Improving hydrochar properties from hydrothermal carbonization of swine manure by recirculation of process water

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Keywords: continuous HTC reactor, hydrochar, hydrothermal carbonization, process water recycle, swine manure.

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***Abstract**: Hydrothermal carbonization allows treating organic wastes, such as swine manure, into a carbonaceous solid with high energy density and better characteristics for use as solid biofuel. Recirculation of process water as a reaction medium increased the hydrochar mass yield, as well as the C content, fixed carbon and higher heating value. The process water was enriched in organic matter and nitrogen-containing compounds in each recirculation cycle, while a decrease in phosphorus content was observed.*

Introduction

Hydrothermal carbonization (HTC) has been stablished as a promise technology to transform biomass waste with high moisture content into a solid biofuel called hydrochar highly appreciated by the high carbon (C) content, fixed carbon (FC), better energy density and higher heating value (HHV), as well improved combustion performance and stability providing to hydrochar with suitable characteristics to energy purposes. This process implies the use of water in subcritical conditions, thus is not mandatory to pre-drying feedstock such as other thermochemical process such as pyrolysis, gasification or incineration (Taskin et al., 2019). The presence of water improves the hydrolysis of less thermal stable organic matter such as volatile matter (VM), as well as the remove of nitrogen, sulfur organic compounds as well solubilization of inorganic compounds into the process water. The soluble molecules obtained in the hydrolysis stage help in the subsequent dehydration and decarboxylation reactions of the initial solid, improving the degree of carbonization of the hydrochar, as well as the energy density and biofuel properties.

Materials and methods

The HTC runs were performed in a continuously operating pilot plant developed in collaboration between the Department of Chemical Engineering of the Autonomous University of Madrid and the company Arquimea (Arquimea, 2023). The reactor, made of stainless steel with a nominal radius of 6 cm and a length of 200 cm, uses a screw pump for the movement of the feedstock. The facility is equipped with an agitation mechanism to prevent solids settling and is divided into five zones, including preheating and reaction sections. External electric resistance heaters and gate valves regulate the temperature, and the resulting wet hydrochar is collected in a cyclone vessel, while water deon process water directed to a storage tank. The first tests were conducted with swine manure (SM) mixed with tap water up to 5% total solids content (TS), at reaction temperatures of 210 °C and 250 °C and with a residence time of 45 min. The following HTC cycles were carried out with the process water obtained in the previous cycle under the same operating conditions.

Results and discussion

The treatment of SM by HTC demonstrated significant improvements in C (4 – 8%) and FC (8 – 10%) content and HHV (2 – 12%), along with a notable reduction in nitrogen, sulfur, and ash content (Table 1). However, the hydrothermal process significantly diminished the mass yield (Y_{HC}) by 21 – 51 wt.%. As expected, high temperature reactions showed greater energy densification. Continuous recycling of process water led to a progressive enhancement of hydrochar characteristics. The most substantial change was observed in the hydrochar mass yield, increasing from 51% and 21% to 82% and 55% at 210 ºC and 250 ºC respectively, over four cycles of process water recycling. The first recycling cycle showed the greatest Y_{HC} increase, while subsequent cycles exhibited a more modest rise. Water recycling also improved the characteristics of subsequent hydrochars, where parameters such as FC, C content and HHV did not show considerable increases. Process water recycling improved the dehydration and decarboxylation reactions, evident in decreasing H/C and O/C ratios in each recycling cycle up to 1.24 and 0.57 and 1.14 and 0.53 at 210 ºC and 250 ºC, respectively. Hydrochars exhibited lignite-like characteristics and fulfilled the ISO/TS 17225-8 standard for graded thermally treated and densified biomass fuels (HHV > 17 MJ kg^{-1}, VM < 75 wt.%, N < 3 wt.%, S < 0.5 wt.%, and ash < 10 wt.%).

Table 1. Main characteristics of swine manure and hydrochars.

