Valorisation of digestate through hydrothermal carbonization (HTC): a preliminary characterization of derived gaseous, liquid, and solid products

V. Benedetti[1], M. Pecchi[1], S. Celletti[1], D. Basso[1,2], F. Patuzzi[1], T. Mimmo[1], S. Cesco[1], M. Baratieri[1]

[1] Faculty of Science and Technology, Free University of Bolzano, piazza Università 5, 39100 Bolzano, Italy.
[2] HBI srl, via Volta 13, 39100 Bolzano, Italy
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Presenting author email: vittoria.benedetti@unibz.it

Anaerobic digestion is a biological process during which methanogenic bacteria convert organic matter into a gas rich in methane and carbon dioxide, in an oxygen-free environment. The gas, also called biogas, is commonly exploited for energetic purposes (Rajendran and Murthy, 2019).

One of the most relevant drawback of anaerobic digestion is associated to the management of digestate, the main by-product of the process. Although digestate, is commonly used as a fertilizing substrate and spread in fields, it may not fulfil the parameters established by legislation for land-spread disposal and nitrate load, depending on the raw material used to feed the digestor. In such cases, it must be disposed of as a waste with relevant economic and environmental costs (Timonen at al., 2019). In particular, it has emerged that digestate produced from agricultural residues can be successfully used as a fertilizer, while digestate produced from other raw materials, such as sewage or industrial sludge, can be dangerous and hazardous.

Moreover, due to its high moisture-content, digestate may not be suitable for treatment with conventional thermochemical processes (i.e. combustion, pyrolysis, gasification) which would require a preliminary cost- and energy-intensive drying step.

For this reasons, the scientific community is currently investigating innovative and efficient approaches for the management of digestate. Among the novelties proposed, hydrothermal treatments are emerging due to their ability to directly handle high-moisture feedstocks and convert it into valuable products.

In particular, hydrothermal carbonization (HTC), is a thermochemical conversion process able to directly treat wet substrates with reduced process efforts, which allows for the recovery of macro- and micro-nutrients (Pecchi and Baratieri, 2019).

This study, part of the project HB Ponics (EFRE-FESR 2014-2020), aims at evaluating the HTC process applied to digestate and characterizing the derived gaseous, liquid (AHL, aqueous HTC liquids) and solid (HC, hydrochar) in order to identify other possible routes for an overall valorisation of the process.

The digestate used as feedstock was taken from an aerobic digester fed with cattle manure and agricultural residues. During each test, about 2.5 L of digestate were subjected to HTC in a 4-litre stainless steel (AISI 316) batch reactor provided by the Italian company HBI srl. The HTC tests were performed at 180, 220 and 250 °C for a residence time of 3 hours to investigate the influence of temperature on the physico-chemical properties of the products. Each experiment was repeated three times to ensure the validity of the results. Gaseous products were collected in gas bags and the composition in terms of CO_2, CO, CH_4, H_2, was analysed off-line by a gas chromatograph (μGC 490, Agilent) equipped with a CP-Molesive 5Å and a PoraPLOT-U column. The obtained hydrochar was dried in an oven for 24 hours at 105 °C, while the liquid product was extracted and stored in a refrigerator at 4 °C. Later, AHL was filtered to remove any remaining hydrochar.

Hydrochar was characterised by ash content (UNI EN 14775:2010), calorific value (calorimeter IKA C200), elemental (analyser Elemental Vario Macro Cube), physisorption (3Flex, Micromeritics) and thermogravimetric analysis (STA 449 F1 Jupiter, Netzsch). The AHL samples were characterised by Total Organic Carbon (TOC) analysis (Shimadzu TOC-V analyser). Moreover, the analysis of the concentration of glucose, lactic acid, formic acid, acetic acid, fumaric acid, hydroxymethylfurfural (HMF), and furfural was determined by High Performance Liquid Chromatography (HPLC), equipped with a cation exchange column Aminex 87-H column (300×7.8 mm, 9 μm, Bio-Rad) and an isocratic elution with 10 mM H_2SO_4 as carrier solution at a flow rate of 0.6 mL/min.

As shown in Table 1, the gas produced during HTC was mainly composed of CO_2 with small amounts of CH_4, CO and H_2. The concentration of CO_2, CH_4 and H_2 increased with temperature due to the increased severity of the reaction, while CO reached a maximum at 200°C.

Table 1: Composition of gaseous products obtained after HTC at 180, 220 and 250 °C for 3 hours

Temperature	CO_2 %	H_2 %	CH_4 %	CO %
180 °C	65.49	0.04	0.26	0.12
220 °C	68.40	0.16	0.41	0.36
250 °C	79.18	0.35	0.70	0.30

According to the results reported in Table 2, the hydrochar obtained at 250 °C featured higher ash content, but the HHV was significantly higher (18.10 MJ/kg), especially if compared to digestate (14.31 MJ/kg). This makes it more suitable for use as biofuel. The carbonization process was also more evident for HC 250, as the C content increased with HTC temperature and O and H weight percentages decreased, due to dehydration and decarboxylation reactions.

Table 2: Composition and HHV of dried HC and carbon content of AHL obtained after HTC at 180, 220 and 250 °C for 3 hours

	Ash [%wt]	HHV [MJ/kg]	C [%wt]	H [%wt]	O [%wt]	N [%wt]	S [%wt]	TOC [g/l]
HC 180	27.76	16.11	40.14	5.01	24.09	2.03	0.71	-
HC 220	29.79	16.70	42.53	4.92	19.71	2.16	0.62	-
HC 250	34.68	18.10	45.03	4.54	12.35	2.59	0.59	-
AHL 180	-	-	-	-	-	-	-	7.06
AHL 220	-	-	-	-	-	-	-	7.42
AHL 250	-	-	-	-	-	-	-	7.89

Concerning AHL composition, results in Table 3 show that lactic acid concentration gradually increased with increasing temperature while glucose, HMF and furfural concentration gradually decreased. Formic acid, acetic acid, and fumaric acid concentration reached a maximum at 220°C.

Table 3: Composition of AHL obtained after HTC at 180, 220 and 250 °C for 3 hours

[mg/L]	Glucose	Lactic acid	Formic acid	Acetic acid	Fumaric acid	HMF	Furfural
AHL 180	695.07	9.19	338.86	349.14	46.31	n.d	4.87
AHL 220	603.78	990.42	1520.54	781.81	79.00	2.74	4.30
AHL 250	571.61	1371.93	502.13	379.94	7.75	1.99	n.d.

The detailed characterization of HTC products carried out in this study represent a useful starting point to understand how to tune up and optimize HTC process conditions to obtain products with the desired characteristics. For instance, when the aim is the production of a HC with a high HHV to be employed for energetic purposes, higher HTC temperatures would be preferred; the same when more lactic acid is desired to be recovered. On the other hand, for recovery of acetic acid, a temperature of 220°C should be considered.

Founding

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References

M. Pecchi, M. Baratieri, Coupling anaerobic digestion with gasification, pyrolysis or hydrothermal carbonization: A review, Renew. Sustain. Energy Rev. 105 (2019) 462–475. doi:10.1016/j.rser.2019.02.003.

K. Rajendran, G.S. Murthy, Techno-economic and life cycle assessments of anaerobic digestion – A review, Biocatal. Agric. Biotechnol. 20 (2019) 101207. doi:10.1016/j.bcab.2019.101207.

K. Timonen, T. Sinkko, S. Luostarinen, E. Tampio, K. Joensuu, LCA of anaerobic digestion: Emission allocation for energy and digestate, J. Clean. Prod. (2019). doi:10.1016/j.jclepro.2019.06.085.