Hydrothermal liquefaction of waste biomass in stirred reactors: one step forward to the integral valorization of municipal sludge

Authors

Claudia Prestigiacomo[a], Vito Armando Laudicina[b], Angelo Siragusa[c], Onofrio Scialdone[a], Alessandro Galia[a,*]

[a]Dipartimento di Ingegneria, Sezione Chimica Ambientale Biomedica Idraulica e dei Materiali, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy.
[b]Dipartimento di Scienze Agrarie, Alimentari e Forestali, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy.
[c]AMAP s.p.a., Via Volturno, 2 90138 Palermo, Italy.

Corresponding author

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

Abstract

Hydrothermal liquefaction (HTL) of municipal sludge (MS) was performed at 350°C for 30 min (subcritical water) and at 400 °C for 0 min (supercritical water) at fixed kinetic severity ($LogR_0$=8.9) in static and stirred batch reactors to study the effect of the flow regime on the energy recovery (ER) of the process and on the quality of the products. With adopted experimental procedures it was possible to reduce to less than 10% the yield of lost organic compounds, termed volatiles (VT), and to collect and quantify a liquid hydrocarbon fraction (HC) separated from the biocrude (BC). The highest value of the HC yield, 25% w/w was obtained in supercritical conditions. The C content of the solid residues (SR) and the H/C ratios of the BC increased when the stirred reactor was used. Quite interestingly in this research we have found, to the best of our knowledge for the first time, that the cumulative ER of the product phases was significantly higher than 100% thus indicating that HTL of MS can be energetically driven by renewable thermal energy, such as solar heat, offering a storage option for it.

Keywords

Hydrothermal liquefaction, waste biomass, municipal sludge, biofuel, energy recovery, energy storage.

Nomenclature

Abbreviations

AP: Aqueous phase; **BC:** Biocrude; **daf:** Dry ash free; **Eq:** Equation; **ER:** Energy recovery; **Fig:** Figure; **GC**: Gas-chromatograph; **HC**: Hydrocarbon; **HHV:** High heating value; **HTL**: Hydrothermal liquefaction; **ICP-OES**: Inductively coupled plasma optical emission spectrometry; **min:** minute; **MS**: Municipal sludge; **SR:** Solid residues; **UWWTP:** Urban wastewater treatment plant; **WSP:** Water soluble products; **GAS:** Gaseous phase; **VT:** Volatiles.

Symbols

H/C: Hydrogen to carbon molar ratio; **N/C:** Nitrogen to carbon molar ratio; **O/C:** Oxygen to carbon molar ratio; **S/C:** Sulphur to carbon molar ratio; **R_0:** Kinetic severity parameter; **rpm:** Rotation per minutes; **T:** Temperature; t: Reaction time; **V_L:** Volume of liquid water; **V_V:** Volume of water vapor; **ϱ:** density g/mL; **% w/w:** percentage by weight

1. Introduction

Hydrothermal liquefaction (HTL) is considered an interesting route to obtain energy from biomass [1-6]. Municipal sludge (MS) obtained from urban wastewater treatment plants (UWWTP) are zero-cost wet raw materials widely available in large quantities [4, 5, 7]. In particular in 2015, 3 millions of metric tons of MS were produced in Italy and just 0.8% was processed to produce energy [8]. HTL can make possible the energetic valorization of the MS and it is considered more interesting than anaerobic digestion because it allows significant reduction of the amount of solids to dispose [9-11]. Furthermore, MS were already proved to be equivalent to microalgae [12-14] in terms of HTL conversion efficiency and their utilization would reduce of 40% the operating expenses of the process [15, 16]. HTL takes place at temperature from 300°C to 400°C and pressure of about 10-40 MPa [17] that are milder operative conditions with respect to other routes for the conversion of wet biomass such as hydrothermal carbonization and hydrothermal gasification [18]. In this aqueous environment, the peculiar properties of dense water at near-critical conditions promote the depolymerization of the bio-macromolecules [19 – 26] resulting in the formation of a wide range of

low molecular weight organic compounds distributed in the produced phases. A heavy oil, named biocrude (BC), is actually considered the main product of the process [5, 6]. An aqueous phase (AP) rich in water soluble products (WSP) – namely organic compounds - a gas phase rich in CO_2 (GAS) and a solid residue (SR) can be identified as co-products. An energetic valorization of the coproducts can be performed to improve economic sustainability of the process. For example the AP can be recycled to the HTL reactor improving the yield and quality of BC [27-29], or it can be converted to a hydrogen rich gas or biogas by aqueous phase reforming or anaerobic digestion respectively [30-32] and the SR can achieve the characteristics of a solid recovered fuel as defined by UNI EN 15359 [33]. Many investigations indicate that the yield and characterization of the products strongly depend on the biochemical composition of the adopted feedstock [34], the biomass loading [35,36] and the reaction temperature and time [4, 24, 37-41]. Some studies about the HTL of lignin compounds [42] and microalgae [43] showed an important correlation between operative conditions and the closing of the mass balance. The main outcome is that the difficulties to achieve quantitative recovery of products increases with the complexity of the phase behavior of the system [5, 34, 44, 45]. To date, significant amount of light fractions of products, termed volatiles (VT), are lost using the work-out procedures reported in literature. The mass percent yield of VT was estimated by difference between 100% and the sum of the mass percent yields determined for BC, SR, WSP and GAS. With microalgae, no VT were estimated at reaction temperature lower than 250°C [43]; this result was never reached with MS. Other studies indicate that, at temperature higher than the critical point of water, part of the formed BC is transformed into a light oil fraction (not quantified) and gases [24]. Quite interestingly a recent study on fast HTL of MS at different reaction temperatures and times showed that, even using optimized operative conditions, the VT yield never decreased below 20% [46]. An important aspect of the HTL is the energy recovery (ER) of the process that affects its economics. Estimation of cumulative ER of the produced phases was not possible yet owing to the large fraction of lost VT reported in studies published till now using microalgae [43, 47], macroalgae [47], lignocellulosic wastes [47] and MS

[12, 36, 43, 46, 47]. Furthermore, the presence of a nonpolar hydrocarbon (HC) fraction in the BC was detected by several techniques but, to the best of our knowledge, an attempt to perform quantization rather than identification of the main components was never addressed [26, 47-49]. To date, many investigations based on HTL of MS were made in stirred [4, 24, 38 - 40] or in static reactors [37, 41] to assess the role of the operating parameters on the distribution and quality of products but there is no comparison between the two different reactors using the same experimental conditions. In our opinion, the reactor configuration and the work-out operations can be adjusted to minimize the amount of VT and to make possible the estimation of the cumulative energy recovery. Under these conditions it is possible to assess the sustainability of industrial application of HTL as possible solution to solve the problem of MS management.

According to this consideration, in this study we adopted work-out procedures that strongly decreased the amount of VT in the HTL of MS comparing the results in static and stirred batch reactors.

