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

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Abstract

Hydrothermal liquefaction (HTL) of municipal sludge (MS) was performed at fixed kinetic severity ($LogR_0$=8.9) in static and stirred batch reactors to study the effect of subcritical and supercritical water conditions and of the flow regime on the energy recovery of the process and on the quality of the products. HTL experiments were done at 350°C for 30 min and at 400 °C for 0 min. The C content of the solid residues (SR) and the H/C ratios of the biocrude (BC) increased when the stirred reactor was used both in sub- and supercritical water conditions. With adopted experimental procedures it was possible the detection and quantification of a liquid hydrocarbon fraction separated from the BC and the reduction of the yield of volatiles, i.e. organics lost during work-out procedures, to 10% w/w or less. The highest value of the hydrocarbon yield, 25% w/w, was obtained in supercritical conditions. Quite interestingly, and to the best of our knowledge for the first time, we have found that the cumulative energy recovery 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.

1. Introduction

The global threats constituted by the climate change, the improving energy demand and the growing challenges concerning waste disposal are highly motivating the research of novel industrial routes to obtain energy from renewable sources such as biomass [1-3]. However, the practical use of biomass as bio-feedstock is strongly affected by its cost. In this context, wet waste biomasses are costless raw materials widely available in large quantities [4-6]. Among them, municipal sludge (MS) from urban wastewater treatment plants (UWWTP) are accumulated as wet solid waste. In particular in 2015, 3 millions of tons of MS were produced in Italy and just 0.8% was processed to produce energy [7] while the majority was disposed in conventional municipal landfill [8] with a cost that can be higher than 80 €/ton [9]. Moreover, traditional disposal strategies such as landfilling and incineration are restricted because of severe directives from environmental authorities [8]. Hydrothermal liquefaction (HTL) is considered an interesting route to convert a wide variety of water rich bio-feedstocks to biocrude (BC), a heavy oil actually considered the main product of the process [5, 10]. In this context, HTL could represent an alternative solution to achieve an integral valorization of the MS since they were already proved to be a zero cost bio-feedstock equivalent to microalgae [9, 11, 12] whose utilization would reduce of 40% the operating expenses of the process. [13, 14]. Indeed BC is not the only added value product of HTL as different co-products can be identified: 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). Utilization of these co-products can be performed with an economic gain: for example the AP can be sent back to the HTL reactor improving the yield and quality of BC [15-17], or it can be converted to a hydrogen rich gas or biogas by aqueous phase reforming or anaerobic digestion respectively [18-20]. Furthermore, HTL of MS was reported to be more interesting than anaerobic digestion because it allows significant reduction of the amount of solids to dispose [21-23] and moreover, using bio-feedstock with low heavy metals content [24, 25] the SR can achieve the characteristics of a solid recovered fuel (SRF) as defined by UNI EN 15359 [26].

HTL takes place at temperature from 300°C to 400°C and pressure of about 10-40 MPa [27] that are milder operative conditions with respect to other routes for the conversion of wet biomass such as hydrothermal carbonization and hydrothermal gasification [28]. In this aqueous environment, the peculiar properties of dense water at near-critical conditions promote the depolymerization of the bio-macromolecules in the biomass [29 – 35, 36] resulting in the formation of a wide range of low molecular weight organic compounds distributed in the produced phases (BC, SR, AP, GAS). It must be underlined that, to date, significant amount of light fractions of aforementioned molecules, termed volatiles (VT), are lost using the work-out procedures reported in literature, and in most of the cases, their yield was estimated as the complement to 100 of the cumulative yield of quantified products.

