

Catalytic hydrothermal liquefaction of municipal sludge assisted by formic acid for the production of next-generation fuels: from experimental results to a techno-economic analysis

Authors

Claudia Prestigiacomo^a, Federica Proietto^a, Vito Armando Laudicina^b, Angelo Siragusa^c, Onofrio Scialdone^a, Alessandro Galia^{a,*}

Nomenclature

Abbreviations

ACF	Activated carbon felt
BC	Biocrude
daf	Dry ash free
EBC	Effective biocrude
Eq	Equation
ER	Energy recovery
FA	Formic acid
Fig	Figure
GC	Gas-chromatograph
GAS	Gaseous phase
HC	Hydrocarbon
HHV	High heating value
HPLC	High performance liquid chromatography
HTL	Hydrothermal liquefaction
min	minute
MS	Municipal sludge
NGF	Next generation fuel
SR	Solid residue
TC	Thermochemical
WSP	Water-soluble products
VT	Volatiles

Symbols

H/C	Hydrogen to carbon molar ratio
m_p	Mass of the product
M_{tot}^0	Total mass of organics loaded in the reactor
N/C	Nitrogen to carbon molar ratio
$N_{HCOOH}^{t=0}$	Mols of FA initially feeded to the reactor,
$N_{HCOOH}^{t=t_r}$	Residual mols of FA
$N_{HCOOH}^{converted}$	Converted mols of FA
O/C	Oxygen to carbon molar ratio
rpm	Rotation per minutes
T	Temperature
t	Reaction time
X_{FA}	Conversion of formic acid
Y_p	Product yields
% w/w	percentage by weight

^aDipartimento di Ingegneria, Sezione Chimica Ambientale Biomedica Idraulica e dei Materiali, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy.

^bDipartimento di Scienze Agrarie, Alimentari e Forestali, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy.

^cAMAP s.p.a., 2 Via Volturmo, 90138 Palermo, Italy.

Corresponding author

E-mail address: alessandro.galia@unipa.it (A. Galia)

Abstract (max 200)

Catalytic hydrothermal liquefaction (HTL) of municipal sludge (MS) was performed to investigate the effect of catalysis on the formation of biocrude (BC) and hydrocarbon (HC) products. HTL experiments were conducted at 325°C and 30 min at 10 and 30% w/w loadings of MS using formic acid (FA) as a green liquid hydrogen donor. Pellets of commercial NiMo/Al₂O₃, CoMo/Al₂O₃ and felt of activated carbon ACF 1600 were used as heterogeneous catalysts. The addition of FA at high MS loading allowed to increase the effective BC (EBC) yields from 39 to 55% 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 EBC yields and quality was obtained at 10% MS loading. This behavior was not observed at 30% w/w concentration probably for the deactivation of the catalytic systems. A techno-economic analysis performed with figures of merit determined in this study, using a mathematical model prepared for solar HTL of microalgae, allowed us to estimate a minimum fuel selling price of the BC of 0.78 USD/kg that is very promising in the perspective of industrial utilization of the process.

Keywords

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

1. Introduction

In the context of waste recycling technologies, thermochemical (TC) conversion processes are considered efficient routes for the energetic valorization of waste biomass by producing crude-like oils classified as next-generation fuels (NGF) [1,2]. To make the NGF 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). Among the TC processes, hydrothermal liquefaction (HTL) performed at 300 - 400°C and pressure in the range of 10-40 MPa [3–5] represents a promising route to transform a wet organic feedstock (bio-feedstock) into a NGF precursor 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. The utilization of a 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 NGF. 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 different additives as potential homogeneous and heterogeneous catalysts in this process finding only slight effects on the BC yield and quality [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 feedstocks leading to fractional cuts rich in paraffinic hydrocarbons. [30] The reactions involved in the hydrotreating of a crude oil distillate can be divided into 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].

The latter is more attractive since it does not consume hydrogen thus increasing the H/C molar ratio of the BC [33].

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 formic acid (FA) as a liquid hydrogen donor the formation of saturated hydrocarbons was promoted [29,34].

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 [35]. Formic acid (FA) is a dense liquid vector for H₂ that can be generated, together with CO₂, by decarboxylation reaction even under mild conditions [36–41]. 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 [42,43]. Biller and Ross [44] demonstrated that FA has effects similar to those of H₂ in the HTL of several biochemical model compounds (such as sunflower oil, albumin and soya protein, starch and glucose), microalgae and cyanobacteria. Furthermore, FA was found the most effective additive to improve the yield of a “heavy oil” fraction in the BC generated by HTL of paper-mill sludge and waste newspapers [45]. Anyway, its use in the HTL of MS was not deeply investigated.

In this study, for the first time, a systematic investigation of the catalytic HTL of MS using FA as a green reducing agent was performed at a relatively mild temperature (325°C). Pellets of commercial CoMo/Al₂O₃ and NiMo/Al₂O₃ and of activated carbon felt (ACF) were selected as heterogeneous catalysts to study their effects on the yield and quality of BC. The obtained experimental results have been used to estimate the minimum fuel selling price (MFSP) of BC in the frame of a techno-economic analysis of solar HTL previously published [9].

