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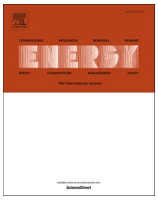

Sewage sludge and olive oil pomace residues as real waste models to feed hydrothermal liquefaction: effect of acid and basic pretreatments

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ABSTRACT

We have studied the possibility of using acid and basic pretreatment with HCOOH and KOH to produce high-quality biocrude (BC) from HTL of sewage sludge (SS) and olive oil pomace (OOP) residues as models of waste. Pretreatments are more effective in improving the BC yield and quality obtained from heterogeneous and mixed SS, whereas they are less effective with more homogeneous matrices, such as OOP. In fact, after the HTL of pretreated SS, we obtained higher yields of BC enriched in aliphatic chains with higher values of H/C ratios and energy recovery. In particular, KOH-pretreatment of SS removed oxygen and nitrogen-bearing chemical species from the feedstock and increased the H/C of the BC obtained after HTL from 1.79 to 1.93 at 300 °C and from 1.67 to 1.85 at 350 °C. A notable increase in BC yield and energy recovery was observed with HCOOH-pretreated SS after HTL at 350 °C, attributed to the beneficial impact of acid pretreatment in enhancing the organic content of the matrix. Collected data indicate that HCOOH-pretreatment and proper kinetic severity of HTL allow a densification of chemical energy in the produced BC.

1. Introduction

The Global Waste Management Outlook of 2024 [1] reported that 2.1 billion tons of municipal solid waste were produced in 2023, and only 13 % of the controlled fraction was effectively disposed of following the waste-to-energy strategy.

Among thermochemical processes, hydrothermal liquefaction (HTL) is a promising route that effectively converts wet bioresources into a valuable fuel oil called biocrude (BC) without the need for an expensive pre-drying step [2].

The BC obtained by HTL is characterized by a larger value of higher heating value (HHV) compared to pyrolysis oil and gasification syn-gas [3] and for this reason, it can be considered a promising substitute for conventional fossil fuels. However, BC has significant heteroatom content and high viscosity [4,5].

To date, most researchers have focused on optimizing HTL operating parameters to achieve high BC yields or improve BC quality. Acid and basic homogeneous catalysts such as KOH, K_2CO_3, and HCOOH were often investigated with microalgae and sewage sludge (SS).

In particular, some authors [6] reported that higher BC yields were obtained in the order K_2CO_3 > KOH > HCOOH when microalgae were used as feedstock. Other authors [7] investigated the use of KOH and HCOOH during HTL of municipal sludge, finding that the H/C molar ratio of the produced BC increased from 1.60 to 1.75 when KOH was added to the reactor at 350 °C for 10 min of reaction time. Despite HTL having been deeply investigated over the last decades, both at the fundamental and technological development levels, there are still poorly explored aspects to study. It was found that sustainable feedstock for industrial HTL is zero, or even negative cost, residual and recalcitrant bioresources, such as SS, food industry waste, and the organic fraction of municipal solid waste [8].

These are complex matrices composed of inorganic, biogenic, and non-biogenic organic compounds, and their random origin makes their composition highly differentiated with time, thus changing the performances of HTL reactors [9] in terms of BC productivity. Attempts have been made to overcome the hurdles of such variability through the use of pretreatment protocols [9]. Literature reports an evident lack of knowledge on the mechanisms and reaction pathways activated in the process and on the mutual interactions between the different bio-feedstock constituents, especially for those of non-biogenic origin. This

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lack is due to the complex nature of real matrices, which cannot always be reproduced by the model compounds used. Then, the effect of the different pretreatments proposed to mitigate the seasonal variability of biofeedstocks has not been sufficiently studied. Pretreatment could contribute to mitigating the composition variation by partial depolymerization or by separating the soluble salts in an aqueous phase. The impact of sodium hypochlorite, ultrasonic, and microwave pretreatments of SS was investigated to understand the reaction mechanisms and BC quality after a subsequent hydrothermal liquefaction step [10]. More specifically, the authors found that even if the elemental chemical composition of the BC remained unchanged, the relative percentage of each compound was affected. Moreover, it was reported that ultrasound pretreatment increased the biocrude yield obtained by HTL by 19 % at 320 °C without changing its composition [11]. Instead, microwave pretreatment led to an improvement in the HHV of BC and a decrease in nitrogen-containing compounds [12].

Co-pretreatment of SS with subcritical water loaded with mixed surfactants was reported to increase the BC yield when a methanol/water mixture (75/25 v/v) was used as reaction medium without separation of the added surfactants [13].

To the best of our knowledge, the current state of the art has only one investigation that addressed the study of the effect of hydrolytic pretreatment on the quality of BC produced by HTL of microalgae [14]. A positive effect on BC yield was found only when KOH and acetic acid were adopted as pretreating agents using a mild HTL reaction temperature between 240 and 300 °C. Instead, Xu et al. analyzed the effectiveness of thermal, alkaline and electrochemical pretreatments of SS to improve biogas production and they found that a NaOH based thermo-alkaline and electrochemical pretreatment enhanced the fraction of volatile solids in the treated matrix [15]. Liu et al. soaked municipal secondary sludge with inorganic and organic acids at room temperature and studied the effect of this treatment on the yield of BC obtained by HTL of the matrix. They found that HCl pretreatment increased the BC yield but no study on the effect of pretreatment on the biofeedstock was reported [16].

Moreover, in the literature, acidic and alkaline additives have been reported to positively affect the biofeedstock degradation during the pretreatments, as well as the BC yield and quality in HTL processes.

This study presents the first comparative analysis of hydrolytic acid and alkaline pretreatment using two different types of real waste biofeedstocks, SS and olive oil pomace residues (OOP) for BC production by HTL. The aim was to conduct an empirical systematic analysis whose results allowed us to understand the effect of selected pretreatments on the distribution of the organic and inorganic fractions of the feed. OOP has scarcely been investigated as a feedstock for HTL. De Filippis et al. have studied the HTL of olive residue at 320 °C and in the absence of added catalyst have obtained a BC yield of 32 % after 30 min [17]. More recently, the use of a transition metal catalyst to optimize the conversion of crude oil pomace through hydrothermal liquefaction (HTL) into valuable products has been studied [18]. None of these studies considered any pretreatment of this feedstock. In our research, we selected it as a model of a more homogeneous and zero-ash feedstock for comparison with SS, since several authors have reported that high inorganic content may affect biocrude production and quality of the products [19]. Product yields, cumulative energy recovery and BC quality were used to study the impact of the pretreatment on the performance of the HTL process.