Many investigations indicate that the yield and characterization of the products strongly depend on the biochemical composition of the adopted feedstock [37], the biomass loading [38, 39] and the reaction temperature and time [4, 24, 34, 40-43]. Indeed some studies about the HTL of lignin compounds [44] and microalgae [45] considered the 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, 37, 46, 47]. With microalgae, it was possible to close the mass balance only when reaction temperature lower than 250°C were used [45]; 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 [34]. 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%[48]. An important aspect of the HTL is the energy recovery of the process that affects its economic sustainability. Estimation of global energy recovery of the produced phases was not possible yet owing to the large fraction of VT reported in studies published till now using real bio-feedstocks as microalgae [45, 49], macroalgae [49], lignocellulosic wastes [49] and MS [9, 39, 45, 48, 49]. Furthermore, the presence of a not-polar hydrocarbon 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 [36, 49, 50, 51]. To date, many investigations based on HTL of MS were made in stirred [4, 34, 40 – 42] or in static reactors [24, 43] 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 control the effects of the complex phase behavior of the system and to minimize the amount of VT to make possible the estimation of the cumulative energy recovery and 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, at fixed kinetic severity, the effect of reaction temperature and time and of the fluid dynamic regime on the final yield and quality of BC, SR and liquid hydrocarbons (HC) finding 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. Moisture and organic content were determined as reported elsewhere [9]. 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) were used as GC standards to build calibration curves for the analysis of hydrocarbon fraction.

Tetrahydrofuran (anhydrous, +99.9% Sigma Aldrich) was used as solvent to prepare liquid samples for the GC analysis [52]. Methyl heptadecanoate (Sigma Aldrich, +99%) was adopted as internal standard.

Proximate analysis of MS (% w/w dry biomass)	
Moisture	76
Organic Content	80 ± 0.2
Elemental analysis	
C	45.2 ± 0.21
H	6.87 ± 0.05
N	5.92 ± 0.03
S	1.46 ± 0.07
HHV (MJ/kg)	20.6 ± 0.2
Hg (mg/kg)	<0.1

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

1.1. Experimental methods

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 [9]. The experimental apparatus described elsewhere [9] 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 [9, 53]. The heating profile of the axially stirred reactor was studied in blank experiments and an 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).

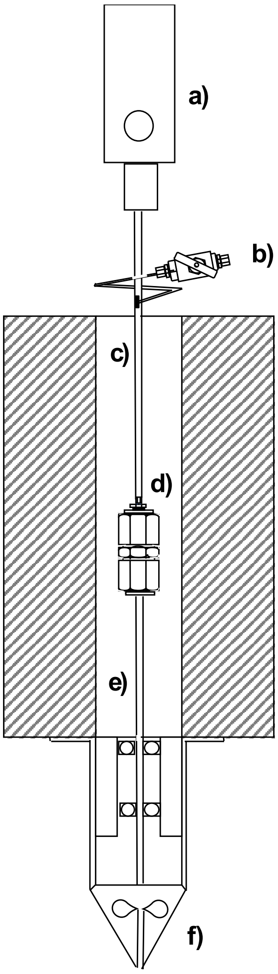

Figure 1: Experimental apparatus: a) IKA RW16 lab stirrer; b) Parker needle valve; c) upper shaft fixed to the reactor; d) reactor body; e) bottom part of the shaft fixed to the cylindrical heating unit; f) fan.

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 [9].

1.2. Work-out procedures

Separation procedures were based on those adopted in our previous work [9], with some modifications aimed to maximize the recovery of the products. The sonication of the reactor after addition of acetone was modified since ultrasounds can heat the system with 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 residual aqueous phase (dissolved in the acetone in the previous procedures) was recovered and added to that obtained by centrifugation. Only at this point the reactor was filled with 5 mL of acetone to recover the residual BC from the inner walls. This step was repeated till the recovered liquid solution was clear.

Another important modification adopted in this study concern the determination of the BC mass. The solvent stripping used in the previous study was modified in a controlled stripping process (Figure 2) performed at 50°C for 6h under a continuous flow of inert gas (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 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.

