Integration of hydrothermal carbonization and anaerobic digestion for energy and nutrient recovery of the valorization of swine manure

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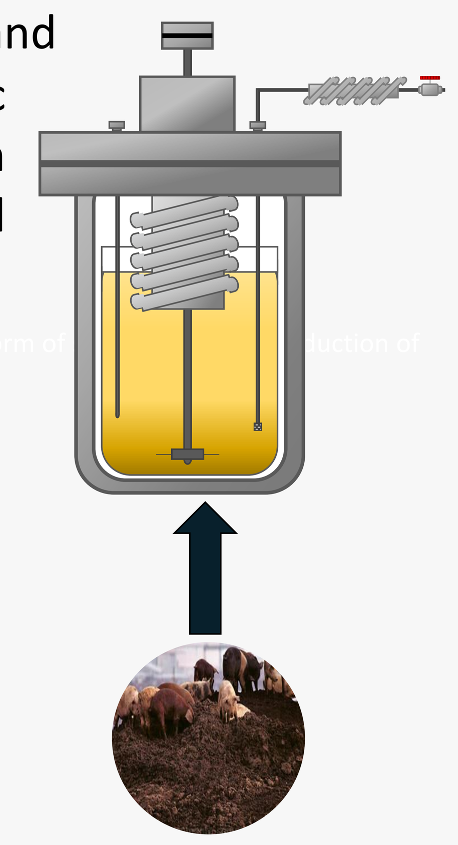
INTRODUCTION

Hydrothermal carbonization (HTC) is a novel process able to treat wet biomass under mild temperatures (180 – 250 °C), low residence time (5 – 120 min) and autogenous pressure. The main product of HTC is a carbonaceous solid called hydrochar (HC), with suitable properties to be used as biofuel and liquid fraction called process water (PW) rich in organic compounds and nutrients. The HC shows higher carbon content, heating value (HHV), combustion behavior and reactivity, which gives it a high potential use as a biofuel.

On other hand, PW appears as a potential source of energy resource by anaerobic digestion (AD) as well as a valuable source of nutrients (especially N and P), in terms of the circular economy.

The present work studies the co-HTC of swine manure (SM) and garden and park waste (GPW) to obtain a HC with suitable characteristics to be used as an alternative biofuel, while the PW can be valorized by nutrient recovery and anaerobic digestion in an approach to the circular economy concept.



METHODS AND MATERIALS

HTC tests were performed in an electrically heated 4 L ZipperClave® pressure vessel loaded with 1.5 kg of SM. The HTC degree was improved with the addition of HCl 0.1-1 M as catalyst at 180 ºC and 1 h. The resulting HC and PW from HTC-A were identified as HC-A or PW-A, respectively, followed by corresponding acid concentration. The HC obtained at 180 ºC was subjected to a washing process (HC-180-W). Two grams of HC were washed for 2 h with 20 mL of: i) a solution 5 M of HCl (HC labelled as HC-180-Wa) or ii) 20, 50 or 75% (v:v) of acetone (HCs labelled as HC-180-Wb followed by acetone concentration). The HCs were evaluated regarding HHV, N, S, and volatile matter (VM) content (HHV > 17 MJ kg^{-1}; N<3 %; S<0.5 %; and VM<75 %) according ISO/TS 17225-8 (2016). PW were valorized through nutrients recovery and AD. To promote struvite formation Mg^{2+} were add in PW in form of $MgCl_2$ and $Mg(OH)_2$ and neutralized until pH 9. The PWs obtained after nutrients precipitation were labeled as PW-S. The PW recovered and unrecovered nutrients were subjected to anaerobic digestion for biogas production and organic matter removal.