2. Experimental

2.1. Materials

The digested SS used in this study was provided by the wastewater treatment plant of "Acqua dei Corsari" A.M.A.P. s.p.a., Palermo, Italy. Native OOP was obtained by an oil mill plant in Bivona, Agrigento, Italy.

Each feedstock was characterized by estimating the moisture content, the organic and ash fractions on a dry basis and by ultimate analyses according to methods reported elsewhere [20–23]. Additionally, the lipid fraction of biofeedstocks was estimated according to EU unified methods [24]. All results of these characterizations are reported in Table 1.

Table 1
Physicochemical properties of raw SS and OOP used in the study.

	SS	OOP
Moisture content (% w/w)	84	6
Organic content[a]	71	99
Ash content[a,b]	29	1
Ultimate analysis [a]		
C	38.2	55.8
H	8.0	8.3
N	5.7	ND
S	2.2	0.8
HHV (MJ/kg)[c]	19.4	24.9
Lipid content[a,d]	10	12

[a] % w/w dry basis.
[b] The ashes are determined by the difference with respect to 100.
[c] Determined by Dulong's formula, considering O = 100-C-H-N-S-ashes.

Ultrapure water (VWR, HPLC grade) was used as a solvent in the HTL reactor and in the preparation of pretreatment acidic and basic solutions. KOH, VWR ≥99.98 % (metal basis) and formic acid (FA) VWR, 99–100 % were used as pretreatment agents. Cyclohexane (Carlo Erba, analytical grade) and acetone (Sigma Aldrich, HPLC grade) were the solvents used to recover the produced BC. Argon (Air Liquide 99.999 % purity) was used for purging steps. Nitrogen used for acetone evaporation and for TGA analyses was Air Liquide 99.999 % purity.

2.2. Experimental methods of the pretreatment

To study the effect of KOH and HCOOH, selected pretreatment trials were conducted using the same procedures adopted by Zimmermann et al. [25]. A batch AISI 316 reactor, with an internal volume of 25 mL, was loaded with 20 g of slurry (6 % w/w of dry biofeedstock in a deionized water solution of the treatment agent at 0.5 mol/L), then it was sealed, purged with argon to remove air, and placed in an oven at 150 °C for 30 min. After the pretreatment, all the content of the vessel was poured into a flask and filtered through commercial cellulose nitrate (pore diameter 40 μm) filter paper to separate the solid residues (SR) from the eluted liquid phase.

Ultrapure water was added to wash the residue from the additive till the pH of the filtrate was neutral. The eluted phase after filtration was analyzed by a total organic carbon (TOC) analyzer (Shimadzu TOC-L). The recovered SR was dried by heating at 60 °C overnight and two

Table 2
Pretreatment of SS and OOP with formic acid (FA) and potassium hydroxide aqueous solutions: yields and organic and inorganic fractions of recovered solid biofeedstock and partitioning of organics between the aqueous solution and the treated solid matrix.

Biofeedstock	T (°C)	Pretreating agent[a]	Y_{PS} (%)	z^{pt}_{SR}	x^{pt}_{SR}	ω_l	ω_s
Native SS	–	–	–	0.71	0.29	–	–
SS	20	FA	69	0.83	0.17	19	81
	150	FA	64	0.81	0.19	27	73
	20	KOH	73	0.72	0.28	25	75
	150	KOH	86	0.51	0.49	38	62
Native OOP	–	–	–	0.99	0.01	–	–
OOP	20	FA	78	1.00	0.00	22	78
	150	FA	77	0.99	0.01	23	77
	20	KOH	75	0.99	0.01	25	75
	150	KOH	76	1.00	0.00	24	76

[a] FA or KOH concentration 0.5 mol/L. Treatment time 30 min.

samples were calcined under air to estimate the ash percentage. Then, the organic content was determined by difference. A further sample of SR was characterized by CHNS elemental composition analyses as described in the following section.

2.3. Experimental methods of HTL

The HTL experiments were performed in a homemade batch reactor with a free volume of 16 mL made from ¾ in. Swagelok® VCR (316SS) male union and caps that were assembled as reported in our previous publications and used under static configuration [20,26].

The reactor sealing was previously tested up to 25 MPa as reported in our previous studies [20,23,26]. To conduct an HTL experiment, 5 g of the aqueous slurry (10 % w/w of dry feedstock in ultrapure water) was poured into the reactor, which was then sealed and purged with argon, leaving a residual pressure of 0.2 MPa. The heating rate of the reactor was estimated to be close to 13 °C/min in blank experiments [20] and the time the reactor was kept at the set-up temperature was considered as the reaction time. After the reaction, the reactor was quenched using a water bath and its upper part was connected to a pre-evacuated gas expansion volume to quantify the produced gaseous phase by pressure deviations [26].

Separation procedures of products were based on those adopted in our previous works [7,20,21,23]. In the case of SS used in previous studies, a hydrocarbon fraction was isolated by controlled evaporation of the solvent used to recover the BC. This fraction was below the detection limit with biofeedstocks used in this study.

2.4. Analytical methods

The effect of the pretreatment process was evaluated by estimating (i) the yield of organics in the solid cake collected after filtration (ω_s); (ii) the yield of compounds dissolved in the eluted phase (ω_l); (iii) the fraction of organic compounds in the solid cake produced by pretreatment (z_{SR}^{pt}) and (iv) the fraction of inorganic compounds in the solid cake produced by pretreatment (x_{SR}^{pt}) by the following equations:

$$\omega_s = 100^*\left(z_{SR}^{pt} Y_{SR}^{pt}\right)/z_{rb} \quad (1)$$

$$\omega_l = 100 - \omega_s \quad (2)$$

where Y_{SR}^{pt} is the yield of the solid residue produced after pretreatment, dry basis, and z_{rb} is the mass fraction of organics in the raw biofeedstock.

The TOC mass content of eluted aqueous phases was determined by a Shimadzu TOC-L analyzer. The sample was diluted 1:100 with ultrapure, HPLC-grade water.