Using these experimental methods, we studied the effect of reaction temperature and time and of the fluid dynamic regime on the final yield and quality of BC, SR and liquid HC. Reaction temperature and time were chosen to keep fixed the kinetic severity R_0 that is a reaction parameter used in complex thermally activated processes [46, 50, 51] to combine the effect of temperature and time on the kinetic behavior of the system. We found experimental conditions that make possible the valorization of any obtained product phase thus supporting the practical feasibility of HTL of MS.

2. Materials and Methods

2.1. Materials

MS used as wet biomass for HTL experiments were provided by the UWWTP of Palermo, Italy (A.M.A.P. s.p.a.). Table 1 lists MS properties. Cyclohexane (Sigma Aldrich, analytical grade) and acetone (Sigma Aldrich, HPLC grade) were the solvents used to recover the produced BC. Tetradecane, 1-tetradecene, hexadecane and 1-hexadecene (Alpha Aesar, analytical grade) and

methyl heptadecanoate (Sigma Aldrich, +99%) were used as gas-chromatographic standards. Tetrahydrofuran (anhydrous, +99.9% Sigma Aldrich) was used as solvent to prepare liquid samples for the gas-chromatographic analysis [52].

Table 1: Proximate and ultimate analyses of MS.

Proximate analysis of MS (% w/w dry biomass)	
Moisture content as received	76 ± 2.0
Organic Content	80 ± 0.2
Ultimate analysis of MS	
C[a]	45.2 ± 0.21
H[a]	6.87 ± 0.05
N[a]	5.92 ± 0.03
S[a]	1.46 ± 0.07
HHV[b] (MJ/kg)	20.6
Hg (mg/kg)	<0.1

[a] % w/w dry basis
[b]HHV: high heating value, estimated by Dulong formula [54];

2.2. Reaction apparatus

The HTL experiments were performed in an axially stirred autoclave reactor with a free volume of 16 mL made from 3/4 in. Swagelok® VCR (316SS) male union and caps. The reactor sealing was previously tested till 25 MPa as reported in our previous study [12]. The experimental apparatus described elsewhere [12] was joined to the shaft of an IKA RW16 lab stirrer to perform experiments under stirring conditions (170 rpm). After the reaction the reactor was quenched using a water bath. The upper part of the reactor was connected, through a 1/16-inch 316SS tube to a

Parker needle valve that allowed to insulate the reactor during the reaction process (maximum operative pressure of 41 MPa) and to join the reaction chamber to a gas expansion system to collect the produced gas phase [12, 53]. The heating profile of the axially stirred reactor was studied in blank experiments and a heating rate of 13 K/min was determined.

Before any HTL experiment, the reactor was filled with 5 g of the aqueous slurry (10% w/w of dry MS in deionized water) and ten quartz spheres (diameter 3 mm) loaded to promote mixing, the reactor was sealed and cleansed with argon (Air Liquide 99.999% purity) whose residual pressure after purging step was 0.2 MPa. Then the reactor was fastened to the bottom part of the shaft (part e in Fig. 1).

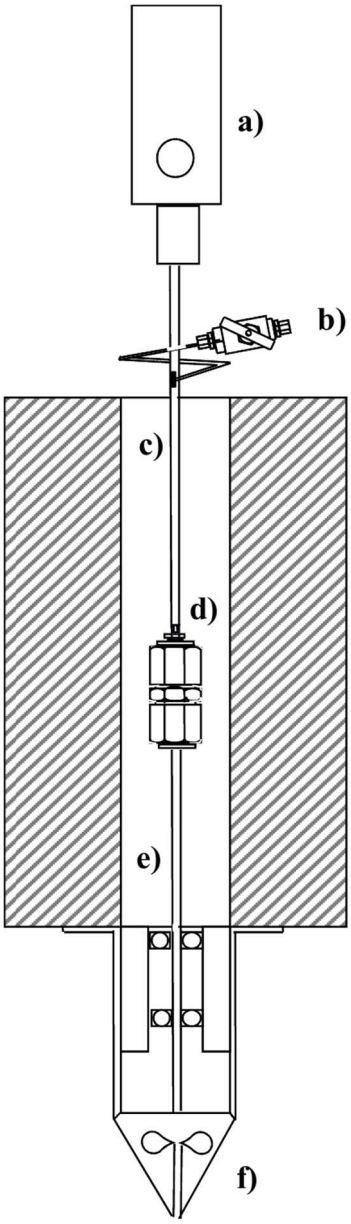

Figure 1: Experimental apparatus: a) IKA RW16 lab stirrer; b) Parker needle valve; c) upper shaft fixed to the reactor; d) reactor body; e) bottom part of the shaft fixed to the cylindrical heating unit; f) fan.

The temperature of the reactor was measured by an infrared thermometer during the experiments. The time during which the reactor was kept at the set-up temperature was considered as reaction time and when 0 min is reported it means that the reactor was quenched immediately after the set-up temperature was reached. At the end of the reaction, the reactor was disconnected from the IKA

RW16 lab stirrer, extracted from the oven and then quenched with cold water as reported elsewhere [12].

2.3. Downstream separation methods

Separation procedures were based on those adopted in our previous work [12], with some modifications aimed to reduce the amount of VT. At the end of each HTL experiment, the reactor was connected to a gas expansion system [53] to collect the produced GAS. Gases were analyzed by Agilent Technology 7890B gas chromatograph (GC) using the method described in detail elsewhere [12]. The reactor was then disconnected from the gas expansion system and opened. All the content was poured in a centrifuge tube. 1 mL of cyclohexane was added to the centrifuge tube containing the recovered AP, BC, and SR to promote the separation of BC fraction from AP. The tube was then centrifuged at 3220 rpm for 20 min using a Thermo Scientific IEC CL10 centrifuge. The three stratified phases ,cyclohexane containing BC, AP and SR, were separated and stored in two different glass vials. In this first stage the SR was mixed with cyclohexane solution because we observed in our previous study [12] that most of the BC was adsorbed on the SR. In our previous study the reactor was cleaned by sonication after adding acetone. This step was modified since heat generated by ultrasounds can promote evaporation of volatile compounds. In the new procedure, the reactor was filled with 5 mL of cyclohexane and stirred in a shaker incubator at 20°C for 3 h. The solvent and the small amount of residual AP were recovered and separated. Only at this point the reactor was filled with 5 mL of acetone to clean the inner walls and recovering the residual BC and SR. This step was repeated till the washing acetone solution was clear. The acetone suspension was added to the vial containing cyclohexane with BC and SR collected after centrifugation. As in our previous study, vacuum filtration on a dry and pre-weighted nylon filter (47 mm diameter with 0.2 µm of pores diameter) was used to separate SR from the mixed solvent containing BC. SR mass was determined after drying at 60°C over night the cake on the filter.