RESULTS AND DISCUSSION

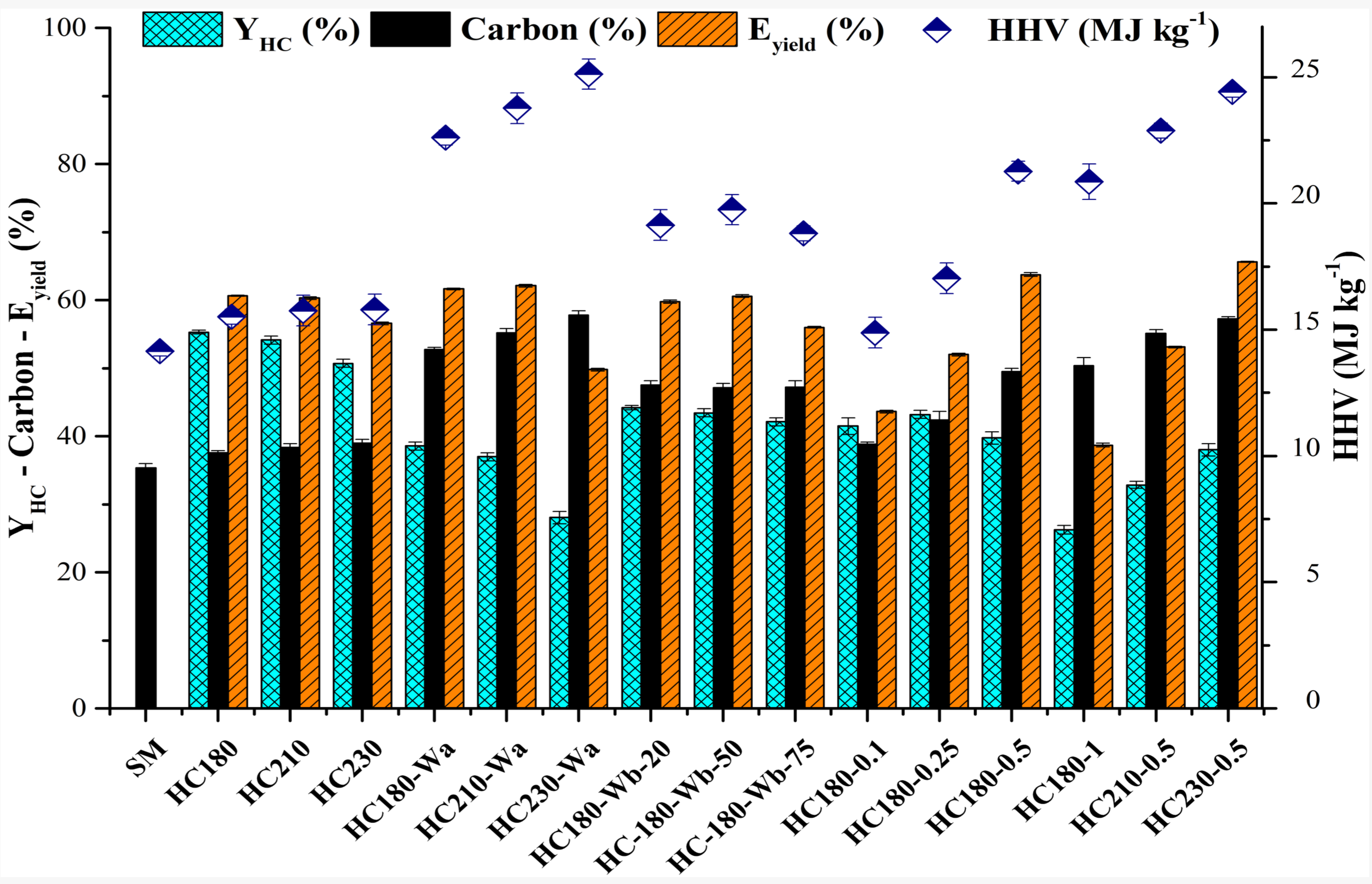
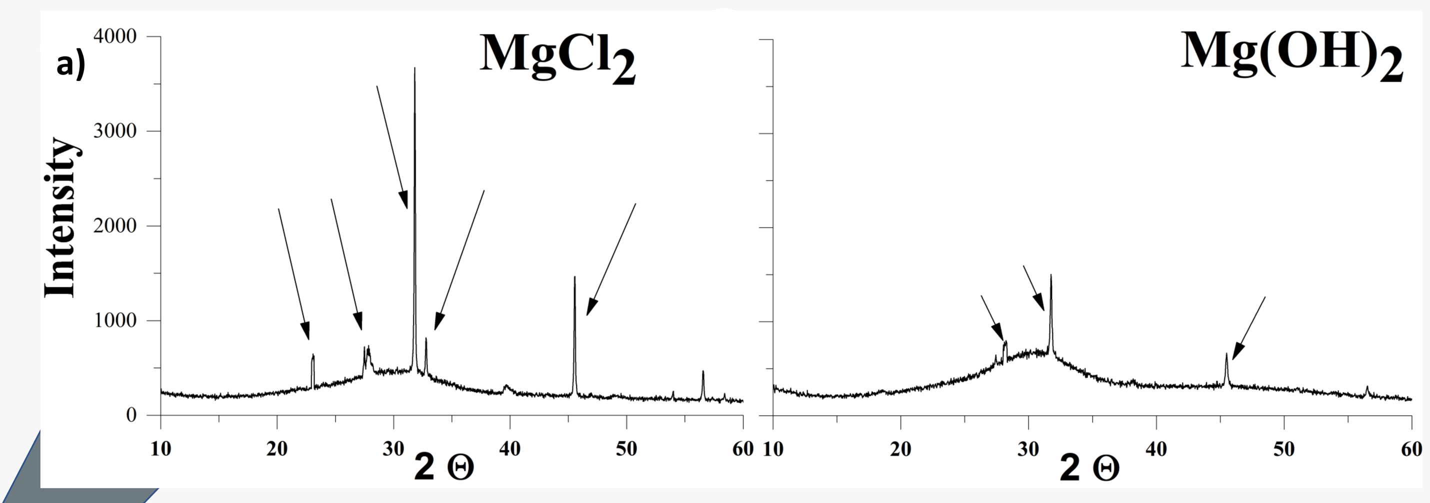
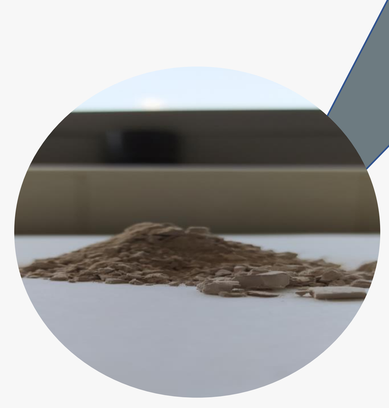