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 received 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. Gravimetric analyses showed that MS had initial moisture of 76% w/w, organic content of $80 \pm 0.2\%$ w/w, and elemental composition of 43.39 % C, 6.48% H, 5.04% N, 0.86% S corresponding to a high heating value (HHV) of 20 MJ/kg. 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 (nota). THF (anhydrous, +99.9% Sigma Aldrich, Italy) was used to dilute liquid samples for gas chromatography (GC) analyses. Tetradecane, 1-tetradecene, hexadecane and 1-hexadecene (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 [46]. Selected experiments were conducted in the presence of an initial partial pressure of H₂, the reactor was then evacuated and

gaseous hydrogen was loaded at 0.2 MPa partial pressure. After this step, other 0.2 MPa of partial pressure of nitrogen were loaded in the reactor as inert diluent.

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 obtain a quantitative closure of the mass balance [17]. Briefly, 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 aqueous phase 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 WSP from the centrifuge tube and from the reactor. The WSP were recovered and stored in a glass vial for further gravimetric analyses. The cyclohexane soluble products were stored in a rounded bottom flask. After the recovery of WSP, 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 biocrude at 50°C. The stripped vapors were collected in a cold

trap at -10°C and analyzed through GC-FID analyses to determine how many hydrocarbons (HC) C14-C18 were stripped with the solvents. Tetradecane, 1-tetradecene, hexadecane and 1-hexadecene (Alpha Aesar, analytical grade) were used to prepare samples to obtain calibration lines.

2.3. Analytical methods

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

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

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

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_{HCOOH}^0 (eq. 2).

The yield of HC was determined using equation (1). It must be considered that the effective amount of BC (EBC) is the sum of BC and HC fractions.

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

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

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.

HC fraction in liquid solutions was detected and quantified 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 using Helium (99.999%, Air Liquide, Italy) as the carrier gas as reported elsewhere [17,27]. Methyl heptadecanoate was used as the internal standard and THF as the solvent to prepare the samples.

The concentration of FA in water after the experiments conducted to study its thermal decomposition in water was detected through liquid chromatography using an Agilent HP 1100

HPLC joined with a Rezex ROA-Organic Acid H+ (8%) column (Phenomenex) at a temperature of 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 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 [47] 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) and the energy consumption ratio (ECR) were the figures of merit used in the work herein 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):

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

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_{HCOOH}^0 are the initial mass of MS and of FA, HHV_{MS} and HHV_{HCOOH} are the high heating value of MS and FA respectively. HHV_{HCOOH} 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.

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) [38,41,48] and the first reaction prevails above 320°C with a rate of consumption following first order kinetics [41]



Yasaka et al. [38] 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 formic acid 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_{HCOOH}) was calculated as in eq. (10):

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

where $N_{HCOOH}^{t=0}$ are the mols of FA initially fed to the reactor, $N_{HCOOH}^{t=t_r}$ represent the residual mols of FA in water detected through HPLC analyses after the reaction time $t_r = 30$ min has passed and $N_{HCOOH}^{converted}$ 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 $N_{HCOOH}^{converted}$ of converted FA, in the eq. (10). Then the FA conversion X_{HCOOH} was calculated as:

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

Table 1: 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

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 1). 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 [49].

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. 1 one can observe that the addition of hydrogen with an initial pressure of 0.2 MPa affected marginally both the BC 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. According to GC analyses, the main components of this fraction are C14 and C16 unsaturated hydrocarbons 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 ratio were only slightly modified (Table 2). 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 confirming the role of the hydrogen vector of the carboxylic acid. With this dosage, we found a significant reduction of both BC 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 formic acid [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 increased from 11 to 24% (Fig.1). We made the hypothesis that the reduction in low volatile product yields (BC and SR) can be attributed to a higher formation of smaller hydrocarbon compounds not detected by the adopted GC method that fictitiously increased the VT yields. Using FA a value of the H/C 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. These results further confirm the role of FA as carrier of hydrogen.

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 and they found that the BC yields increased up to a maximum and then decreased when the SS 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 BC 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 2). In these conditions, the ER of BC, generally close to 70%, reached a value of 108% 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. 1). These results are interesting since a lower mass of solids has to be disposed of or devoted to other kinds of energetic valorization as solid recovered fuels.