Also the method to estimate the BC mass was changed. Instead of using solvent stripping by a nitrogen stream bubbled in the liquid solution and vented to the atmosphere under hood, in this

study we adopted a controlled stripping process (Fig. 2) performed at 50°C for 6h under a continuous flow of nitrogen (approximate flow-rate 1 L/min) condensing the produced vapors in a cold trap cooled at -10°C by a chiller. At the end of the 6 h the rounded bottom glass flask with the remaining BC (Fig. 2ii, part a), and the glass jacketed flask, full of trapped liquid phase, were disconnected from the system. This experimental set-up allowed us to detect and quantify by gas-chromatographic analyses hydrocarbon compounds in the condensed vapors.

Then, the rounded bottom flask containing the residual BC was weighted and the BC yield was determined.

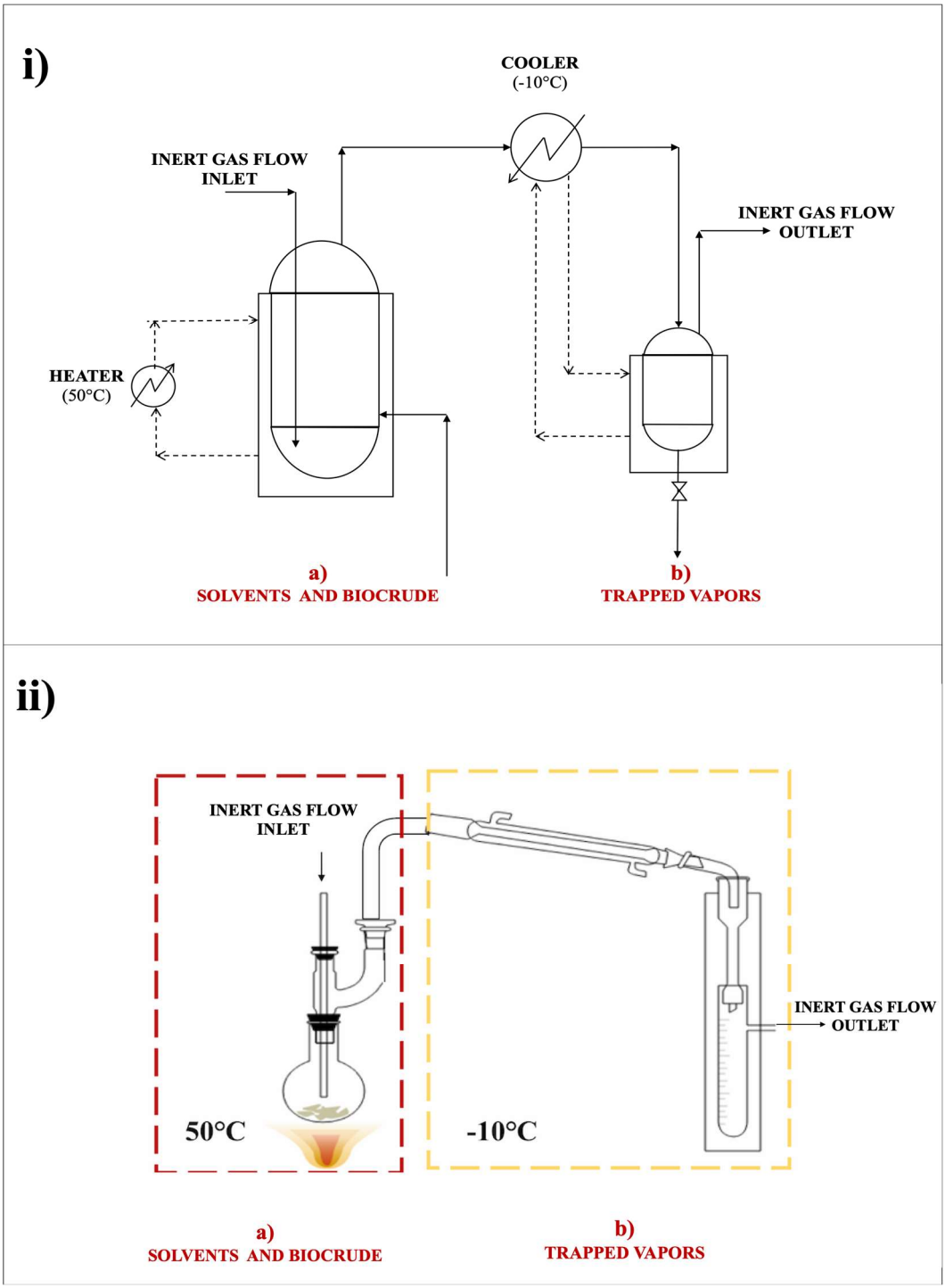

Figure 2: i) flowsheet diagram of the controlled evaporation process, ii) detailed scheme of the system: a) rounded bottom flask in which the solvents and BC were initially loaded; b) jacketed flask from which the condensed vapors were recovered at the end of the process

2.4. Analytical Methods

Moisture and organic content of MS were determined as reported in detail elsewhere [9]. Hg content in the MS was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis made by A.M.A.P. s.p.a. laboratory. Elemental analyses of the MS, of the BC and SR to determine carbon (C), hydrogen (H), nitrogen (N) and Sulphur (S) content were performed by Perkin Elmer 2400 Series II elemental analyzer and O (% w/w) was determined by eq. (1):

$$O = 100 - C - H - N - S - ashes \quad (1)$$

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 at 550°C, for 6h. The same calcination process was performed on BC samples finding an ash percentage below detection limits (0.5% w/w).

The high heating values (HHV) of BC and SR were calculated by the expanded Dulong formula [54]:

$$HHV(MJ/kg) = 0.338\,C + 1.44\,(H - O/8) + 0.094\,S \quad (2)$$

All HTL experiments were repeated twice to determine the reproducibility and reported yields are mean values. The standard errors of product yields in % units were 1.1 for BC, 3.0 for the hydrocarbons (HC), 1.0 for the WSP, 1.0 for the GAS and 5.0 for the SR.

The yields of products were calculated according to equation (3) in the dry ash free form (daf):

$$Yield^{product}_{(daf)(\%\,w/w)} = (mass_{daf}\ of\ product / mass_{daf}\ of\ MS) \times 100 \quad (3)$$

The yield of VT ($Yield^{VT}$) was determined by the equation (4):

$$Yield^{VT}(\%) = 100 - Yield^{BC}(\%) + Yield^{HC}(\%) + Yield^{SR}(\%) + Yield^{WSP}(\%) \quad (4)$$

Liquid solutions recovered in the cold trap were analyzed using a Perkin Elmer Autosystem XL GC, equipped with a capillary column ZB-FFAP (30 m x 0,25 mm x 0,25 µm) Phenomenex. Calibration of the chromatograph was performed using GC standards of tetradecane, 1-tetradecene, hexadecane and 1-hexadecene. The standard error for the % w/w composition of hydrocarbon

fraction amounted to 1.5. The amount of products and the composition of the gas phase were determined as in our previous study [12]. Molar percentage of the components of the produced gas were obtained with an average standard error of 0.1 per cent unit.