Figure 1. Energy characteristics of HC, HC-W and HC-A

Table 1. Process water characterization

	PW180	PW210	PW230	PW180-0.1	PW180-0.25	PW180-0.5	PW180-1.0	PW210-0.5	PW230-0.5	PW180-S	PW180-0.5-S
pH	8.6±0.1	9.3±0.1	9.2±0.1	6.2±0.1	5.4±0.1	2.8±0.1	1.1±0.1	2.6±0.1	2.9±0.1	9.2±0.1	9.1±0.1
TS (g L^{-1})	24.0±0.2	21.7±0.7	18.9±0.6	27.1±0.2	32.8±0.2	38.4±0.1	68.9±0.4	37.7±0.3	37.0±0.2	18.6±0.2	29.6±0.4
VS (g L^{-1})	18.3±0.1	15.0±0.7	12.1±0.2	20.3±0.2	23.7±0.1	24.7±0.1	43.8±0.2	25.6±0.2	24.5±0.1	15.6±0.2	22.5±0.5
TCOD (g L^{-1})	30.5±1.2	27.3±0.2	27.8±0.6	29.2±0.4	24.8±0.4	28.4±0.9	29.2±0.8	33.3±0.8	33.8±0.6	23.5±0.3	21.3±0.2
TOC (g L^{-1})	9.6±0.1	9.2±0.1	9.1±0.1	7.5±0.1	8.1±0.1	9.0±0.1	8.2±0.1	8.8±0.1	8.3±0.1	6.2±0.2	4.9±0.1
TVFA (g acetic acid L^{-1})	1.8±0.1	2.0±0.1	1.9±0.1	1.9±0.2	1.6±0.1	1.7±0.3	1.5±0.2	1.8±0.1	1.7±0.1	1.1±0.1	0.9±0.1
P-PO_4^{3-} (mg L^{-1})	15.6±0.1	12.7±0.1	10.6±0.1	112.6±0.5	125.5±0.2	116.5±0.7	147.6±0.1	74.7±0.1	71.9±0.2	0.6±0.1	3.7±0.1
TKN (g L^{-1})	1.7±0.1	2.1±0.2	1.9±0.1	3.1±0.1	3.9±0.1	3.5±0.1	3.9±0.1	3.7±0.1	3.7±0.1	0.8±0.0	1.0±0.1
N-NH_4 (g L^{-1})	1.1±0.1	1.6±0.1	1.4±0.1	2.4±0.1	3.3±0.1	3.4±0.1	3.8±0.1	3.8±0.1	3.7±0.1	0.6±0.0	0.9±0.1
N-Org. (g L^{-1})	0.6±0.1	0.5±0.1	0.5±0.1	0.7±0.1	0.6±0.1	0.1±0.0	0.1±0.0	0.1±0.0	0.0±0.0	0.2±0.0	0.1±0.1
Cl^- (mg L^{-1})	147±1.0	162±1.0	169.1±1.0	732.1±1.0	942.7±1.0	1357.9±1.0	2998.1±1.0	1674.6±1.0	1640.5±1.0	84.7±1.0	626.4±1.0
Y_{PW} (%)	82.5±2.1	81.0±4.1	80.4±1.6	81.0±2.3	79.0±2.0	73.5±3.1	83.5±1.3	74.7±2.0	78.8±1.0	-	-





b) Minerals metals (g kg^{-1})	Al	Ca	Fe	K	Mg	Na	P
$MgCl_2$	1.0	6.6	2.0	4.5	133.0	1.1	167.3
$Mg(OH)_2$	1.0	19.0	1.3	3.7	67.4	0.7	41.8
Heavy metals (mg kg^{-1})	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
$MgCl_2$	1.34	2.64	59.93	2.23	43.92	21.24	114.17
$Mg(OH)_2$	0.78	1.75	46.17	1.23	22.53	12.52	28.05