The yields of condensed products after HTL were calculated with the following formulas:

$$Y_{p_{dry}}(\%) = m_p \Big/ m_f \times 100 \quad (3)$$

$$Y_{p_{daf}}(\%) = m_{p_{daf}} \Big/ m_{f_{daf}} \times 100 \quad (4)$$

while the yield of volatiles (VT) was determined by the following equation (5):

$$Y_{VT_{daf}} = 100 - \left(Y_{BC_{daf}} + Y_{SRHTL_{daf}} + Y_{WSP_{daf}} + Y_{GAS_{daf}} \right) \quad (5)$$

Where Y_{pdry} is the yield of products in the dry mass basis, m_p is the dry mass of the product, m_f is the dried initial mass of the feedstock used to perform HTL, m_{pdaf} is the dry ash-free mass of the products (obtained by calcination at 550 °C for 6 h of the dry samples under air), Y_{pdaf} is the product yields calculated in the dry ash free form, m_{fdaf} is the dry ash free mass of the feedstock.

The pretreatments and HTL experimental runs were conducted at least twice to assess the reproducibility. All the reported yields are mean values. The standard deviations of yields in % units for the hydrolysis were 4.0 for the pretreated solid yield and 3.2 for the dry residue in the liquid phase. For HTL experimental trials, standard deviations were 3.2 for BC, 3.1 for the SR, 0.9 for the water-soluble products (WSP), 2.4 for the gas (GAS). Product yields from HTL were calculated according to equation (3) in the dry ash-free form (daf). SRHTL defines the solid residue collected after HTL. The gas phase produced by HTL experiments was analyzed by Agilent Technology 7890B Gas Chromatograph using the method described elsewhere [20,23,26].

The amount of products and the composition of the gas phase were determined as in our previous study [26]. The molar percentages of the components in the produced gas were obtained with an average standard deviation of 0.7 percentage points.

The BC obtained by separation procedures after HTL was redissolved in 5 mL of acetone and poured into a borosilicate glass test tube together with 1g of anhydrous Na_2SO_4. After the sonication for 30 min and centrifugation at 3000 rpm for 10 min, the acetone-BC solution was separated from the hydrated solid Na_2SO_4.

CHNS elemental composition analyses of the feedstocks, of the BC and of the SRHTL were performed by a PerkinElmer 2400 Series II elemental analyzer, and O (% w/w) was determined by difference.

The HHV of BC and SRHTL were calculated by the expanded Dulong formula:

$$HHV(MJ/kg) = 0.338\,C + 1.44\,(H - O/8) + 0.094\,S \quad (6)$$

The energy recovery (ER) of each collected product was estimated by equation (7):

$$ER(\%) = \frac{HHV_p \times Y_{p_{daf}}(\%)}{HHV_{feedstock}} \times 100 \quad (7)$$

The cumulative energy recovery (ER_c) was calculated by the following equation, summing the energy recovery of each product:

$$ER_C(\%) = ER_{BC}(\%) + ER_{SRHTL}(\%) \quad (8)$$

Anhydrous BC samples were obtained after acetone evaporation under a continuous N_2 flow and were characterized by ATR-FTIR spectroscopy and thermogravimetric analysis (TGA). ATR-FTIR spectra were collected in the 450-4000 cm^{-1} range, with a scan resolution of 1 cm^{-1} and 16 scan accumulations. The data were analyzed in absorbance mode by using as an internal reference the resonance band of the sp^3 hybridized stretching of CH_3 and CH_2 groups related to long carbon chains associated with phenolics (2923 cm^{-1}), which is detected in all the analyzed BC. The following equation was used to normalize the absorbances:

$$R_{i/std} = Int\,A_i / Int\,A_{std} \quad (9)$$

where $R_{i/std}$ identifies the value of the ratio between the integrals (*Int*) of the absorbance of the resonance band of each i-esim functional group *Int* A_i and of the selected reference group *Int* A_{std}.

The TGA analyses of selected anhydrous BC samples, produced at 350 °C for 30 min, were conducted from 30 to 600 °C under a N_2 atmosphere (60 mL/min) with a heating rate of about 20 °C/min using a PerkinElmer STA 6000 analyzer. To perform the analyses, a mass of 5 ± 2 mg of BC was charged in an alumina crucible.

3. Results and discussion

3.1. Pretreatment of biofeedstocks

Pretreatment experiments were conducted at 20 and 150 °C for 30 min. Table 2 presents the results obtained in terms of yield in solid biofeedstock recovered from the pretreatment Y_{PS}, along with its organic and inorganic content given in terms of weight fractions z_{SR}^{pt} and x_{SR}^{pt} respectively and partitioning of the organics of the native

Table 3
List of produced yields obtained from HTL experiments conducted at 300 and 350 °C with untreated SS and OOP using 30 min as reaction time.

Exp.	biofeedstock	T (°C)		Product yields (daf %wt bases)				
			KSF	BC (±3)	SRHTL (±3)	WSP (±1)	GAS (±2)	VT
1	SS	300	8	15	40	25	3	17
2		350	9	19	33	26	13	9
3	OOP	300	8	27	45	8	2	19
4		350	9	37	23	6	9	25

Table 4
Elemental analysis of BC and SR obtained in experiments reported in Table 2.

Exp.	Elemental analysis of BC									Elemental analysis of SRHTL								
	C	H	N	S	O	H/C	O/C	N/C	S/C	C	H	N	S	O	H/C	O/C	N/C	S/C
1	65.0	9.7	6.7	1.8	16.9	1.79	0.20	0.09	0.01	28.8	3.7	10.4	0.4	13.0	1.56	0.34	0.31	0.005
2	72.3	9.1	3.9	2.1	12.6	1.51	0.13	0.05	0.01	25.9	2.4	2.6	1.8	16.3	1.12	0.47	0.09	0.025
3	66.5	7.8	ND	1.9	23.9	1.41	0.27	ND	0.01	49.4	5.5	ND	1.4	39.9	1.33	0.61	ND	0.011
4	76.5	9.4	ND	2.2	12.0	1.48	0.12	ND	0.01	57.8	5.0	ND	1.3	31.4	1.03	0.41	ND	0.008

biofeedstock between the aqueous phase and the treated biofeedstock.

Sludge is a complex, multiphase system constituted by microbial aggregates, organic and inorganic particles and extracellular polymeric substances generated from microbial activity or from the wastewater itself. These are considered the main constituents of its organic fraction [27].