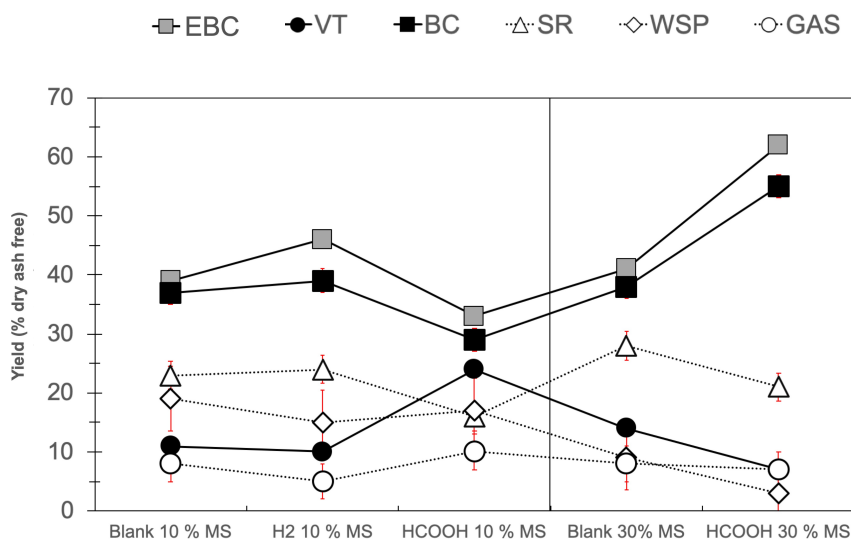


Figure 1: Product yields obtained from HTL experiments conducted at 325°C as reaction temperature, 30 min as reaction time, 10% - 30 % w/w of dry MS loading in water , 0.2 MPa of H₂ or 0.4 M of HCOOH. MS: municipal sludge; daf: dry ash free; EBC: effective amount of BC; BC: biocrude; HC: hydrocarbon fraction; SR: solid residues; WSP: water soluble products; VT: volatiles; HHV: high heating value; ER: energy recovery.

Table 2: Elemental molar ratios of the EBC produced from HTL experiments at 325°C 30 min of reaction time, 0.2 MPa of H₂ or 0.4 M of HCOOH.

Exp.	MS loading (% w/w)	Reducing agent	H/C ^a	O/C ^a	N/C ^a	HHV ^b	ER	
							ER% BC	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	HCOOH	1.95	0.08	0.04	42	68	11
4	30	–	1.85	0.10	0.06	39	74	8
5	30	HCOOH	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.

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

The behavior of catalysts in the HTL of MS was investigated 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 BC 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 EBC (sum of BC and HC yields) that reached 61% compared with 39% obtained in the pure thermal experiment (Fig. 2a). 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 EBC yields were estimated to 42% and 37% respectively together with quite high VT yields of 18 and 22% that could be due to the presence in the HC fraction of components with less than 12 carbon atoms not detected by GC analysis.

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. 2c), the higher biomass loading did not change BC and HC yield. When heterogeneous catalysts were added, the highest EBC 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 has added alone it strongly enhanced the EBC yields at 30% MS loading (Fig. 2d). When both FA and catalysts were added, BC yields increased with respect to pure thermal HTL at both investigated MS loadings (Fig. 2b and 2d). 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 all experiments with heterogeneous catalysts were mainly constituted by n-C16 saturated hydrocarbons.

In Fig. 3 are reported the Van Krevelen diagrams of EBC obtained at the two different MS loadings together with the initial composition of adopted MS as a reference. In the most diluted system, the elemental composition of EBC 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.

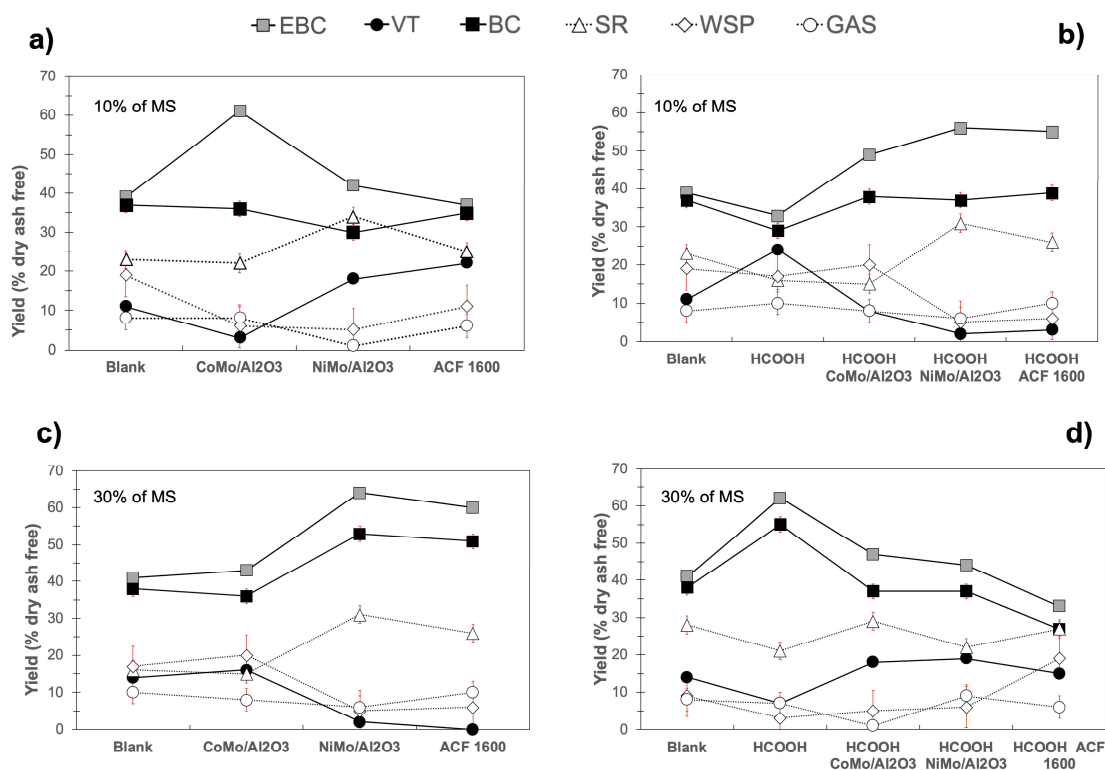
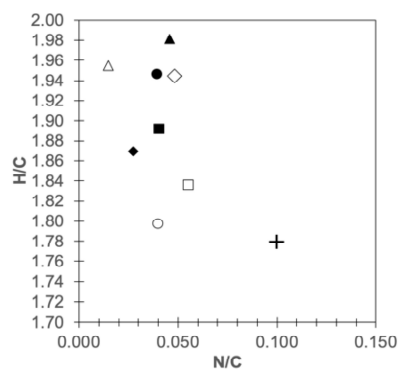
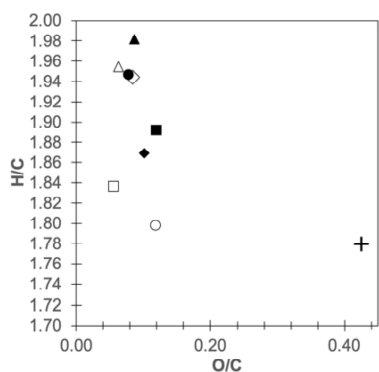