Figure 2. Analysis of solid recovered from PW: a) 2-theta XRD graph b) mineral and heavy metals content

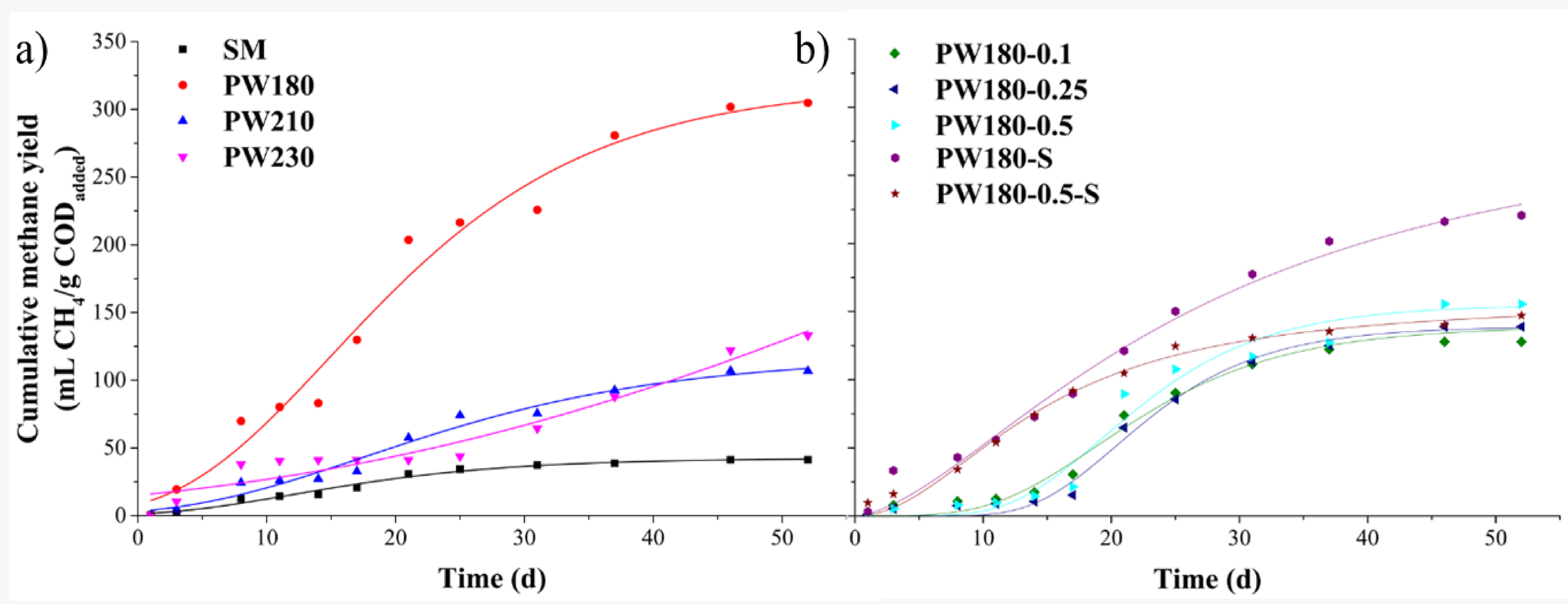


Figure 3. Cumulative methane production a) PW from HTC b) PW from HTC-A and nutrients recovery. Symbols represent experimental values and solid lines indicate theoretical value

CONCLUSIONS

- HC washed (HC-Wa and HC-Wb) and HC-A (an exception of HC-180-0.5 and HC230-0.5) are upgraded carbonaceous material with HHV 18 – 25 MJ kg^{-1} as well as low N, S, and ash contents, suitable for combustion according to ISO 17225-8, being acetone washing the most effective in N, S, and ash removal as well as heavy metals.
- The addition of acid to reaction promote up to 75% the solubilization of phosphorus content in SM to the PW, however, plain HTC of SM retained up to 85% of the phosphorus in the HC.
- The structure of the recovered solid presents peaks belonging to struvite, but also other peaks that could be related to the presence of other salts such as apatite or hydroxyapatite, being $MgCl_2$ which allowed to obtain the highest amount of P and other minerals in the struvite.
- Both solid precipitated had minimum heavy metals content according to ecological criteria for the award of the EU Ecolabel for growing media, soil improvers and mulch Decree No. 2015/2099 (European Parliament, 2015)
- Biomethane potential shows that highest methane yield (≈ 310 mL CH_4/g COD_{added}) was obtained with the PW at lowest temperature (PW180) without acid assistant. The increase of HTC temperature, the addition of acid or the neutralization step produced a stressing effect on anaerobic microorganisms reducing their methane production by up to 50%. Anaerobic digestion removed 40 – 60% of organic matter in PW.