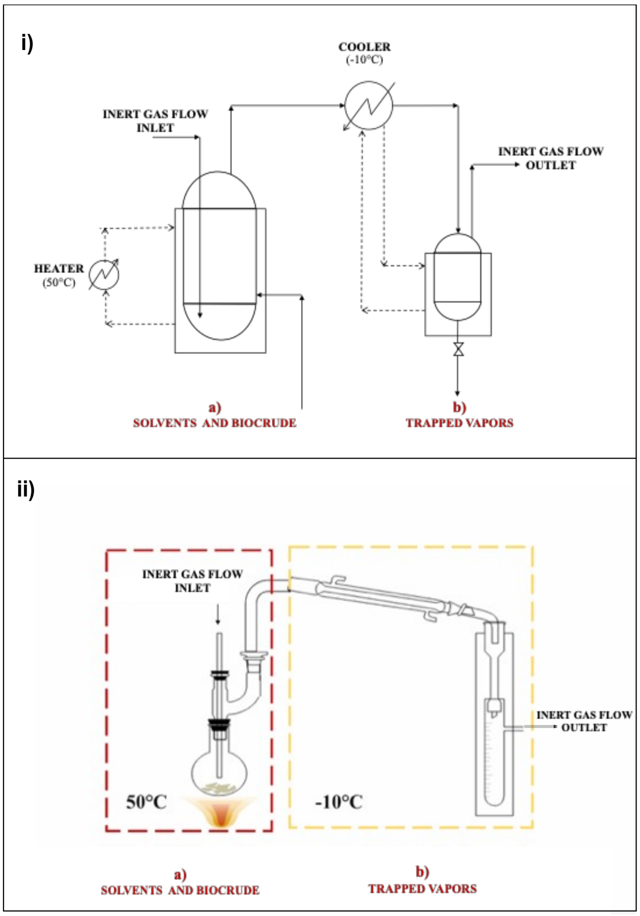

Figure 2: i) flowsheet diagram of the controlled evaporation process, ii) detailed scheme of the system: a) rounded bottom flask in which the solvents and BC were initially loaded; b) jacketed flask from which the condensed vapors were recovered at the end of the process

1.3. Elemental analysis

All HTL experiments were repeated twice to determine the reproducibility and reported yields are mean values. The standard deviations 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 (1) in the dry ash free form (daf):

$$Yield^{product}_{(daf)(\%\,w/w)} = (mass_{daf}\ of\ product/\ mass_{daf}\ \ of\ MS)\ \times\ 100 \qquad (1)$$

The yield of VT (Yield^{VT}) was determined by the equation (2):

$$Yield^{VT}(\%) = 100 - Yield^{BC}(\%) + Yield^{HC}(\%) + Yield^{SR}(\%) + Yield^{WSP}(\%) \qquad (2)$$

Gases were analyzed by Agilent Technology 7890B GC using the method described in detail elsewhere [9].

Liquid solutions recovered in the cold trap were analyzed using a Perkin Elmer Autosystem XL Gas Chromatograph, 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 deviation 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 [9]. Molar percentage of the components of the produced gas were obtained with an average standard deviation of 0.1 per cent unit. CHNS elemental composition analyses of the MS, of the BC and of the SR were performed by Perkin Elmer 2400 Series II elemental analyzer and O (% w/w) was determined by difference (eq. (3)):

$$O = 100 - C - H - N - S - ashes \tag{3}$$

Where C, H, N, S are the % w/w detected by the elemental analyzer and the ashes are the ash average percentage obtained, as previous described, by 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]:

$$HHV(MJ/kg) = 0.338\,C + 1.44\,(H - O/8) + 0.094\,S \tag{4}$$

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):

$$\varrho_L V_L + \varrho_V V_V = M_{water}^{tot} \tag{5}$$

$$V_L + V_V = V_{tot} \tag{6}$$

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. [55] 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) [56]:

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

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

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

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

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

2. Results and discussion

2.1. Effect of reactor stirring

Preliminary runs were performed in static batch reactors to assess how the yields in the products changes with respect to those obtained in our previous study [9] for 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 [57, 58].