Acid and alkaline pretreatments have been extensively studied to destructure such a complex system to increase the digestion efficiency in its anaerobic treatments, even if the pretreatment is carried out at room temperature [28].

Prompted by these considerations we pretreated SS with FA and KOH and then we investigated the reactivity of the treated feedstock during HTL.

It is possible to observe that when SS were pretreated with FA and KOH solutions at 20 °C, 19 and 25 % of their initial organic content, respectively, were solubilized by the pretreating aqueous solution. These yields increased when the pretreating temperature was raised to 150 °C, particularly with KOH, probably due to a deeper effect in hydrolyzing the organic matter in the feedstock. SS residue collected after FA-based pretreatment was enriched in organic content as this fraction increased from 0.71 in native SS to 0.83–0.81 in treated solid SS. Differently, when alkaline pretreatment with KOH was performed, recovered SS had an organic fraction similar to the native sludge at 20 °C and were significantly enriched in inorganic content after pretreatment at 150 °C probably owing to the significant dissolution of lignocellulosic fraction as confirmed by the value of organic compounds in the liquid phase after pretreatment (ω_l) that is close to 40 %.

OOP is a matrix that is less differentiated than SS, and it is mainly composed by extractives, triglycerides, pigments, polysaccharides and lignin [29,30]. In the case of OOP, pretreatments led to about 25 % of liquefied organics, yet at room conditions, and the increase in temperature did not significantly change this value. As this biofeedstock is almost entirely constituted of organic compounds, no bias of the organic fraction can be detected in this case.

According to the collected results, both formic acid and potassium hydroxide generated significant fractions of soluble organics which are indicative of the deconstruction of biofeedstocks through the depolymerization and liquefaction of biopolymers such as polysaccharides, proteins and lignin together with the decomposition of bacterial cells and release of intracellular fluids.

3.2. HTL of biofeedstocks

A set of HTL experiments was performed using the raw matrices to study the effect of the nature of the feedstock on the product yields (daf w/w%) in the absence of any pretreatment (Table 3). Firstly, we observed an increase in BC and GAS yields with both biofeedstocks with increasing reaction temperature, i.e. kinetic severity of the process [8]. However, higher reaction temperatures decreased the SRHTL yields. The positive effect of higher reaction temperature on BC yields was also observed by other researchers who investigated the HTL of digested SS, obtaining BC yields in the range of 29–58 wt%, daf but with much longer reaction times, 2–6 h, than that adopted in our study [31,32]. On the other hand, yields close to 18 % have been obtained in HTL of digested SS at 330 °C with 20 min reaction time by Amadei et al. [33]. BC yields close to 20 % were also reported for HTL of secondary SS carried out at 350 °C with a fast heating rate of the reactor and 10 min isothermal reaction time [34]. From this comparison we can conclude that the

Table 5
Results from HTL experiments conducted at 300 and 350 °C for 30 min, with 10 % of dry feedstock concentration, with native and pretreated biofeedstocks.

Exp	organic matrices	T (°C)	Pretreated agent	Product yields (daf %wt bases)				
				BC (±3)	SRHTL (±3)	WSP (±1)	GAS (±2)	VT
1	SS	300	_	16	40	25	3	16
2			KOH	15	61	15	3	6
3			FA	16	59	23	1	1
4		350	_	18	33	25	13	11
5			KOH	23	43	16	3	14
6			FA	34	22	27	10	7
7	OOP	300	_	27	45	8	2	19
8			KOH	9	60	5	2	25
9			FA	19	42	5	2	32
10		350	_	37	23	6	9	25
11			KOH	22	51	5	2	21
12			FA	21	33	1	7	38

behavior and yields observed in our study are consistent with those obtained by other independent researchers.

From the comparison of the two matrices, SS and OOP, it is possible to observe that the latter gave higher yields in BC, 37 % instead of 19 % at 350 °C, and lower production of WSP. Also, in the case of OOP, BC yields obtained in our study are coherent with those found by other researchers that reported BC yields of about 30 % from HTL of olive oil residue carried out at 330 °C for 15–30 min [17,18].

Generally, as shown in Table 4, the BC obtained by HTL of SS has a higher H/C molar ratio than that obtained from OOP, even if the difference was mitigated at 350 °C. It was also found that an increase in reaction temperature significantly decreased the O/C, from 0.20 to 0.13 in the case of SS and from 0.27 to 0.12 in the case of OOP.

3.3. HTL of pretreated biofeedstocks

Further experimental campaigns were designed to explore the reactivity of the pretreated biofeedstocks during HTL experiments. Table 5 reports the results obtained with pretreated SS and OOP at 300 °C and 350 °C and 30 min as reaction time together with those found from the HTL of the two raw matrices.

Also in this context, the two different natures of the biofeedstock affected the performance of the HTL process.

In the case of SS, similar BC yields, of about 15–16 %, were obtained at 300 °C with all kinds of matrices while the basic and acid pretreatment of SS produced an increase in the SRHTL yield from 40 % of the raw feed to 61 % and 59 % respectively. It is interesting to observe that in the case of pretreated biofeedstocks a better closure of mass balances was achieved as the yield of volatiles decreased from 16 % to 6 % and 1 %.

Differently, when the reaction temperature was increased to 350 °C, pretreated SS were characterized by higher BC yields than the native matrix. This effect is more evident particularly when FA was used in the pretreatment.

It is worthwhile to mention that the product distribution of uncatalyzed HTL processes can be correlated with the concept of kinetic severity factor (KSF) which cumulates the effects of reaction time and temperature [35]. Values of KSF in the range of 8.5–9.5 are necessary to have high BC yields, while higher severity decreases BC yields owing to the activation of secondary reactions [8]. In our study, experiments at 300 °C and 30 min correspond to KSF = 8 while those at 350 °C correspond to KSF = 9.

The collected experimental results are compatible with the hypothesis that treated SS have a higher concentration of organics, which exhibit a higher apparent activation energy in the HTL process. Consequently, an increase in temperature has a significant effect in accelerating the kinetics of their conversion, resulting in a larger yield of BC.

Different behavior was observed in the case of OOP as pretreated feedstocks were characterized by lower BC yields than native OOP at all investigated values of KSF.