The volume of vapor and liquid water inside the reactor in subcritical condition were determined by solving the system composed by the equations (5) and (6):

$$\varrho_L V_L + \varrho_V V_V = M_{water}^{tot} \quad (5)$$

$$V_L + V_V = V_{tot} \quad (6)$$

Where ϱ_L and ϱ_V are the densities (g/mL) of liquid and vapor water at 350°C, V_L and V_V are the volumes (mL) of liquid and vapor water, M_{water}^{tot} is the total mass (g) of water initially loaded inside the reactor and V_{tot} is the total volume (mL) of the reactor.

The kinetic severity factor defined by Overend et al. [50] was used as parameter to choose the operating conditions (temperature and reaction time) for the batch HTL experiments. To calculate the value of this parameter taking into account the heating transient, the numerical integration of the equation was used considering the temperature profile inside the reactor (eq. 7) [51]:

$$R_0 = \int_{t_0}^{t_f} \exp(\left(T_{(t)_{[°C]}} - 14.75\right)/100_{[°C]})\, dt \quad (7)$$

The energy recovery (ER) of each collected product was estimated by the equation (8):

$$ER(\%) = \frac{HHV_{product} \times Yield_{(daf)(\%\, w/w)}^{product}}{HHV_{feedstock}} \times 100 \quad (8)$$

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

$$ER_C(\%) = ER_{BC}(\%) + ER_{HC}(\%) + ER_{SR}(\%) + ER_{WSP}(\%) \quad (9)$$

3. Results and discussion

3.1. Effect of reactor stirring

Preliminary runs were performed with the reactor apparatus showed in Fig. 1 without stirring to assess how product yields change [12] using the new downstream recovery procedures.

This step was considered important because HTL of a biomass produces a multiphase product mixture whose fractionation requires very complex procedures that can strongly affect the determination of yields and compositions of the products [55, 56].

Table 2: Effect of work-out procedures on product yields and composition. Comparison of results obtained with the procedures used in our previous study [12] and those adopted in the present study. HTL experiments performed at 325°C and 30 min of reaction time in static regime.

Proc.	Products yield (daf % w/w)					Elemental Analyses (mol ratios)				HHV (MJ/kg)
	BC	SR	WSP	GAS	VT	H/C	O/C	N/C	S/C	
Previous study [12]	27	15	14	12	32	1.42	0.16	0.02	0.01	34.6
Present study	34±0.3	27±2	10±3	13±3	15	1.68±0.03	0.10±0.01	0.05±0.01	0.01	38.3

Proc: procedure; daf: dry ash free; BC: biocrude; SR: solid residues, WSP: water soluble products; VT: volatiles. HHV: high heating value.

In this study we removed any heating process during product phase recovery from the reactor, like sonication [12], under the hypothesis that most of VT are lost in this step.

Moreover the stripping of acetone and cyclohexane solvents from BC was performed using a closed evaporation system (Fig. 2) to trap any BC component volatilized during this unit operation. Experiments in Table 2 only differs for the work-out procedures. The effect of the extraction solvent on the yields of products obtained from HTL of MS has been studied by Qian et al. [36]. They found that even using good solvents such as trichloromethane or dichloromethane the cumulative yields in isolated products was much lower than 100% and the yield of lost VT only decreased to about 30 %. As shown in Table 2, in this study an improvement of the BC and SR yields from 27 to 34% and from 15 to 27% respectively was observed and the VT yields decreased from 32 to 15%.

These results clearly demonstrate that the new adopted downstream processing procedures significantly reduce the VT yield leading to a better closing of the mass balance and a better description of the HTL outcome that was never reported before to the best of our knowledge. To this regard the optimized work-out also allowed to increase the H/C ratio of the BC from 1.42 to 1.68 leading to an enhancement of calculated HHV from 34.6 to 38.3 MJ/kg.

It seems interesting to underline that also the SR yields improved (Table 2). This result could be related with the elimination of the sonication step that promotes the extraction of adsorbed organics from the SR. Elemental analyses of the SR recovered from experiments in Table 2 showed that the H/C increased from 1.10 to 1.24 suggesting enrichment in lighter compounds.

One drawback for the development of a biorefinery process for HTL of wet biomass can be the mass transfer resistance inside the reactor due to the presence of four different phases. For this reason, we decided to perform batch experiments with MS at 350°C and 30 min and 400 °C and 0 min to compare the effect of sub-critical and super-critical water in static and stirred regime at fixed kinetic severity of the HTL process ($LogR_0$=8.9). To be sure that under adopted sub-critical conditions the liquid phase would be a significant reaction locus, its volume fraction in the reactor at 350°C was estimated as reported in the experimental section. We found that 40% v/v of the reactor volume was filled with liquid water and then stirring should affect the performances of the process.

For what concern the BC, SR, WSP and GAS yields, no significant effect of the different fluid dynamic conditions was observed at sub-critical temperature (Table 3).Obtained values of BC yields were in agreement with the literature findings reported by Dimitriadis et al. [5]. When we analyzed liquid solution recovered from the cold trap of the evaporation system we detected the presence of significant amounts of C14-C16 hydrocarbons (Table 4). By considering their cumulative mass, almost quantitative closer of the product mass balance was achieved. When the same experiments were repeated at 400°C in supercritical regime the BC yield decreased from 42 to 32% under stirred conditions, a value that seems coherent with that obtained by Ma et al. [57] at similar experimental conditions. In all experiments the VT yields are much lower than those reported in studies on the

HTL of MS previously published [12, 36, 46]. Furthermore, stirring of supercritical water at 400°C decreased VT yield from 8 to 4% that is significantly lower than the lowest reported in the literature (30%) at similar operative conditions [36] but with different work-out procedures.

Aforementioned contraction of VT yield was accompanied by an enhancement of the HC yield from 15 to 25%. This result is in agreement with the enrichment in light components in the BC observed in supercritical conditions [44, 58] and it could be attributed to faster decarboxylation reactions that drive the oxygen transfer from the BC to the GAS as reported by Pedersen et al. [56]. This hypothesis is supported by the increase of the carbon dioxide molar fraction in the gas phase collected from the stirred reactor (Table 5).

Elemental analyses of BC collected in these experimental runs are showed in Table 6. It can be observed that the H/C of the produced BC increased with stirring from 1.69 to 1.74 and from 1.60 to 1.69 both in sub and supercritical water conditions. Moreover an higher HHV of the BC was achieved in subcritical water. Quite interestingly the H/C ratio of the produced BC are in the range accepted for liquid transportation fuels which has to range between 1 and 2.3 [59]. Also the HHV and the organic content of produced SR increased when stirred reactor was employed at both investigated temperatures as a consequence of the higher fraction of C detected in this product (Table 6).