	SM	HC210	HC210-C1	HC210-C2	HC210-C3	HC210-C4	HC250	HC250-C1	HC250-C2	HC250-C3	HC250-C4
Y_{HC} (%)	-	50.7 (1.3)^a	78.1 (1.0)^b	75.9 (1.7)^b	77.7 (2.4)^b	82.1 (3.8)^c	20.7 (2.5)^a	41.9 (0.8)^b	48.0 (1.3)^c	56.2 (1.0)^d	54.6 (3.0)^d
FC (%)	13.4 (0.2)	21.2 (0.2)^a	19.7 (0.2)^b	23.1 (0.1)^c	21.9 (0.3)^{a,b}	23.2 (0.3)^d	23.2 (0.2)^a	25.3 (0.2)^b	25.5 (0.2)^b	26.3 (0.2)^c	22.4 (0.3)^d
VM (%)	76.2 (0.4)	75.0 (0.2)^a	73.6 (0.3)^b	71.8 (0.2)^c	71.0 (0.2)^c	71.5 (0.4)^c	72.9 (0.3)^a	66.3 (0.2)^b	66.9 (0.3)^b	65.2 (0.4)^c	66.4 (0.2)^b
Ash (%)	10.4 (0.3)	3.7 (0.2)^a	6.7 (0.2)^b	5.1 (0.3)^c	7.1 (0.3)^b	5.3 (0.1)^c	3.9 (0.1)^a	8.4 (0.1)^b	7.6 (0.2)^c	8.5 (0.3)^b	11.2 (0.3)^d
C (%)	44.4 (0.3)	47.5 (0.5)^a	50.1 (0.2)^b	50.8 (0.3)^c	51.5 (0.3)^c	52.2 (0.2)^d	51.7 (0.2)^a	53.0 (0.2)^b	53.9 (0.1)^c	53.8 (0.3)^c	54.2 (0.3)^d
N (%)	1.5 (0.1)	1.2 (0.2)^a	1.6 (0.0)	1.8 (0.1)	2.0 (0.0)	2.0 (0.1)	1.2 (0.0)^a	1.5 (0.1)^b	1.8 (0.1)^c	1.8 (0.1)^c	1.6 (0.0)^{b,c}
S (%)	0.6 (0.1)	0.3 (0.1)^a	0.4 (0.0)^a	0.4 (0.0)^a	0.5 (0.0)^b	0.5 (0.0)^b	0.4 (0.0)^a	0.5 (0.0)^a	0.5 (0.0)^a	0.5 (0.0)^a	0.4 (0.0)^a
H/C	1.50	1.44	1.34	1.28	1.26	1.24	1.36	1.23	1.18	1.15	1.14
O/C	0.64	0.72	0.63	0.61	0.59	0.57	0.59	0.56	0.53	0.54	0.53
HHV (MJ kg^{-1})	18.5 (0.3)	18.9 (0.2)^a	19.6 (0.2)^b	19.8 (0.2)^b	20.2 (0.1)^c	20.4 (0.2)^c	20.7 (0.6)^a	20.8 (0.2)^a	21.0 (0.3)^b	20.7 (0.2)^a	21.1 (0.2)^b
E_{yield} (%)	-	51.9 (0.4)^a	56.5 (0.6)^b	58.8 (0.8)^c	64.5 (1.2)^d	70.5 (1.5)^e	23.2 (1.4)^a	33.7 (0.6)^b	38.1 (0.6)^c	46.0 (0.4)^d	45.6 (0.9)^d

The changes in hydrochar characteristics are primarily attributed to process water, where solubilized molecules (which are thermally less stable) are transferred to the liquid fraction along with mineral salts and nutrients. Table 2 shows the main characteristic of the process water. The pH of the process waters was acidic (<5), attributed to the presence of short-chain acids, such as acetic acid. The organic matter content is high as shown by the SCOD (10 - 40 g L-1) and TOC (6 - 31 g L-1) values. Process water recycling shows a gradual increase in organic matter content in the liquid fraction, unlike hydrochar, where statistically significant changes were no longer observed in certain characteristics. The highest temperature tested (250 ºC) exhibited a greater migration of organic compounds from feedstock to the liquid fraction, with higher SCOD and TOC values in all cases compared to the lower temperature tested (210 ºC). This same trend is observed in total nitrogen (TN: 189 – 863 mg L^{-1}) and ammoniacal nitrogen (N-NH_4: 98 – 323 mg L^{-1}) content, gradually increasing with reaction temperature and process water recycling cycles. This indicates an accumulation of organic and nitrogenous matter in process water. However, it is worth noting that more than half of the TN belongs to organic nitrogen (proteins and amino acids solubilized into the process water). The P content as PO_4-P contradicts the accumulation of organic and nitrogenous matter. This may be due to the high reactivity of PO_4^{3-} with ions such as Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} present in SM, which also accumulate with process water recycling cycles, evident in the increase in conductivity.

Table 2. Main characteristics of process water.