Exp	**T (°C)**	**t (min)**	**Config.**	**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**	
1[a]	325	30	Static	27	15	14	12	32	1.42	0.16	0.02	0.01	34.6
2	325	30	Static	34	27	10	13	15	1.68	0.10	0.05	0.01	38.3

[a] results obtained from (Prestigiacomo et al., 2019)
BC: biocrude; SR: solid residues, WSP: water soluble products; VT: volatiles. HHV: high heating value.

Table 2: Effect of work-out procedures on product yields and composition.

In this study we removed any heating process during product phase recovery from the reactor, like sonication [9], under the hypothesis that most of volatiles are lost in this step.

Moreover the stripping of acetone and cyclohexane solvents from biocrude was performed using a closed evaporation system (Figure 3) to trap any BC component volatilized during this unit operation. Experiments 1 and 2 in Table 2 only differs for the adopted work-out procedure so that any difference in yields and composition must be attributed to physical separation procedures rather than to different operative conditions during HTL reactions. As shown in Table 2, using the new separation procedure an improvement of the BC and SR yields from 27 to 34% and from 15 to 27% respectively was observed.

When the optimized work-out was used the H/C ratio of the BC increased from 1.42 to 1.68 leading to an enhancement of calculated HHV from 34.6 to 38.3 MJ/kg.

These results clearly demonstrate that the new adopted downstream processing procedures reduce loss of mass and lead to a better closing of the mass balance.

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. In this study we performed elemental analyses of the solid residues recovered from experiments 1 and 2 finding that the H/C of this materials increased from 1.10 to 1.24 when the optimized procedures were employed 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, in this study we decided to perform HTL 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 regime in static and stirred batch reactors to examine the effect of water physical state (liquid or gaseous) at fixed kinetic severity of 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 this make reasonable to think that stirring should affect the performances of the process.

On the other hand 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). 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 yields decreased from 42 to 32% under stirred conditions. This modification was accompanied by an enhancement of the hydrocarbon yields from 15 to 25%. This result could be attributed to faster rates of decarboxylation reactions that drive the oxygen transfer from the BC to the GAS [58]. This hypothesis is supported by the increase of the carbon dioxide molar fraction in the gas phase when the stirred reactor was used (Table 6) .

Elemental analyses of BC collected in these experimental runs are showed in Table 5. It can be observed that the H/C of the produced BC increased from 1.69 to 1.74 and from 1.60 to 1.69 when the stirred reactor was used both in sub and supercritical water conditions. Furthermore 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]. It is worthwhile to highlight that 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 detected C fraction in this product (Table 5).

Exp	**T (°C)**	**t (min)**	**Type of reactor**	**Products yield (daf % w/w)**					
				BC	**HC**	**SR**	**WSP**	**GAS**	**VT**
3	350	30	Static	39	14	16	12	12	7
4	350	30	Stirred	40	9	22	11	10	8
5	400	0	Static	42	15	12	14	12	5
6	400	0	Stirred	32	25	18	13	8	4

BC: biocrude, HC hydrocarbons, SR: solid residue, WSP: water soluble products, VT: volatiles.

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	**HC composition % w/w**			
	$C_{14}H_{30}$	**$C_{14}H_{28}$**	**$C_{16}H_{34}$**	**$C_{16}H_{32}$**
3	5.2	83.6	2.0	9.2
4	6.3	76.8	5.6	11.3
5	ND	90.8	ND	9.2
6	ND	88.8	ND	11.2

Exp 3, 4: performed at 350°C and 30 min in static and respectively stirred conditions.
Exp 5, 6: performed at 400°C and 0 min in static and respectively stirred conditions.
ND: not detected.

Table 4: Hydrocarbon fraction composition (%w/w) for experiments conducted at 350°C and 30 min and 400°C, 0 min in static and stirred reactor configuration.