Table 3: Product yields (daf % w/w) for experiments conducted at 350°C and 30 min and 400°C, 0 min in static and stirred reactor configuration. Exp 1, 2: performed at 350°C and 30 min in static and respectively stirred conditions. Exp 3, 4: performed at 400°C and 0 min in static and respectively stirred conditions.

Exp	T (°C)	t (min)	Type of reactor	Products yield (daf % w/w)					
				BC (±1.1)[a]	HC (±3.0)[a]	SR (±5.0)[a]	WSP (±1.0)[a]	GAS (±1.0)[a]	VT
1	350	30	Static	39	14	16	12	12	7

2	350	30	Stirred	40	9	22	11	10	8
3	400	0	Static	42	15	12	14	12	5
4	400	0	Stirred	32	25	18	13	8	4

[a]the value inside the brackets are the mean values of standard errors.
Ep: experiment; daf: dry ash free; BC: biocrude, HC hydrocarbons, SR: solid residue, WSP: water soluble products, VT: volatiles.

Table 4: Composition of hydrocarbon fractions collected in experiments reported in Table 3.

Exp	**HC composition % w/w** (±1.5)[a]			
	$C_{14}H_{30}$	**$C_{14}H_{28}$**	**$C_{16}H_{34}$**	**$C_{16}H_{32}$**
1	5	84	2	9
2	6	77	6	11
3	ND	91	ND	9
4	ND	89	ND	11

[a]the value inside the brackets are the mean values of standard errors.
Exp: experiment; HC: hydrocarbons; ND: not detected.

Table 5: Composition of gas phases collected in experiments reported in Table 3.

Exp	**mol % of produced gas phase**					
	CH_4 (±0.05)	**C_2H_4** (±0.08)	**C_2H_6** (±0.02)	**CO_2** (±3.0)	**CO** (± 1.0)	**H_2** (±1.4)
1	7.9	2.1	2.1	72.8	8.5	6.6
2	1.5	0.4	0.4	92.1	2.2	3.4
3	9.3	1.8	2.6	65.6	11.8	8.9
4	0.1	0.1	<0.1	98.3	1.0	0.5

Exp: experiment;

Table 6: Elemental analyses of BC and SR obtained in experiments reported in Table 3.

Exp	BC										SR										Organic fraction (% w/w) (±3)
	Elemental Analyses (% w/w)					Elemental Analyses (mol ratios)				HHV (MJ/kg)	Elemental Analyses (% w/w)					Elemental Analyses (mol ratios)				HHV (MJ/kg)	
	C (±0.01)	H (±0.02)	N (±0.21)	S (±0.28)	O[b]	H/C	O/C	N/C	S/C		C (±0.59)	H (±0.09)	N (±0.12)	S (±0.07)	O[b]	H/C	O/C	N/C	S/C		
1	76.08	10.78	4.25	1.11	7.78	1.69	0.08	0.05	0.01	40.0	24.19	1.49	1.18	1.03	8.42	0.73	0.26	0.04	0.02	8.9	36
2	74.60	10.90	5.63	2.03	6.85	1.74	0.07	0.07	0.01	39.9	27.64	2.58	1.52	0.80	15.04	1.11	0.41	0.05	0.01	10.4	48
3	69.65	9.38	3.83	1.78	15.37	1.60	0.17	0.05	0.01	34.5	20.33	1.17	0.91	1.10	10.27	0.69	0.38	0.04	0.02	6.8	33
4	71.39	10.11	3.86	2.20	14.44	1.69	0.13	0.05	0.01	36.7	30.08	1.54	1.68	1.12	17.50	0.61	0.44	0.05	0.01	9.4	51

[a] the value inside the brackets are the mean values of standard errors.
[b] Percentage calculated by difference using equation (2)
BC: biocrude; SR: solid residues;

3.2. Energy recovery in the products

The hydrothermal liquefaction of MS has been proposed as a possible solution for the disposal of MS since 1992 [60, 61]. The assessment of the economic sustainability of this process was hurdled by the complex characterization of the products.

With the work-out procedures adopted in this study, it was possible to discuss about the energy recovery potential of all the products of HTL of MS in different fluid dynamic conditions. In Figure 3 the energy recoveries of the four different product phases are compared with that of the initial biomass feedstock. In a previous investigation on HTL of MS we found evidence of endothermic reactions occurring during the process [12]. Under all operative conditions adopted in this study, the cumulative energy recovery ER_c (%) was higher than 100%. The result indicates that aforementioned endothermic reactions have a significant effect on the energy capture of the process.

As reported elsewhere [45, 60, 61] HTL could be assessed as energy producer, but in a waste to fuel scenario in which the process is driven by renewable thermal energy i.e. coupled with a concentrating solar plant, one can think that the fraction of ER_c exceeding 100% represents the amount of solar energy that can be stored in the products.

According to obtained experimental data, BC and SR can be valorized as biofuel. The water phase can be recycled to the HTL reactor or used to produce hydrogen by aqueous phase reforming. The gas phase, rich in pressurized carbon dioxide, can be valorized by a CO_2 conversion process such as, just to make an example, its electrochemical reduction to formic acid [62] that can be used as additive during the HTL step. By this strategy, complete valorization of MS is possible.

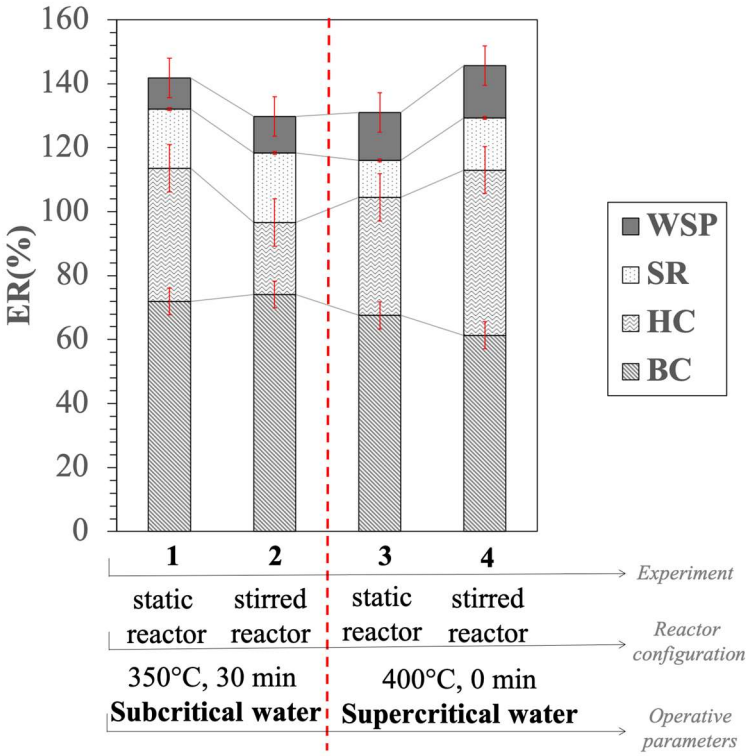

Figure 3: Energy recovery distribution for experiments conducted with MS at different fluid dynamics conditions. BC: biocrude, HC hydrocarbons, SR: solid residue, WSP: water soluble products, VT: volatiles.