These results suggest that pretreatment is more effective in improving the BC yield for heterogeneous and mixed biofeedstocks such as SS, while it is less effective with more homogeneous matrices like OOP.

3.4. Biocrude characterization

BC and SRHTL were characterized by elemental analysis to study the effect of pretreatments on their atomic composition (Table 6).

In the case of SS, the BC obtained from HTL of pretreated matrices was characterized by higher H/C ratios at both studied KSF values which led to higher values of HHV. In particular with both additives, the H/C ratio increased from 1.79 to 1.93 at 300 °C. At higher severity when KOH was used, the H/C changed from 1.51 to 1.85 while it increased from 1.51 to 1.63 with FA.

In the case of OOP, BC from treated biofeedstock had lower H/C

Table 6
Elemental analyses of BC and SR obtained in experiments in Table 4.

Exp	Feed	T (°C)	Pretreatment agent	Elemental analysis of BC									Elemental analysis of SR								
				C	H	N	S	O	H/C	O/C	N/C	S/C	HHV (MJ/kg)	C	H	N	S	O	ash (%)	H/C	O/C	N/C	S/C	HHV (MJ/kg)
1	SS	300	_	65.0	9.7	6.7	1.8	16.9	1.79	0.20	0.09	0.01	33.1	28.8	3.8	10.4	0.4	13.0	43.7	1.56	0.34	0.31	0.01	12.8
2			KOH	64.8	10.4	7.3	1.6	15.8	1.93	0.18	0.10	0.01	34.2	24.7	3.3	5.5	0.9	17.8	47.9	1.59	0.54	0.19	0.01	10.0
3			FA	66.8	10.7	2.5	2.1	17.8	1.93	0.20	0.03	0.01	35.1	37.9	4.8	4.8	1.6	31.8	19.1	1.52	0.63	0.11	0.02	14.2
4		350	_	72.30	9.1	3.9	2.1	12.6	1.51	0.13	0.05	0.01	35.4	25.9	2.4	2.6	1.7	16.3	51.0	1.12	0.47	0.09	0.03	9.5
5			KOH	65.76	10.1	2.3	1.6	20.2	1.85	0.23	0.03	0.01	33.3	23.1	2.5	0.6	0.8	17.2	55.8	1.28	0.56	0.02	0.01	8.3
6			FA	71.30	9.7	6.0	2.7	10.3	1.63	0.11	0.07	0.01	36.4	29.4	2.6	3.1	1.4	12.2	51.4	1.08	0.31	0.09	0.02	11.7
7	OOP	300	_	66.51	7.8	ND	1.9	23.8	1.41	0.27	ND	0.01	29.6	49.4	5.5	ND	1.4	39.9	4.0	1.33	0.61	ND	0.01	17.6
8			KOH	64.81	7.2	ND	1.9	26.1	1.34	0.31	ND	0.01	27.6	49.3	5.0	ND	1.5	44.8	0.2	1.21	0.68	ND	0.01	15.9
9			FA	68.77	7.5	ND	1.9	21.8	1.31	0.24	ND	0.01	30.4	54.2	5.2	ND	1.4	30.3	8.6	1.16	0.42	ND	0.01	20.6
10		350	_	76.5	9.4	ND	2.2	11.9	1.48	0.12	ND	0.01	37.5	57.8	5.0	ND	1.3	31.4	3.9	1.03	0.41	ND	0.01	21.2
11			KOH	71.1	8.7	ND	2.1	18.0	1.48	0.20	ND	0.01	33.5	49.0	5.0	ND	1.5	42.1	3.1	1.22	0.64	ND	0.01	16.3
12			FA	77.5	8.8	ND	2.0	11.5	1.37	0.10	ND	0.01	37.2	62.7	4.5	ND	1.2	30.6	0.6	1.16	0.42	ND	0.01	22.4

Table 7
Energy recovery ER from HTL experiments of raw and pretreated SS and OOP conducted at 300 and 350 °C and 30 min as reaction temperature and time. Pretreatments were conducted at 150 °C for 30 min.

KSF = 8		ER (%)		
		BC	SRHTL	Cumulative
SS	Raw	27.1	26.4	53.5
	KOH	33.9	28.3	62.2
	FA	30.2	42.8	73.0
OOP	Raw	31.9	31.7	63.5
	KOH	20.9	31.7	52.6
	FA	11.7	38.5	50.2
KSF = 9				
SS	Raw	35.5	15.5	51.0
	KOH	33.3	19.2	52.5
	FA	68.1	13.5	81.6
OOP	Raw	56.2	19.9	76.1
	KOH	35.6	33.8	69.4
	FA	29.2	29.6	58.8

ratios. With both biofeedstocks, the O/C value seemed not affected by the pretreatments but mainly dependent on the KSF of the process as its value generally decreased when it was higher with the only exception of BC from KOH-treated SS whose O/C increased with KSF.

SRHTL recovered after FA pretreatment of the biofeedstocks showed the highest value of HHV.

Product yields and HHV were used to estimate the energy recovery of each single fraction, BC and SRHTL (Table 7). The highest values of cumulative energy recoveries were obtained with FA-pretreated SS: at KSF = 8 the SRHTL was the main contributor with 42.8 % compared to a value of 30.2 % for BC, and the enhancement of KSF to 9 biased this partitioning in the direction of BC whose ER increased from 35.5 to 68.1 %. In comparison, the SRHTL decreased to 13.5 %.

These data indicate that FA pretreatment, combined with the optimal value of kinetic severity of HTL [8], makes it possible to densify the chemical energy in the BC product.

To obtain additional information on the composition of BC, selected samples were analyzed by FT-ATR (Figs. 1 and 2). Attention was focused on the main detected resonance bands according to BC characterization reported in the literature.

The spectra of BC exhibited resonance bands at about 2923 and 2853 cm^{-1} that are associated with sp^3 hybridized stretching of C-H bonds along with the C-C peak at about 1450 cm^{-1} and other absorption bands at 1375 cm^{-1} and 720 cm^{-1} which are indicative of paraffinic hydrocarbon chains [36,37].