Figure 2: Product yields obtained from catalyzed HTL experiments conducted with a MS loading of 10% and 30% w/w at 325°C and 30 min as reaction temperature and time. CoMo/Al₂O₃, NiMo/Al₂O₃, ACF 1600 were used as catalysts, formic acid (FA) was added as liquid hydrogen donor. Heterogeneous catalysts loading was 10% w/w with respect to mass of municipal sludge. MS: municipal sludge; daf: dry ash free; BC: biocrude; HC: hydrocarbon fraction; 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 1600: activated carbon felt.

a) 10% MS



- +MS
- Blank
- △ CoMo/Al₂O₃
- NiMo/Al₂O₃
- ◇ ACF 1600
- HCOOH
- ▲ HCOOH CoMo/Al₂O₃
- HCOOH NiMo/Al₂O₃
- ◆ HCOOH ACF 1600

b) 30% MS

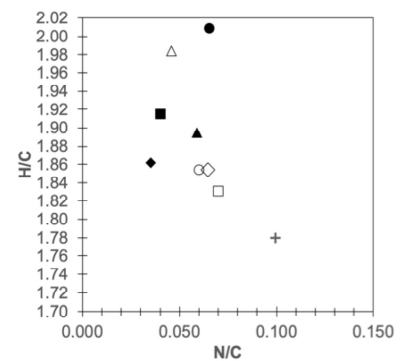
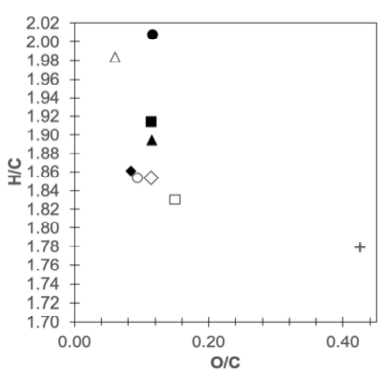


Figure 3 : Elemental molar ratio diagram for the **EBC** obtained from the experiments with a MS loading of a) 10% and b) 30% w/w at 325°C, 30 min as reaction temperature and time. CoMo/Al₂O₃, NiMo/Al₂O₃, ACF 1600 were used as catalysts at 10% loading with respect to biomass, formic acid (FA) was added as liquid hydrogen donor.