	PW210	**PW210-C1**	**PW210-C2**	**PW210-C3**	**PW210-C4**	**PW250**	**PW250-C1**	**PW250-C2**	**PW250-C3**	**PW250-C4**
pH	4.5 (0.1)^{a}	4.6 (0.1)^{a}	4.3 (0.1)^{b}	4.0 (0.1)^{b}	4.1 (0.1)^{b}	4.2 (0.1)^{a}	4.4 (0.1)^{b}	4.3 (0.1)^{a,b}	4.4 (0.1)^{b}	4.4 (0.1)^{b}
TS (g L^{-1})	6.8 (1.0)^{a}	10.3 (1.3)^{b}	13.4 (0.7)^{c}	17.3 (0.7)^{d}	20.0 (0.8)^{e}	9.6 (0.6)^{a}	11.3 (0.3)^{b}	12.8 (0.9)^{c}	14.1 (1.6)^{c}	16.2 (0.7)^{d}
VS (g L^{-1})	6.0 (0.7)^{a}	9.3 (1.1)^{b}	11.6 (0.8)^{c}	15.4 (0.7)^{d}	18.6 (0.2)^{e}	7.8 (0.4)^{a}	10.0 (0.2)^{b}	10.9 (1.0)^{c}	13.2 (0.9)^{c}	14.4 (0.3)^{d}
SCOD (g L^{-1})	10.2 (0.5)^{a}	12.1 (1.6)^{a}	20.4 (0.4)^{b}	28.4 (0.8)^{c}	32.3 (0.5)^{d}	12.5 (0.8)^{a}	19.0 (0.7)^{b}	23.5 (0.3)^{c}	29.6 (0.5)^{c}	37.9 (0.3)^{c}
TOC (g L^{-1})	6.4 (0.0)^{a}	9.1 (0.2)^{b}	16.2 (0.3)^{c}	20.3 (0.5)^{d}	25.2 (0.8)^{e}	10.3 (0.6)^{a}	16.4 (0.6)^{b}	20.6 (0.4)^{c}	25.7 (0.7)^{d}	30.8 (0.6)^{e}
PO_4-P(mg L^{-1})	69.4 (2.7)^{a}	100.5 (1.0)^{b}	92.5 (2.5)^{c}	86.3 (3.3)^{d}	73.9 (1.3)^{e}	81.9 (0.5)^{a}	159.5 (2.4)^{b}	86.3 (2.0)^{c}	129.6 (0.4)^{d}	149.8 (0.9)^{e}
TN (mg L^{-1})	189.1 (3.9)^{a}	335.8 (6.9)^{b}	455.8 (5.9)^{c}	540.0 (12.6)^{d}	623.4 (14.6)^{e}	287.6 (12.8)^{a}	439.2 (6.3)^{b}	655.0 (5.8)^{c}	863.0 (5.4)^{d}	859.2 (8.6)^{d}
NH_4-N (mg L^{-1})	98.0 (1.6)^{a}	274.8 (2.9)^{b}	161.0 (4.5)^{c}	145.6 (1.5)^{d}	191.8 (4.3)^{e}	163.8 (0.9)^{a}	284.2 (7.3)^{b}	303.8 (10.1)^{c}	323.4 (3.4)^{d}	272.4 (6.1)^{b}
Conductivity (ms cm^{-1})	1.3 (0.2)^{a}	1.1 (0.1)^{b}	1.4 (0.1)^{c}	1.7 (0.0)^{c}	1.9 (0.1)^{d}	1.2 (0.2)^{a}	1.1 (0.2)^{b}	2.9 (0.1)^{c}	2.8 (0.0)^{d}	3.2 (0.1)^{e}

Conclusions

Hydrothermal carbonization has proven to be an effective process for converting swine manure into a value-added carbonaceous solid. The continuous reactor facilitates a significant enhancement of the swine manure characteristics. Additionally, process water recycling further improved hydrochar properties and notably increased the hydrochar mass yield. The use of a continuous HTC reactor represents an advance that could contribute to a better management and utilization of swine manure to obtain a carbonaceous solid with suitable characteristics for industrial use as biofuel. In addition, the liquid fraction could be used for the recovery of nutrients such as P and N, or by anaerobic treatment to eliminate the organic load and produce methane-rich biogas, closing the cycle in the use of swine manure in a circular economy framework.

Acknowledgements

Authors greatly appreciate funding from Spain's MICINN (PID2019-108445RB-I00), MINECO (PDC2021-120755-I00 and TED2021-130287B-I00), Madrid Regional Government (Project S2018/EMT-4344) and Grupo Kerbest Company. R.P. Ipiales acknowledges financial support from Community of Madrid (IND2019/AMB-17092) and Arquimea Agrotech Company.

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