4. Conclusions

In this study on the HTL of MS we have adopted optimized work-out procedures that made possible to reduce the VT yield below 10% also at the highest investigated reaction temperature that is much lower with respect the values to date reported in literature. This result was obtained thanks to the detection and quantification of a hydrocarbon fraction separated from the BC. Using a stirred reactor the energy content of the BC and of the SR increased as indicated by the higher H/C ratio of the BC and by the higher organic content of the SR. When supercritical conditions were adopted carbon dioxide molar fraction in the gas phase and hydrocarbon yields increased simultaneously suggesting that faster rate of decarboxylation reactions can occur, promoting the *in-situ* up-grading of the produced biocrude.

A more reliable estimation of the energy recovery of the products was possible thank to the better closing of the mass balances. By these calculations cumulative ER% higher than 100% was calculated that means that, if the HTL reactions would be driven by solar thermal energy, the process can be used to store solar energy in BC, SR and HC. Moreover all generated products can be valorized as biofuels or concentrated source of carbon dioxide or recycled back to the HTL reactor.

These results suggest that HTL of MS in continuous flow reactor at supercritical conditions can be considered a promising option to solve the problem of their disposal by achieving their integral valorization.

Acknowledgments

The financial support of project PON BIOFEEDSTOCK ARS01_00985 is gratefully acknowledged.

References

[1] Goyal, H.B., Seal, D., Saxena, R.C., Renew. Sustain. Energy Rev., Bio-fuels from thermochemical conversion of renewable resources: A review, 2008, 12, 504-517. https://doi.org/10.1016/j.rser.2006.07.014

[2] Zappa, W., Junginger, M., Broek, M. Van Den, Cover, C.L., Appl. Energy, Is a 100 % renewable European power system feasible by 2050? 2019, 233–234, 1027–1050. https://doi.org/10.1016/j.apenergy.2018.08.109

[3] Cantero, D., Jara, R., Navarrete, A., Pelaz, L., Queiroz, J., Rodriguez-Rojo, S., Cocero M.J., Annu. Rev. Chem. Biomol. Eng., Pretreatment processes of biomass for biorefineries: current status and prospects, 2019, 10, 1-22. https://doi.org/10.1146/annurev-chembioeng-060718-030354

[4] Lemoine, F., Maupin, I., Lemée, L., Lavoie, J.M., Lemberton, J.L., Pouilloux, Y., Pinard, L.,

Bioresour. Technol., Alternative fuel production by catalytic hydroliquefaction of solid municipal wastes, primary sludges and microalgae, 2013, 142, 1–8. https://doi.org/10.1016/j.biortech.2013.04.123

[5] Dimitriadis, A., Bezergianni, S., Renew. Sustain. Energy Rev., Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review, 2017, 68, 113–125. https://doi.org/10.1016/j.rser.2016.09.120

[6] Kruse, A., Maniam, P., Spieler, F., Ind. Eng. Chem. Res., Influence of Proteins on the Hydrothermal Gasification and Liquefaction of Biomass. 2. Model Compounds, 2007, 46, 87 - 96. https://doi.org/10.1021/ie061047h

[7] Anastasakis, K., Biller, P., Madsen, R.B., Glasius, M., Johannsen, Ib, Energies, Continuous Hydrothermal Liquefaction of Biomass in a Novel Pilot Plant with Heat Recovery and Hydraulic Oscillation, 2018, 11, 2695. https://doi.org/doi:10.3390/en11102695

[8] Mundo, F., Adella, L., Lupica, I., Mariotta, C., Aragona, G., D'Alessandro, P., Muto, L., Frittelloni, V., C.M., 2017. Rapp. Rifiuti Speciali - Dati di sintesi. http://www.isprambiente.gov.it/files2017/pubblicazioni/rapporto/RapportoRifiutiUrbani_Ed.2017_n.272_Vers.Integrale_rev08_02_2018.pdf

[9] Suzuki A., Nakamura, T., Yokoyama, S., Ogi, T., Koguchi, K., J. Chem. Eng. Japan, Conversion of sewage sludge to heavy oil by direct thermochemical liquefaction, 1988, 21, 288-293. https://doi.org/10.1252/jcej.21.288

[10] Marrone, P.A., Moeller, J, Water Environ. & Reuse Found., Genifuel Hydrothermal Processing BENCH-scale Technology Evaluation Report, 2016, 15. https://doi.org/10.2166/9781780408408

[11] Mulchandani, A., Westerhoff, P., Bioresour. Technol., Recovery opportunities for metals and energy from sewage sludges, 2016, 215, 215-226. http://dx.doi.org/10.1016/j.biortech.2016.03.075

[12] Prestigiacomo, C., Costa, P., Pinto, F., Schiavo, B., Siragusa, A., Scialdone, O., Galia, A., J. Supercrit. Fluids, Sewage sludge as cheap alternative to microalgae as feedstock of catalytic hydrothermal liquefaction processes, 2019, 143, 251–258. https://doi.org/10.1016/j.supflu.2018.08.019

[13] Jarvis, J.M., Billing, J.M., Hallen, R.T., Schmidt, A.J., Schaub, T. M., Energy Fuels, Hydrothermal Liquefaction Biocrude Compositions Compared to Petroleum Crude and Shale Oil, 2017, 31, 2896-2906. http://dx.doi.org/10.1021/acs.energyfuels.6b03022

[14] Marrone, P.A., Elliott, D.C., Billing, J.M., Hallen, R.T., Hart, T.R., Kadota, P., Moeller, J.C., Randel, M.A., Schmidt, A.J, Water Environ. Res., Bench-Scale evaluation of Hydrothermal Processing technology for conversion of wastewater solids to fuels, 2018, 90, 329-342. https://doi.org/10.2175/106143017X15131012152861

[15] Giaconia, A., Caputo, G., Ienna, A., Mazzei, D., Schiavo, B., Scialdone, O., Galia, A., Appl. Energy, Biorefinery process for hydrothermal liquefaction of microalgae powered by a concentrating solar plant: A conceptual study, 2017, 0–1. https://doi.org/10.1016/j.apenergy.2017.09.038

[16] Ranganathan, P., Savithri, S., Bioresour. Technol., Techno-economic analysis of microalgae-based liquid fuels production from wastewater via hydrothermal liquefaction and hydroprocessing, 2019, 284, 256–265. https://doi.org/10.1016/j.biortech.2019.03.087

[17] Yeh, T.M., Dickinson, J.G., Franck, A., Linic, S., Levi, T., Jr, T., Savage, P.E., J. Chem.Technol Biotechnol., Hydrothermal catalytic production of fuels and chemicals from aquatic biomass, 2012, 88.

https://doi.org/10.1002/jctb.3933

[18] Tekin, K., Karagöz, S., Bektaş, S., Renew. Sustain. Energy Rev., A review of hydrothermal biomass processing, 2014, 40, 673-687. http://dx.doi.org/10.1016/j.rser.2014.07.216

[19] Elliott, D. C., Sealock, L. J., Jr., Baker, E., G., Ind. Eng. Chem. Res., Chemical Processing in High-Pressure Aqueous Environments. 3. Batch Reactor Process Development Experiments for Organics Destruction, 1994, 33, 558-565.