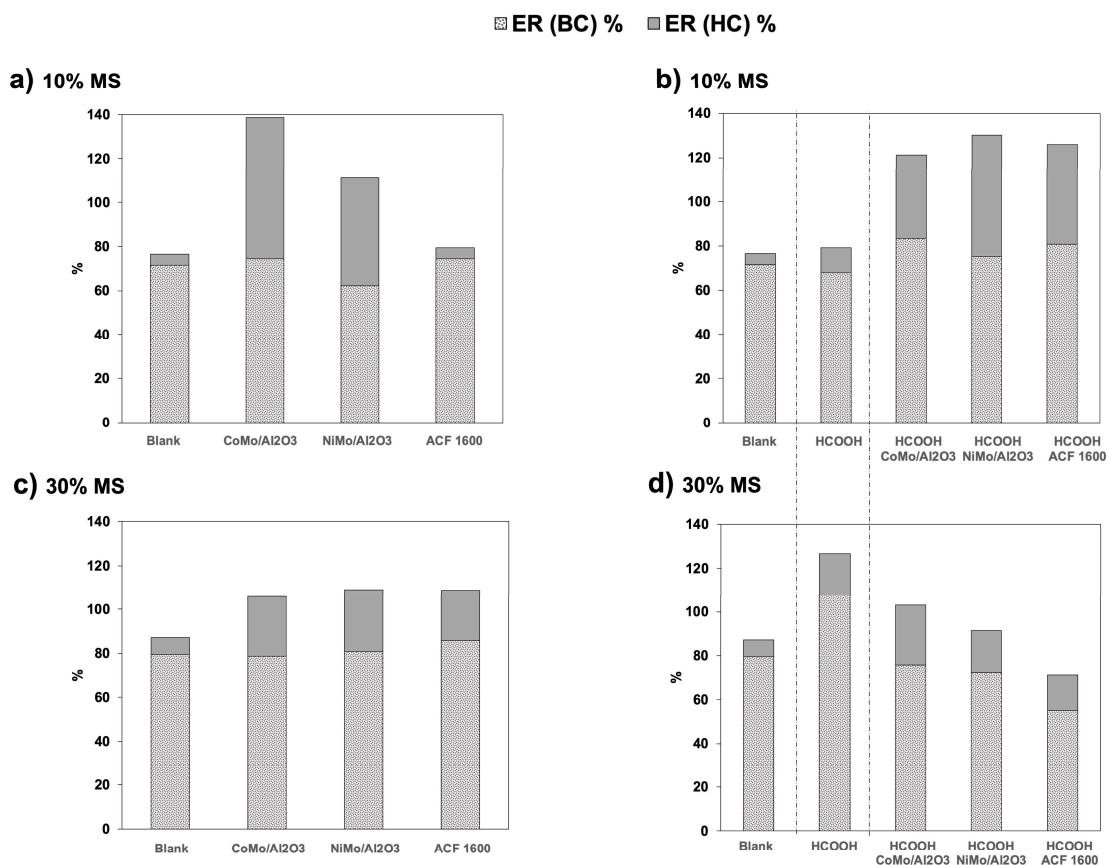


Figure 4: ER distribution for catalytic experiments with a MS loading of a) 10% and d) 30% w/w at 325°C, 30 min as reaction temperature and time in absence of FA and a MS loading of c) 10% and d) 30% w/w at 325°C, 30 min as reaction temperature and time in the presence of FA. CoMo/Al₂O₃, NiMo/Al₂O₃, ACF 1600 were used as catalysts, formic acid (FA) was added as liquid hydrogen donor. In the experiments conducted with catalyst their loading was of 10% w/w with respect to MS.

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 BC and HC fractions are reported in Fig. 4. In general CoMo and NiMo 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. Techno-economic analyses were then conducted choosing operating parameters that in the work herein allowed us to obtain higher productivity and high-quality BC. Therefore, the experiment conducted in the presence of formic acid and 30% w/w

of MS loading was selected to this purpose since a BC yield of 55 % w/w with a H/C ratio of 1.99 was produced.

3.4. Techno-economic analysis

The mathematical model developed to perform the conceptual techno-economic analysis of the HTL of microalgae powered by concentrated solar heat [9] was used in this study to perform a first estimation of the economic sustainability of the HTL of MS using FA as a green liquid vector of hydrogen. In the last years a lot of interest was devoted to investigate the feasibility of solar-assisted hydrothermal processes [50].

Giaconia et al. [9] calculated a minimum fuel selling price (MFSP) of BC of 2.19 USD/kg whose value is strongly affected by the cost of the microalgae as clearly indicated by the reduction of MFSP to 1.31 USD/kg obtained considering in the model a zero-cost bio-feedstock.

In the case here investigated, the yield of the products of HTL of MS were taken from experiments carried out with MS at 30% loading in the presence of FA (Fig. 1). The market price of the carboxylic acid, with a purity of 80%, ranged in the interval 0.8-1.2 €/kg [9,51] and for this techno-economic analysis, we selected the mean value of 1 €/kg. Two scenarios were implemented: the first considering the HTL plant totally driven by combustion of part of the produced BC; the second one in which concentrated solar heat was used to power the reactor using the same solar plant configuration previously adopted [9]. Quite interestingly, we found that the improvement of the BC yield from 31 to 55 %w/w together with the use of zero cost MS led to a MFSP of 0.72 USD/kg in the first scenario and of 0.67 USD/kg in the second one. These values are comparable to the market price of diesel fuel in 2020 that is assessed at 0.79 USD/kg. However, it has to be considered that the BC produced by HTL has to be further refined and the return of the investment must be added to make the comparison meaningful from the commercial point of view.

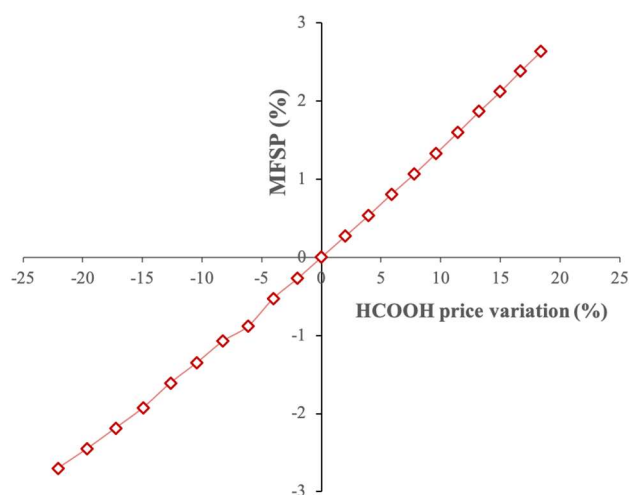


Figure 5: Sensitivity analysis: % of variation of the FA price versus the % of variation of the obtained minimum fuel selling price (MFSP)

In the plant, FA is used as a sacrificial additive and for this reason a sensitivity analysis of its cost on the value of the MFSP was performed (Fig.5). As it is possible to observe in the Fig. 5, FA price variation does not affect in a significant way the economic sustainability of the HTL plant powered by concentrated solar heat.