Exp	BC										SR										
	Elemental Analyses									HHV (MJ/kg)	Elemental Analyses									HHV (MJ/kg)	Organic fraction (% w/w)
	(% w/w)					(mol ratios)					(% w/w)					(mol ratios)					
	C	H	N	S	O[a]	H/C	O/C	N/C	S/C		C	H	N	S	O[a]	H/C	O/C	N/C	S/C		
3	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
4	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
5	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
6	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] Percentage calculate by difference using equation (2)

Exp 3, 4: performed at 350°C and 30 min in static and respectively stirred conditions.

Exp 5, 6: performed at 400°C and 0 min in static and respectively stirred conditions.

Table 5: Elemental analyses of produced BC and SR

Exp	**mol % of produced gas phase**					
	CH_4	**C_2H_4**	**C_2H_6**	**CO_2**	**CO**	**H_2**
3	7.9	2.1	2.1	72.8	8.5	6.6
4	1.5	0.4	0.4	92.1	2.2	3.4
5	9.3	1.8	2.6	65.6	11.8	8.9
6	0.1	0.1	<0.1	98.3	1.0	0.5

Exp 3, 4: performed at 350°C and 30 min in static and stirred conditions respectively.
Exp 5, 6: performed at 400°C and 0 min in static and stirred conditions respectively.

Table 6: Gas phase composition. CH_4, C_2H_4, C_2H_6, CO_2, CO and H_2 mol % produced

2.2. 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.

As a consequence of 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 hydrothermal conversion process [9]. 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 [47, 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.

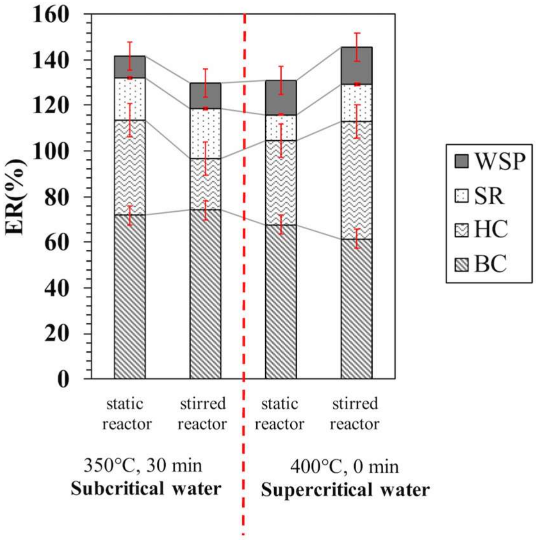

Figure 3: Energy recovery distribution for experiments conducted with MS at different fluid dynamics conditions.

3. 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

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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] 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

[7] 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

[8] Gherghel, A., Teodosiu, C., De Gisi, S., J. Clean. Prod., A review on wastewater sludge valorization and its challenges in the context of circular economy, 2019, 228, 244-263. https://doi.org/10.1016/j.jclepro.2019.04.240

[9] 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

[10] 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

[11] 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

[12] 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

[13] 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

[14] 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

[15] 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

[16] 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

[17] 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

[18] 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

[19] 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

[20] 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

[21] 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

[22] 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

[23] 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

[24] 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

[25] Huang, H.J., Yuan X. Z., Bioresour. Technol., The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge, 2016, 200, 991-998. http://dx.doi.org/10.1016/j.biortech.2015.10.099

[26] 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

[27] 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

[28] 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

[29] 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.

[30] 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

[31] 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

[32] 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

[33] 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

[34] 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

[35] 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

[36] 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

[37] 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.

[38] 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

[39] 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

[40] 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

[41] 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

[42] 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

[43] 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

[44] 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

[45] 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

[46] 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

[47] 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

[48] 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

[49] 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

[50] 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

[51] 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

[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] 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

[56] 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

[57] 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

[58] 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

[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