Absorption bands in the range 1650–1720 cm^{-1} related to C=O groups [36] were clearly detectable: in BC obtained from OOP (Fig. 2) the peak was mainly located at 1710 cm^{-1} with a shoulder at 1735 cm^{-1} while in the BC from SS (Fig. 1) two peaks were detectable: the first one at 1710 cm^{-1}, as in OOP, and a second located at about 1650 cm^{-1}. The

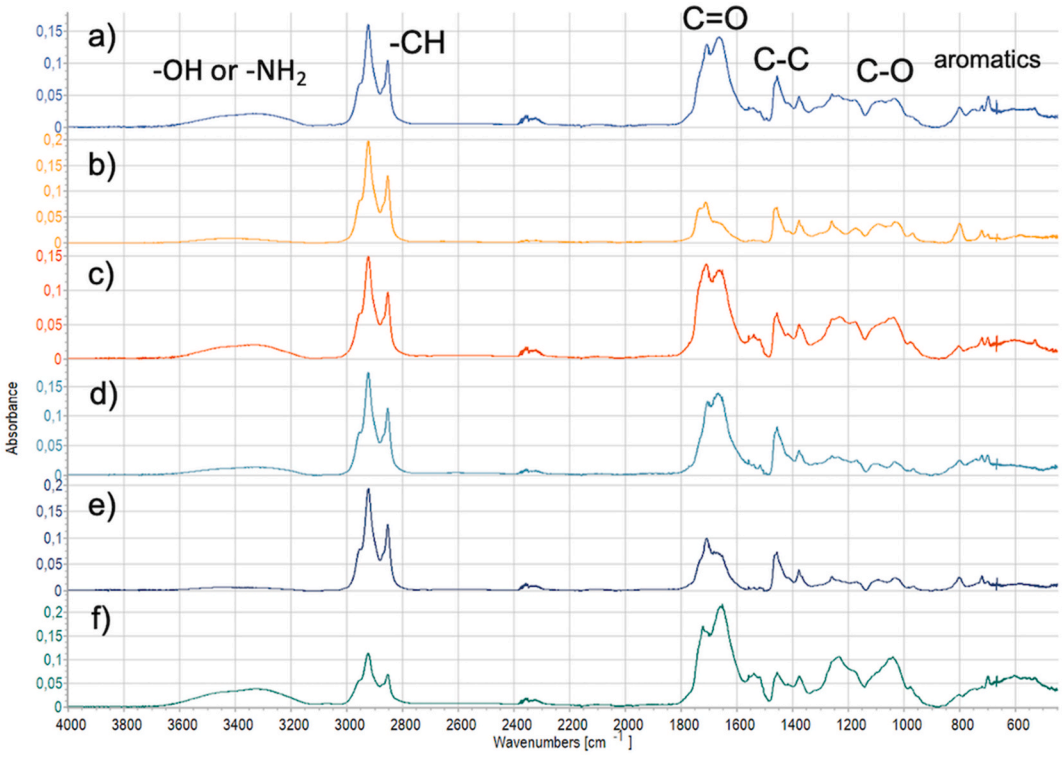

Fig. 1. FTIR spectra of BC obtained from HTL of SS at KSF = 8: a) non treated SS, b) SS treated with KOH, c) SS treated with FA; KSF = 9: d) non treated SS, e) SS treated with KOH, f) SS treated with FA.

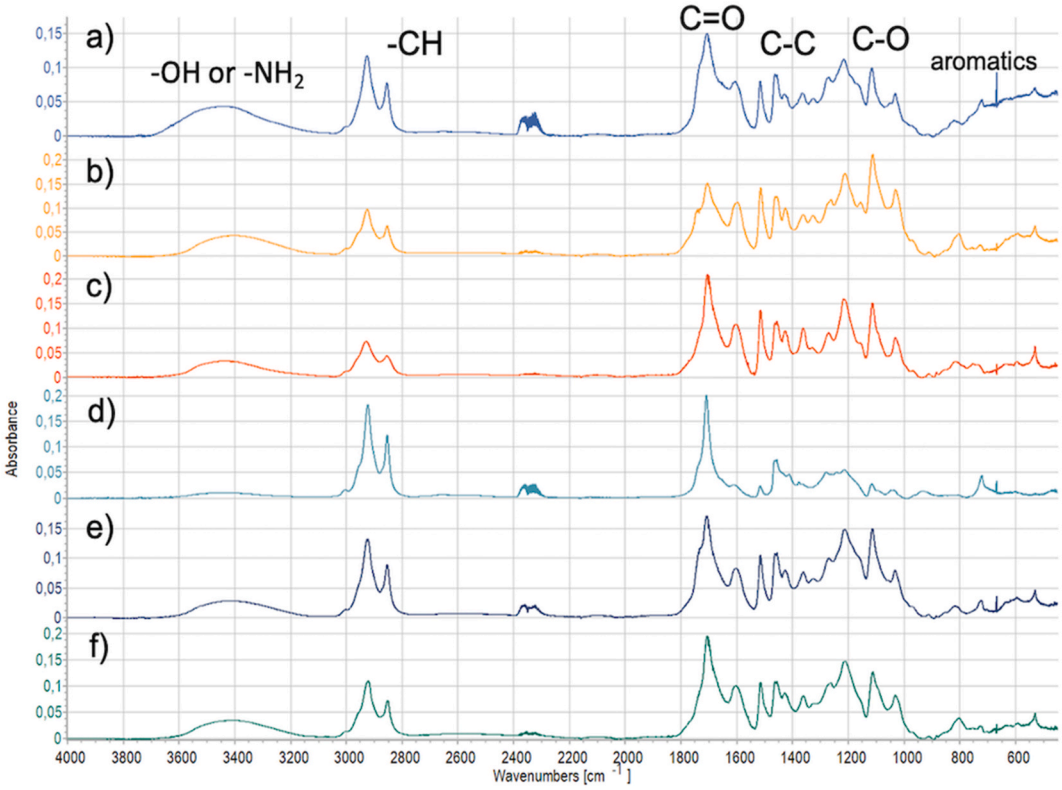

Fig. 2. FTIR spectra of BC obtained from HTL of OOP at KSF = 8: a) non treated OOP, b) OOP treated with KOH, c) OOP treated with FA; KSF = 9: d) non treated OOP, e) OOP treated with KOH, f) OOP treated with FA.

Table 8
Integrals of resonance peaks related to carbonyl functional groups (1600-1800 cm^{-1}), and O-H and N-H bonds (3100-3600 cm^{-1}) of BC from SS normalized with respect to $-CH_2$ and $-CH_3$ sp^3 groups (2800-3000 cm^{-1}). The ratios between the integrals of resonance peaks at 1660 and 1719 cm^{-1} are also reported.