4. Conclusions

The combined utilization of commercial heterogeneous catalysts and FA as green hydrogen donor in the HTL of a zero-cost wet bio feedstock as MS can increase both BC yield and quality.

Experiments at high biomass loading give an indication of catalyst deactivation that becomes a crucial issue for the practical exploitation of the approach. More promising in this perspective was the addition of FA as a green sacrificial hydrogen donor, that can be produced also by the electrochemical reduction of carbon dioxide driven by green energy. In fact it allowed to work at MS loading as high as 30% with EBC yield higher than 50% and ER higher than 100%. A techno-economic analysis based on a mathematical model developed for solar HTL of microalgae allowed us to estimate a minimum fuel selling price of the BC of 0.67 USD/kg that coupled with the ER higher than 100 % is very promising for the exploitation of the process on the industrial scale.

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References

- [1] Zinoviev S, Müller-Langer F, Das P, Bertero N, Fornasiero P, Kaltschmitt M, et al. Next-generation biofuels: Survey of emerging technologies and sustainability issues. *ChemSusChem* 2010; 3:1106–33. <https://doi.org/10.1002/cssc.201000052>
- [2] Kumar N, Sonthalia A, Pali HS, Sidharth. *Next-Generation Biofuels: Opportunities and Challenges*. Green Energy and Technology, Springer Singapore, 2020; 171–91. https://doi.org/10.1007/978-981-13-9012-8_8
- [3] Yeh TM, Dickinson JG, Franck A, Linic S, Thompson LT, Savage PE. Hydrothermal catalytic production of fuels and chemicals from aquatic biomass. *Journal of Chemical Technology and Biotechnology* 2013;88:13–24. <https://doi.org/10.1002/jctb.3933>
- [4] Demirbas A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy conversion and management*, 2001; 42: 1357-1378. [https://doi.org/10.1016/S0196-8904\(00\)00137-0](https://doi.org/10.1016/S0196-8904(00)00137-0)
- [5] Dimitriadis A, Bezergianni S. Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review. *Renewable and Sustainable Energy Reviews* 2017;68:113–25. <https://doi.org/10.1016/j.rser.2016.09.120>
- [6] Peterson AA, Vogel F, Lachance RP, Fröling M, Antal MJ, Tester JW. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy and Environmental Science* 2008;1:32–65. <https://doi.org/10.1039/b810100k>
- [7] Yang J, Hong C, Xing Y, Zheng Z, Li Z, Zhao X, et al. Research progress and hot spots of hydrothermal liquefaction for bio-oil production based on bibliometric analysis. *Environmental Science and Pollution Research* 2021; 28: 7621-7635. <https://doi.org/10.1007/s11356-020-11942-2>
- [8] Zhang X, Li X, Li R, Wu Y. Hydrothermal Carbonization and Liquefaction of Sludge for Harmless and Resource Purposes: A Review. *Energy and Fuels* 2020;34:13268–13290. <https://doi.org/10.1021/acs.energyfuels.0c02467>
- [9] Giaconia A, Caputo G, Ienna A, Mazzei D, Schiavo B, Scialdone O, et al. Biorefinery process for hydrothermal liquefaction of microalgae powered by a concentrating solar plant: A conceptual study. *Applied Energy* 2017;208:1139–1149. <https://doi.org/10.1016/j.apenergy.2017.09.038>
- [10] Ranganathan P, Savithri S. Techno-economic analysis of microalgae-based liquid fuels production from wastewater via hydrothermal liquefaction and hydroprocessing. *Bioresource Technology* 2019;284:256–265. <https://doi.org/10.1016/j.biortech.2019.03.087>
- [11] Biller P, Ross AB. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. *Bioresource Technology* 2011;102:215–225. <https://doi.org/10.1016/j.biortech.2010.06.028>
- [12] Madsen René B., Glasius Marianne. no_Madsen, 2019, How Do Hydrothermal Liquefaction Conditions and Feedstock Type Influence Product Distribution and Elemental

Composition? *Ind Eng Chem Res* 2019;58:17583–17600.