[20] Akiya, N., Savage, P.E., Chem. Rev., Roles of water for chemical reactions in high-temperature water, 2002, 102, 2725–2750. https://doi.org/10.1021/cr000668w

[21] Kruse, A., Dinjus, E., J. Supercrit. Fluids, Hot compressed water as reaction medium and reactant. Properties and synthesis reactions., 2007, 39, 362–380. https://doi.org/10.1016/j.supflu.2006.03.016

[22] Lachance, R.P., Fro, M., Antal, M.J., Peterson, A.A., Tester, J.W., Energy Environ. Sci., Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies, 2008, 32–65. https://doi.org/10.1039/b810100k

[23] Peterson, A. A., Vogel, F., Lachance, R. P., Fröling, M., Antal, M. J., Tester, Jr., Tester, J.W., Energy Environ. Sci., Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies, 2008, 1, 32-65. https://doi.org/10.1039/b810100k

[24] Wang, Y., Chen, G., Li, Y., Yan, B., Pan, D., Waste Manag., Experimental study of the bio-oil production from sewage sludge by supercritical conversion process, 2013, 33, 2408-2415. http://dx.doi.org/10.1016/j.wasman.2013.05.021

[25] Tu, Y., Huang, J., Xu, P., Wu, X., Yang, L., Peng, Z., Bioresour., Subcritical water hydrolysis treatment of waste biomass for nutrient extraction, 2016, 11, 5389-5403. https://doi.org/10.15376/biores.11.2.5389-5403

[26] Elliott, D.C., Biller, P., Ross, A.B., Schmidt, A.J., Jones, S.B., Bioresour. Technol., Hydrothermal liquefaction of biomass: developments from batch to continuous process, 2015, 178, 147–156. https://doi.org/10.1016/j.biortech.2014.09.132

[27] Biller, P., Madsen, R.B., Klemmer, M., Becker, J., Iversen, B.B., Glasius, M., Bioresour. Technol., Effect of hydrothermal liquefaction aqueous phase recycling on bio- crude yields and composition, 2016, 220, 190–199. https://doi.org/10.1016/j.biortech.2016.08.053

[28] Zhu, Z., Rosendahl, L., Sohail, S., Yu, D., Chen, G., Appl. Energy, Hydrothermal liquefaction of barley straw to bio-crude oil : Effects of reaction temperature and aqueous phase recirculation, 2015, 137, 183–192. https://doi.org/10.1016/j.apenergy.2014.10.005

[29] Wu, S., Liu, F., Huang, S., Wu, Y, Gao, J., Fuel Process. Technol., Direct n-hexane extraction of wet sewage sludge at thermal and pressurized conditions: A preliminary investigation on its process and product characteristics, 2017, 156, 90-97. http://dx.doi.org/10.1016/j.fuproc.2016.07.020

[30] Pipitone, G., Zoppi, G., Ansaloni, S., Bocchini, S., Deorsola, F.A., Pirone, R., Bensaid, S., Chem. Eng. J., Towards the sustainable hydrogen production by catalytic conversion of C-laden biorefinery aqueous streams, 2019, https://doi.org/10.1016/j.cej.2018.12.137

[31] Si, B., Li, J., Zhu, Z., Shen, M., Lu, J., Duan, N., Zhang, Liao, Q., Huang, Y., Liu, Z., Sci. Total Environ., Inhibitors degradation and microbial response during continuous anaerobic conversion of hydrothermal liquefaction wastewater, 2018, 630, 1124-1132. https://doi.org/10.1016/j.scitotenv.2018.02.310

[32] Hao, S., Ren, S., Zhou, N., Chen, H., Usman, M., He, C., Shi, Q., Luo, G., Zhang, S., J. Hazard. Mater., Molecular composition of hydrothermal liquefaction wastewater from T

sewage sludge and its transformation during anaerobic digestion, 2020, 383, 121163. https://doi.org/10.1016/j.jhazmat.2019.121163

[33] D.lgs. n. 22/2013- Ministero dell'ambiente e della tutela del territorio e del mare, GU *Serie Generale* n.62 del 14-03-2013. https://www.gazzettaufficiale.it/eli/id/2013/03/14/13G00061/sg

[34] Biller, P., Ross, A.B., Bioresour. Technol., Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content, 2011, 102, 215-22 http://dx.doi.org/10.1016/j.biortech.2010. 06.0285.

[35] Madsen R.B., Glasius M., Ind. Eng. Chem. Res., How Do Hydrothermal Liquefaction Conditions and Feedstock Type Influence Product Distribution and Elemental Composition?, 2019, 58, 17583-17600. http://dx.doi.org/10.1021/acs.iecr.9b02337

[36] Qian, L., Wang, S., Savage, P.E., Bioresour. Technol., Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions, 2017, 232, 27-34. http://dx.doi.org/10.1016/j.biortech.2017.02.017

[37] Xu, D., Lin, G., Liu, L., Wang, Y., Jing, Z, Wang, S., Energy, Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of sewage sludge at different temperatures, 2018, 159, 686-695. https://doi.org/10.1016/j.energy.2018.06.191

[38] Malins, K., Kampars, V., Brinks, J., Neibolte, I., Murnieks, R., Kampare, R., Bioresour. Technol., Bio-oil from thermo-chemical hydro-liquefaction of wet sewage sludge, 2015, 187, 23-29. http://dx.doi.org/10.1016/j.biortech.2015.03.093

[39] Ma, W., Du, G., Li, J., Fang, Y., Hou, L., Chen, G., Ma, D., Waste Manag., Supercritical water pyrolysis of sewage sludge, 2017, 59, 371-378. http://dx.doi.org/10.1016/j.wasman.2016.10.053

[40] Kapusta, K., Waste Manag., Effect of ultrasound pretreatment of municipal sewage sludge on characteristics of bio-oil from hydrothermal liquefaction process, 2018, 78, 183-190. https://doi.org/10.1016/j.wasman.2018.05.043