T (°C)	Pretreatment agent	$R_{1600\text{-}1800/C\text{-}H}$	$R_{3100\text{-}3600/C\text{-}H}$	$R_{1650/1710}$
300	_	1.2	0.5	1.6
	KOH	0.4	0.2	0.7
	FA	1.3	0.5	1.1
350	_	1.0	0.4	2.0
	KOH	0.6	0.2	1.0
	FA	1.0	1.3	2.0

former can be mainly associated with carbonyl groups of ketones, aldehydes, carboxylic acid and their esters, while the latter can be associated with carbonyl groups in amide [37]. These results are consistent with the outcomes of elemental analysis of the BC which showed N content below the detection limit when OOP was used as the biofeedstock (Table 6).

The C-O absorbance peak at 1113 cm^{-1} indicated the presence of phenols or alcohols in all the analyzed BC [38].

In some of the analyzed BC samples, a broad band in the range 3300–3600 cm^{-1} was detected that can be related to -OH stretches from alcohols or phenols or to $-NH_2$ resonance of amine and amide, as the analyzed BC was carefully dehydrated by addition of sodium sulfate (as reported in the methodology section). If related to -OH groups, this peak should be associated with bands at 1113 cm^{-1} that are generated by resonance with the C-O stretch.

Absorbance bands at about 1515 cm^{-1} and 1600 cm^{-1} and resonance bands located in the range 700–850 cm^{-1} indicate aromatic compounds [39].

In the case of SS we observed that BC obtained from KOH treated SS (Fig. 1b and e) is characterized by a lower area of peaks related to -OH, -NH and carbonyl functional groups (Table 8), indicating that the alkaline pretreatment removed oxygen and nitrogen bearing chemical species from the SS matrix. These IR indications seem not to be coherent with the outcomes of elemental analyses that estimated higher O/C values for BC produced from KOH treated SS.

A possible explanation for this discrepancy can be proposed according to the results of Jedynak et al. [40] who studied the effect of KOH on the structure of sawdust. In particular, they found that in the presence of KOH intercalation of potassium oxide occurs in the biofeedstock structure according to the following reaction between potassium hydroxide and the carbon sites of the matrix:

$$4KOH + C \rightarrow K_2CO_3 + K_2O + 2H_2 \quad (10)$$

It is possible that during HTL part of these inorganic compounds are transferred to the BC and are responsible for an overestimation of the oxygen content of the BC that is determined as the complement to 100 % of the quantified C, H, N and S atoms.

In the case of BC from OOP, in which no N atom was detected by elemental analysis, we obtained a good linear correlation between the summation of the integral areas of carbonyl and hydroxyl peaks

Table 9
Integrals of resonance peaks related to carbonyl functional groups (1630-1800 cm^{-1}), and O-H bonds (3100-3600 cm^{-1}) of BC from OOP normalized with respect to $-CH_2$ and $-CH_3$ sp^3 groups (2800-3000 cm^{-1}).

T (°C)	Pretreatment agent	$R_{1630\text{-}1800/C\text{-}H}$	$R_{3100\text{-}3600/C\text{-}H}$
300	_	0.7	1.1
	KOH	0.9	1.2
	FA	0.7	0.5
350	_	0.6	0.2
	KOH	0.8	0.2
	FA	0.9	0.9

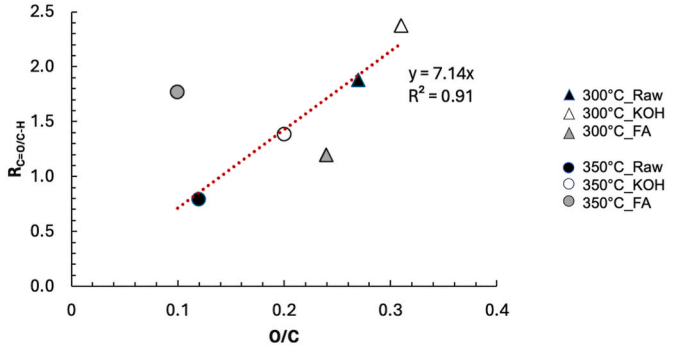

Fig. 3. Diagram of the summation of the integral areas of carbonyl and hydroxyl peaks normalized to sp^3 methyl or methylenic groups ($\mathbf{R_{C=O/C-H}}$) vs. the O/C parameter estimated from elemental analysis of HTL experiments of raw and pretreated OOP conducted at 300 and 350 °C and 30 min as reaction temperatures and time.

normalized to sp^3 methyl or methylenic groups ($\mathbf{R_{C=O/C-H}}$), which values are reported in Table 9, and the O/C parameter estimated from elemental analysis (Fig. 3).

This result indicates that the aforementioned functional groups are the main contributors to the oxygen content of BC from OOP.

Moreover, the resonance peak located at 1600 cm^{-1}, indicative of aromatic rings, was more evident in the case of BC obtained from pretreated OOP, which could explain the absence of an observed effect of the pretreatments on the H/C ratios.

TGA analyses of BC samples produced at 350 °C were performed to investigate their volatilization behavior and the results are shown in Table 10 and Fig. 4 a) and b). The TGA results demonstrated that the BC from KOH pretreated matrices had a higher fraction of residues at temperatures higher than 550 °C, which was measured at around 25 % with respect to a residual obtained mass fraction of approximately 15 % and 9 % for raw SS and OOP, respectively.

Furthermore, Figs. 1 and 2 also show that the relative intensity of the olefinic and aromatic C=C stretching band was lower with both hydrolyzed feedstocks at 350 °C, suggesting a potential efficacy of the pretreatment in increasing the aliphatic character of BC generated from hydrolyzed feedstocks.

4. Conclusions

The use of hydrolytic pretreated SS as feedstock of HTL induced several improvements: (i) an increase of the BC yield that changed from 18 %, obtained with the raw matrix, to 23 and 34 %; (ii) an increase of the H/C ratios that led to higher values of HHV; (iii) a reduction of the relative intensity of the olefinic and aromatic C=C stretching bands, suggesting a potential efficacy of the pretreatment in increasing the aliphatic character of BC generated from hydrolyzed biofeedstocks.