<https://doi.org/10.1021/acs.iecr.9b02337>

- [13] Qian L, Wang S, Savage PE. Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions. *Bioresource Technology* 2017;232:27–34. <https://doi.org/10.1016/j.biortech.2017.02.017>
- [14] Ali Shah A, Sohail Toor S, Hussain Seehar T, Sadetmahaleh KK, Helmer Pedersen T, Haaning Nielsen A, et al. Bio-crude production through co-hydrothermal processing of swine manure with sewage sludge to enhance pumpability. *Fuel* 2021;288:119407. <https://doi.org/10.1016/j.fuel.2020.119407>
- [15] Conti F, Toor SS, Pedersen TH, Seehar TH, Nielsen AH, Rosendahl LA. Valorization of animal and human wastes through hydrothermal liquefaction for biocrude production and simultaneous recovery of nutrients. *Energy Conversion and Management* 2020;216:112925. <https://doi.org/10.1016/j.enconman.2020.112925>
- [16] Yang J, He Q (Sophia), Corscadden K, Niu H. The impact of downstream processing methods on the yield and physiochemical properties of hydrothermal liquefaction bio-oil. *Fuel Processing Technology* 2018;178:353–361. <https://doi.org/10.1016/j.fuproc.2018.07.006>
- [17] Prestigiacomo C, Laudicina VA, Siragusa A, Scialdone O, Galia A. Hydrothermal liquefaction of waste biomass in stirred reactors: One step forward to the integral valorization of municipal sludge. *Energy* 2020;201:117606. <https://doi.org/10.1016/j.energy.2020.117606>
- [18] Madsen RB, Zhang H, Biller P, Goldstein AH, Glasius M. Characterizing Semivolatile Organic Compounds of Biocrude from Hydrothermal Liquefaction of Biomass. *Energy&Fuels* 2017;31:4122–4134. <https://doi.org/10.1021/acs.energyfuels.7b00160>
- [19] Lemoine F, Maupin I, Lemée L, Lavoie JM, Lemberton JL, Pouilloux Y, et al. Alternative fuel production by catalytic hydroliquefaction of solid municipal wastes, primary sludges and microalgae. *Bioresource Technology* 2013;142:1–8. <https://doi.org/10.1016/j.biortech.2013.04.123>
- [20] Xu D, Lin G, Liu L, Wang Y, Jing Z, Wang S. Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of sewage sludge at different temperatures. *Energy* 2018;159:686–695. <https://doi.org/10.1016/j.energy.2018.06.191>
- [21] Wang Y, Chen G, Li Y, Yan B, Pan D. Experimental study of the bio-oil production from sewage sludge by supercritical conversion process. *Waste Management* 2013;33:2408–2415. <https://doi.org/10.1016/j.wasman.2013.05.021>
- [22] Malins K, Kampars V, Brinks J, Neibolte I, Murnieks R, Kampare R. Biooil from thermochemical hydroliquefaction of wet sewage sludge. *Bioresource Technology* 2015;187:23–29. <https://doi.org/http://dx.doi.org/10.1016/j.biortech.2015.03.093>
- [23] Ma W, Du G, Li J, Fang Y, Hou L, Chen G, et al. Supercritical water pyrolysis of sewage sludge. *Waste Management* 2017;59:371–378. <https://doi.org/10.1016/j.wasman.2016.10.053>
- [24] Kapusta K. Effect of ultrasound pretreatment of municipal sewage sludge on characteristics of bio-oil from hydrothermal liquefaction process. *Waste Management* 2018;78:183–190. <https://doi.org/10.1016/j.wasman.2018.05.043>
- [25] Couto EA, Pinto F, Varela F, Reis A, Costa P, Calijuri ML. Hydrothermal liquefaction of biomass produced from domestic sewage treatment in high-rate ponds. *Renewable Energy* 2018;118:644–653. <https://doi.org/10.1016/j.renene.2017.11.041>
- [26] Wu B, Berg SM, Remucal CK, Strathmann TJ. Evolution of N-Containing Compounds during Hydrothermal Liquefaction of Sewage Sludge. *ACS Sustainable Chemistry and Engineering* 2020;8:18303–18313. <https://doi.org/10.1021/acssuschemeng.0c07060>
- [27] Prestigiacomo C, Costa P, Pinto F, Schiavo B, Siragusa A, Scialdone O, et al. Sewage sludge as cheap alternative to microalgae as feedstock of catalytic hydrothermal liquefaction processes. *Journal of Supercritical Fluids* 2019;143:251–258. <https://doi.org/10.1016/j.supflu.2018.08.019>

