the hypothesis that catalyst fouling occurs during the HTL process particularly when the concentration of MS is large.

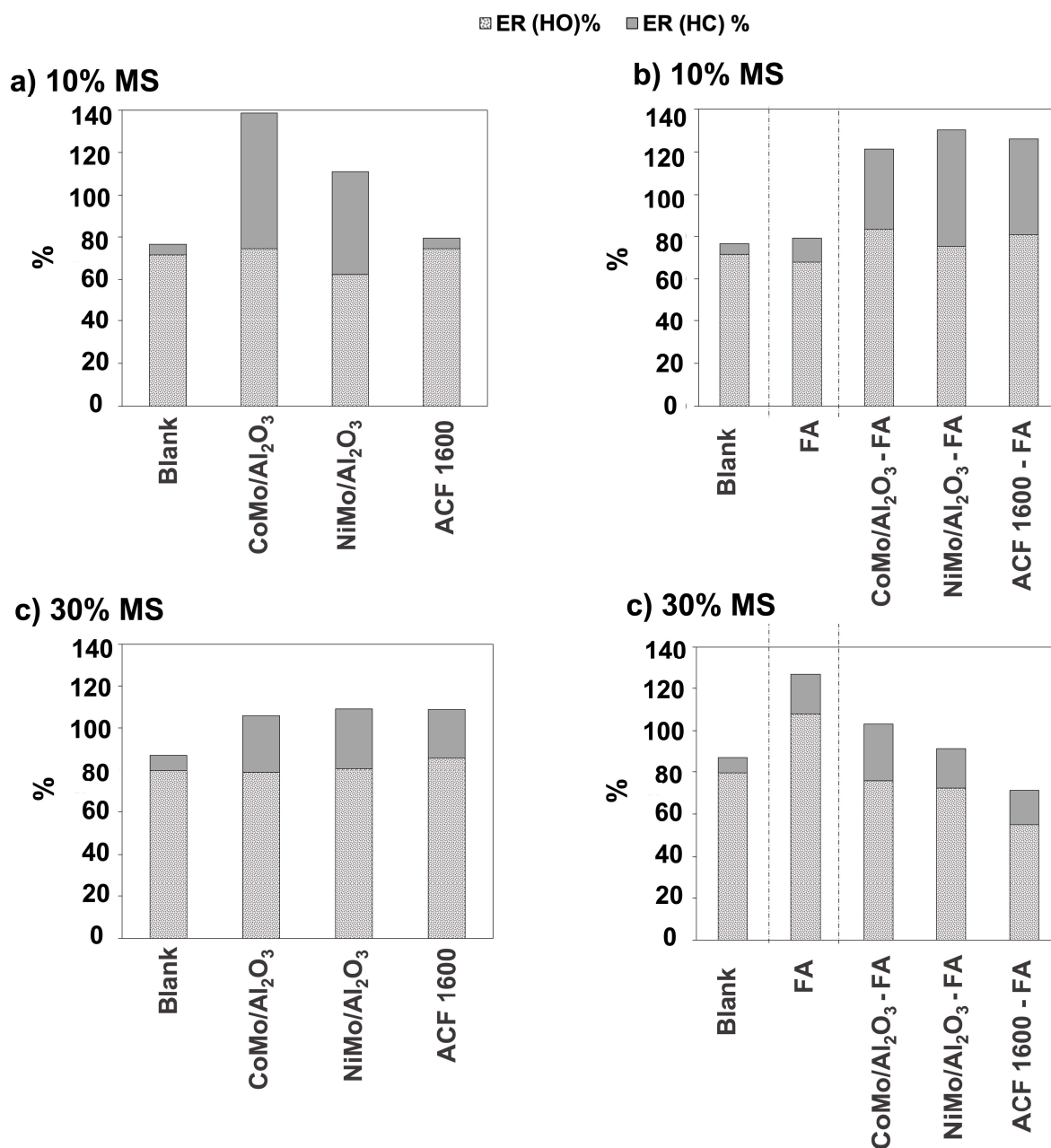


Figure 8: ER distribution for catalytic experiments with a MS loading of a) 10% and d) 30% w/w at 325°C, 30 min as reaction temperature and time in absence of FA and a MS loading of c) 10% and d) 30% w/w at 325°C, 30 min as reaction temperature and time in the presence of FA. CoMo/Al₂O₃, NiMo/Al₂O₃, ACF 1600 were used as catalysts, FA was added as liquid hydrogen donor. In the experiments conducted with catalyst their loading was of 10% w/w with respect to MS. FA: Formic acid; HO: heavy oil; HC: hydrocarbon fraction; ACF: activated carbon felt.

ER is the figure of merit that can be used to evaluate the energy that is stored in the produced phases and values estimated for HO and HC fractions are reported in Fig. 8. In general CoMo and NiMo based catalysts, both in the absence and in the presence of FA, allowed to increase the cumulative ER with respect to pure thermal HTL mainly due to the contribution of generated HC fraction. Also, FA alone gave cumulative ER higher than 100 % indicating that a fraction of the energy used to drive the process can be stored in the products.

In the last years significant interest was devoted to investigate the feasibility of hydrothermal processes [57]. Giaconia et al. [9] calculated a minimum fuel selling price (MFSP) of BC of 2.19 USD/kg. This value was demonstrated to be strongly affected by the cost of the biofeedstock as the MFSP of BC decreased to 1.31 USD/kg considering in that model a zero-cost bio-feedstock. In the same study it was found that the BC yield is another parameter strongly affecting the economic sustainability, since it determines the fraction of starting material transformed in valuable products. In the case here investigated, the yield of the products of HTL of MS were significantly improved by the addition of FA as indicated by experiments carried out with MS at 30% loading (Fig. 2). Both the nominal zero cost of MS and the higher BC yields promotes the possibility of practical exploitation of the technology.

On the other hand FA is used as sacrificial additive and it seems reasonable to question if its use is economically sustainable. To get a first indication on this aspect, the mathematical model developed to perform the conceptual techno-economic analysis of the HTL of microalgae powered by concentrated solar heat [9] was used as a reference. In the model the yield of BC was considered unaffected by the addition of FA that is a conservative choice with respect to the enhancement observed at higher MS loadings. The market price of the carboxylic acid, with a purity of 80%, ranged in the interval 0.6-1.0 €/kg [9,58] and to estimate its impact on the economics of the HTL process, we selected the mean value of 0.8 €/kg. The operating cost of the solution 0.4 M of FA was substituted to that of water in the previously developed cash flow analysis calculation [9]. By this approach it was found that MFSP increases just by 10%, from 2.19 to 2.43 USD/kg, when a

solution of 0.4 mol/L of FA is substituted to demineralized water that is a quite limited economic penalty.

4. Conclusions

The utilization of FA as green hydrogen donor in the HTL of a zero-cost wet bio feedstock as MS can significantly increase both BC yield and quality. Results of catalytic experiments at high biomass loading give an indication of catalyst deactivation by fouling with compounds that, differently from BC, are not soluble in acetone and are a major drawback for the practical exploitation of this approach. More promising in this perspective was the use of FA alone as a green sacrificial hydrogen donor. In fact it allowed to work with native MS at loading as high as 30% reaching BC yield and ER higher than 60% and 100% respectively. A mathematical model developed for solar HTL of microalgae indicated that the use of FA increases by only 10% the minimum fuel selling price of the BC with respect to the process performed without addition of the hydrogen donor. All these findings suggest that FA can be a promising additive to transfer the process from the laboratory to the industrial plant.

Acknowledgments

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