When SS were pretreated with FA we observed an enhancement of the organic fraction from the 0.71 value of the raw matrix to 0.83–0.81. HTL of the treated SS at KSF = 9 produced a BC with an energy recovery of 68.1 % significantly higher than the 35.5 % obtained with native SS. This indicates that FA pretreatment, combined with HTL performed at optimized values of kinetic severity [8], makes it possible to densify chemical energy in the produced BC.

Also, KOH pretreatment of SS positively affected the H/C ratio of the BC as this parameter increased from 1.79 to 1.93 at 300 °C and from 1.51 to 1.85 at 350 °C. Moreover, FTIR spectra of produced BC are characterized by lower normalized areas of peaks related to -OH, -NH and carbonyl functional groups, indicating that the alkaline pretreatment removed oxygen and nitrogen-bearing chemical species from the SS matrix.

Different behavior was observed in the case of OOP as pretreated feedstocks were characterized by lower BC yields than the native ones, with no significant improvement of HHV.

These results suggest that pretreatments are more effective in

Table 10
Fraction of volatilized mass recorded as a function of temperature interval in TGA of BC produced by HTL experiments 4–6 and 10–12 in Table 4.

Distillate Range (°C)	Potential application	SS (% w/w)			OOP (% w/w)		
		NP	KOH	FA	NP	KOH	FA
35-185	gasoline	7.00	5.51	7.40	5.27	0.77	5.37
185-240	kerosene	11.65	10.38	10.42	11.12	4.94	9.92
240-350	diesel	37.14	31.34	34.67	43.05	22.80	39.31
350-570	heavy gas oil	29.75	25.94	29.34	30.11	47.59	33.22
>570	residual fuel oil	14.46	26.83	18.17	10.45	23.89	12.17

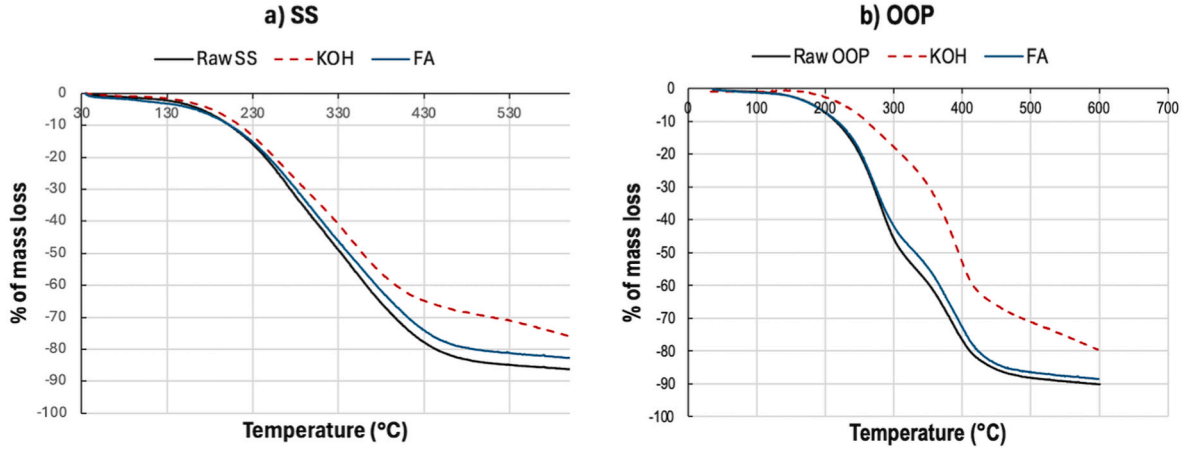

Fig. 4. TGA analyses of the BC obtained by HTL experiments of a) SS and b) OOP at 350 °C.

improving the BC yield for heterogeneous and mixed biofeedstocks such as SS, while they are less useful for more homogeneous matrices like OOP.

CRediT authorship contribution statement

Claudia Prestigiacomo: Writing – original draft, Visualization, Supervision, Data curation, Conceptualization. **Elisa Ciccarello Cicchino:** Data curation. **Federica Proietto:** Formal analysis. **Onofrio Scialdone:** Writing – review & editing. **Alessandro Galia:** Writing – review & editing, Visualization, Validation, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Glossary

ATR-FTIR attenuated total reflectance-Fourier transform
BC biocrude
ER Energy recovery
ER_{BC}: Energy recovery of BC
ER_{SRHTL}: Energy recovery of SRHTL
ER_c Cumulative energy recovery
FA formic acid
FT-IR Fourier transform infrared spectroscopy
GAS gas phase of HTL
HHV higher heating value
HTL: hydrothermal liquefaction
Int A_i integral of i-esim functional group Int A_i
Int A_{std}: integral of the selected reference group
KSF kinetic severity factor
m_p: dry mass of the product
m_f dry initial mass of the feedstock used to perform HTL
m_{pdaf} dry ash-free mass of the products (obtained by calcination at 550 °C for 6 h of the dry samples)
m_{fdaf} dry ash free mass of feedstock
OOP Olive Oil Pomace
$R_{i/std}$: value of the ratio between the integrals (Int) of the absorbance of the resonance band of each i-esim functional group Int A_i and of the selected reference group Int A_{std}
SR solid residues
SRHTL: solid residues from HTL
SS Sewage Sludge
T Temperature
TGA thermogravimetric analyses
TOC total organic Carbon
VT volatiles
x_{SR}^{pt}: the fraction of inorganic compounds in the solid cake produced by pretreatment
Y_{SR}^{pt} : yield of the solid residue produced after pretreatment, dry basis
$Y_{p_{dry}}$: yields of condensed products after HTL, dry basis
$Y_{p_{daf}}$: yields of condensed products after HTL, dry ash free basis
$Y_{VT_{daf}}$: yields of volatiles, dry ash free basis
WSP water soluble products
z_{SR}^{pt}: fraction of organic compounds in the solid cake produced by pretreatment
ω_s yield of organics in the solid cake collected after filtration
ω_l: the yield of compounds dissolved in the eluted phase

Data availability

Data for this article, including FT-IR and TGA are available at OneDrive at https://unipa-my.sharepoint.com/:f:/g/personal/alessandro_galia_unipa_it/EpX8-vZdL1ZHu2qA9jc1WlYBORH6F-Xomcuy5BZHQWIZxQ?e=CUzhJC.

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