[41] Couto, E. A., Pinto, F., Varela, F., Reis, A., Costa, P., Calijuri, M. L., Renew. Energy, Hydrothermal liquefaction of biomass produced from domestic sewage treatment in high-rate ponds, 2018, 118, 644-653. https://doi.org/10.1016/j.renene.2017.11.041

[42] Hardi, F., Mäkelä, M., Yoshikawa, K., App. En., Non-catalytic hydrothermal liquefaction of pine sawdust using experimental design: Material balances and products analysis, 2017, 204, 1026-1034. http://dx.doi.org/10.1016/j.apenergy.2017.04.033

[43] Valdez, P.J., Nelson, M.C., Wang, H.Y., Lin, X.N., Savage, P.E., Biomass and Bioenergy, Hydrothermal liquefaction of Nannochloropsis sp.: Systematic study of process variables and analysis of the product fractions, 2012, 46, 317–331. https://doi.org/10.1016/j.biombioe.2012.08.009

[44] Zhai, Y., Chen, H., Xu, B., Xiang, B., Chen, Z., Li, C., Zeng, G., Bioresour. Technol., 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, 2014, 159, 72-79. http://dx.doi.org/10.1016/j.biortech.2014.02.049

[45] Yang, T., Liu, X., Li, R., Li, B., Kai, X., J. of Supercrit. Fluids, Hydrothermal liquefaction of sewage sludge to produce bio-oil: Effect of co- pretreatment with subcritical water and mixed surfactants, 2019, 144, 28-38. https://doi.org/10.1016/j.supflu.2018.10.005

[46] Qian, L., Wang., S., Savage, P.E., Appl. Energy, Fast and isothermal hydrothermal liquefaction of sludge at different T severities: Reaction products, pathways, and kinetics, 2020, 260, 114312.
https://doi.org/10.1016/j.apenergy.2019.114312

[47] Madsen R.B., Zhang H., Biller P., Goldstein A. H., G.M., Energy Fuels, Characterizing Semivolatile Organic Compounds of Biocrude from Hydrothermal Liquefaction of Biomass, 2017, 31, 4122–4134.
https://doi.org/10.1021/acs.energyfuels.7b00160

[48] Huang, H.J., Yuan, X.Z., Zhu, H., Liu, Y., Wang, X., Zeng, G:, Energy, Comparative studies of thermochemical liquefaction characteristics of microalgae, lignocellulosic biomass and sewage sludge, 2013, 56, 52-60.
http://dx.doi.org/10.1016/j.energy.2013.04.065

[49] Vardon, D.R., Sharma, B.K., Scott, J., Yu, G, Wang, Z., Schideman, L., Zhang, Y., Strathmann, T.J., Bioresour. Technol., Chemical Properties of biocrude oil from the hydrothermal liquefaction of spirulina algae, swine manure, and digested anaerobic sludge, 2011, 102, 8295-8303.
https://doi.org/10.1016/j.biortech.2011.06.041

[50] Overend, R.P., Chornet, E., Gascoigne, J.A., Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.,. Fractionation of Lignocellulosics by Steam-Aqueous Pretreatments [and Discussion], 1987, 321, 523–536. https://doi.org/10.1098/rsta.1987.0029

[51] Faeth, J.L., Valdez, P.J., Savage, P.E., Energy Fuels, Fast hydrothermal liquefaction of Nannochloropsis sp. To produce biocrude, 2013, 27, 1391–1398.
https://doi.org/10.1021/ef301925d

[52] Villadsen, S.R., Dithmer, L., Forsberg, R., Becker, J., Rudolf, A., Iversen, S.B., Iversen, B.B., Glasius, M., Energy Fuels, Development and Application of Chemical Analysis Methods for Investigation of Bio-Oils and Aqueous Phase from Hydrothermal Liquefaction of Biomass,

2012, 26, 6988-6998.
https://doi.org/10.1021/ef300954e

[53] Bleta, R., Schiavo, B., Corsaro, N., Costa, P., Giaconia, A., Interrante, L., Monflier, E., Pipitone, G., Ponchel, A., Sau, S., Scialdone, O., Tilloy, S., Galia, A., ACS Appl. Mater. Interfaces, Robust Mesoporous CoMo/γ-Al2O3 Catalysts from Cyclodextrin-Based Supramolecular Assemblies for Hydrothermal Processing of Microalgae: Effect of the Preparation Method, 2018, 10, 15, 12562 – 12579.
https://doi.org/10.1021/acsami.7b16185

[54] Marlair, G., Cwiklinski, C., Tewarson, A., Interflam 99, An analysis of some practical methods for estimating heats of combustion in fire safety studies, 1999, ineris-00972167.
https://hal-ineris.archives-ouvertes.fr/ineris-00972167

[55] Yang, J., Sophia, Q., Corscadden, K., Niu, H., Fuel Process. Technol., The impact of downstream processing methods on the yield and physiochemical properties of hydrothermal liquefaction bio-oil. 2018, 178, 353–361.
https://doi.org/10.1016/j.fuproc.2018.07.006

[56] Pedersen, T.H., Jensen, C.U., Sandström, L., Rosendahl, L.A., Appl. Energy, Full characterization of compounds obtained from fractional distillation and upgrading of a HTL biocrude, 2017, 202, 408–419.
https://doi.org/10.1016/j.apenergy.2017.05.167

[57] Ma, W., Du, G., Li, J., Fang, Y., Hou, L., Chen, G., Ma, D., Waste Manag., Supercritical water pyrolysis of sewage sludge, 2017, 59, 371-378.
http://dx.doi.org/10.1016/j.wasman.2016.10.053

[58] Xu, D., Lin, G., Liu, L., Wang, Y., Jing, Z., Wang, S., Energy, Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of sewage sludge at different temperatures, 2018, 159, 686-695.
https://doi.org/10.1016/ j.energy.2018.06.191.

[59] Vennestrøm, P.N.R., Osmundsen, C.M., Christensen, C.H., Taarning, E., Angew. Chemie, Beyond petrochemicals: The renewable chemicals industry, 2011, Int. Ed. 50, 10502–10509. https://doi.org/10.1002/anie.201102117

[60] Itoh, S., Suzuki, A., Desalination, Production of heavy oil from sewage sludge by direct thermochemical liquefaction. 1994, 98, 127–133.

[61] Itoh, S., Suzuki, A., Nakamura, T., Yokoyama, S., Water Sci. Technol., Direct thermochemical liquefaction of sewage sludge by a continuous plant, 1992, 26, 1175–1184.

[62] Proietto, F., Schiavo, B., Galia, A., Scialdone O., Electrochimica Acta, Electrochemical conversion of CO_2 to HCOOH at tin cathode in a pressurized undivided filter-press cell, 2018, 277, 30-40. https://doi.org/10.1016/j.electacta.2018.04.159