- [28] Zhai Y, Chen H, Xu BB, Xiang B, Chen Z, Li C, et al. Influence of sewage sludge-based activated carbon and temperature on the liquefaction of sewage sludge: Yield and composition of bio-oil, immobilization and risk assessment of heavy metals. *Bioresource Technology* 2014;159:72–79. <https://doi.org/10.1016/j.biortech.2014.02.049>
- [29] Popov S, Kumar S. Rapid hydrothermal deoxygenation of oleic acid over activated carbon in a continuous flow process. *Energy and Fuels* 2015;29:3377–3384. <https://doi.org/10.1021/acs.energyfuels.5b00308>
- [30] Castello D, Haider MS, Rosendahl LA. Catalytic upgrading of hydrothermal liquefaction biocrudes: Different challenges for different feedstocks. *Renewable Energy* 2019;141:420–430. <https://doi.org/10.1016/j.renene.2019.04.003>.
- [31] Laurent E, Delmon B. Influence of Water in the Deactivation of a Sulfided NiMo/ γ -Al₂O₃ Catalyst during Hydrodeoxygenation. *Journal of Catalysis* 1994; 146: 281– 291. [https://doi.org/10.1016/0021-9517\(94\)90032-9](https://doi.org/10.1016/0021-9517(94)90032-9)
- [32] Popov S, Kumar S. Renewable fuels via catalytic hydrodeoxygenation of lipid-based feedstocks. *Biofuels* 2013;4:219–239. <https://doi.org/10.4155/bfs.12.89>
- [33] Laurent E, Delmon B. Study of the hydrodeoxygenation of carbonyl, carboxylic and guaiacyl groups over sulfided CoMo/ γ -Al₂O₃ and NiMo/ γ -Al₂O₃ catalysts. *Applied Catalysis A* 1994;109:77–96. [https://doi.org/10.1016/0926-860x\(94\)85004-6](https://doi.org/10.1016/0926-860x(94)85004-6)
- [34] Isa KM, Abdullah TAT, Ali UFM. Hydrogen donor solvents in liquefaction of biomass: A review. *Renewable and Sustainable Energy Reviews* 2018;81:1259–1268. <https://doi.org/10.1016/j.rser.2017.04.006>
- [35] Dalebrook AF, Gan W, Grasemann M, Moret S, Laurenczy G. Hydrogen storage: Beyond conventional methods. *Chemical Communications* 2013;49:8735–8751. <https://doi.org/10.1039/c3cc43836h>
- [36] Nelson WJ, Rl C, Exgelder J. The Thermal Decomposition Of Formic Acid. *The Journal of Physical Chemistry* 1926; 30, 4: 470-475. <https://doi.org/10.1021/j150262a003>
- [37] Saito K, Kakumoto T, Kuroda H, Torii S, Imamura A. Thermal unimolecular decomposition of formic acid. *The Journal of Chemical Physics* 1984;80:4989–4996. <https://doi.org/10.1063/1.446521>
- [38] Yasaka Y, Yoshida K, Wakai C, Matubayasi N, Nakahara M. Kinetic and equilibrium study on formic acid decomposition in relation to the water-gas-shift reaction. *Journal of Physical Chemistry A* 2006;110:11082–11090. <https://doi.org/10.1021/jp0626768>
- [39] Akiya N, Savage PE. Role of Water in Formic Acid Decomposition. *AIChE Journal* 1998;44:405-415. <https://doi.org/10.1002/aic.690440217>
- [40] Saito K, Kakumoto T, Kuroda H, Torii S, Imamura A. Thermal unimolecular decomposition of formic acid. *The Journal of Chemical Physics* 1984;80:4989–4996. <https://doi.org/10.1063/1.446521>
- [41] Yu J, Savage PE. Kinetics, Catalysis, And Reaction Engineering, Decomposition of Formic Acid under Hydrothermal Conditions. *Industrial and Engineering Chemistry Research* 1998; 37:2-10. <https://doi.org/10.1021/ie970182e>
- [42] Proietto F, Schiavo B, Galia A, Scialdone O. Electrochemical conversion of CO₂ to HCOOH at tin cathode in a pressurized undivided filter-press cell. *Electrochimica Acta* 2018;277:30–40. <https://doi.org/10.1016/j.electacta.2018.04.159>
- [43] Ma P, Hao X, Proietto F, Galia A, Scialdone O. Assisted reverse electrodialysis for CO₂ electrochemical conversion and treatment of wastewater: A new approach towards more eco-friendly processes using salinity gradients. *Electrochimica Acta* 2020;354. <https://doi.org/10.1016/j.electacta.2020.136733>.
- [44] Ross AB, Biller P, Kubacki ML, Li H, Lea-Langton A, Jones JM. Hydrothermal processing of microalgae using alkali and organic acids. *Fuel* 2010;89:2234–2243. <https://doi.org/10.1016/j.fuel.2010.01.025>.

- [45] Zhang L, Champagne P, (Charles) Xu C. Bio-crude production from secondary pulp/paper-mill sludge and waste newspaper via co-liquefaction in hot-compressed water. *Energy* 2011;36:2142–2150. <https://doi.org/10.1016/j.energy.2010.05.029>.
- [46] Bleta R, Schiavo B, Corsaro N, Costa P, Giaconia A, Interrante L, et al. Robust Mesoporous CoMo/ γ -Al₂O₃ Catalysts from Cyclodextrin-Based Supramolecular Assemblies for Hydrothermal Processing of Microalgae: Effect of the Preparation Method. *ACS Applied Materials and Interfaces* 2018;10:12562–12569. <https://doi.org/10.1021/acsami.7b16185>.
- [47] Marlair G, Cwiklinski C, Tewarson A. An analysis of some practical methods for estimating heats of combustion in fire safety studies. 2014. <https://hal-ineris.archives-ouvertes.fr/ineris-00972167>
- [48] McCollom TM, Seewald JS. Experimental constraints on the hydrothermal reactivity of organic acids and acid anions: I. Formic acid and formate. *Geochimica et Cosmochimica Acta* 2003;67:3625–3644. [https://doi.org/10.1016/S0016-7037\(03\)00136-4](https://doi.org/10.1016/S0016-7037(03)00136-4).
- [49] Pray A, Schweickert CE, Minnich BH. Solubility of Hydrogen, Oxygen, Nitrogen, and Helium in Water at elevated temperatures 1952; 44: 1146-1151.
- [50] Ayala-Cortés A, Arcelus-Arillaga P, Millan M, Arancibia-Bulnes CA, Valadés-Pelayo PJ, Villafán-Vidales HI. Solar integrated hydrothermal processes: A review. *Renewable and Sustainable Energy Reviews* 2020;139:110575. <https://doi.org/10.1016/j.rser.2020.110575>
- [51] Reutemann W, Kieczka H. Formic Acid 2000. https://doi.org/10.1002/14356007.a12_013.pub3