Valorization of swine manure by hydrothermal carbonization

R.P. Ipiales[1,2], M.A. de la Rubia[1], E. Díaz-Portuondo[2], E. Díaz[1], A.F. Mohedano[1]
[1]Chemical Engineering Department, Universidad Autónoma de Madrid, 28049, Spain
[2]Arquimea-Agrotech, Collado Villalba, Madrid, 28400, Spain

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Presenting author email: ricardo.ipiales@estudiante.uam.es

Abstract: *In this study, two alternatives for treating swine manure by hydrothermal carbonization are analyzed. The first involves the use of raw swine manure, while the second involves the treatment of the solid fraction of swine manure, subsequently mixed with water. The difference between these two substrates lies in the fact that the liquid fraction contained a high content of salts and solid particles, which negatively affected the characteristics of the solid fraction of the manure. The hydrothermal treatment was carried out in a continuous flow tubular reactor at three temperatures: 210, 230 and 250 ºC, with a residence time of 45 minutes. After the hydrothermal process, both hydrocarbons presented improved properties, showing their potential for use as biofuel and, in most cases, fulfilling the criteria for solid biofuels.*

Introduction

Swine manure (SM) management is one of the major challenges on pig farms. Traditionally, SM contains only 10 wt.% of total solids. This solid fraction is usually composted for use as a source of organic matter and nutrients that are returned to agricultural soils. On the other hand, the treatment of the liquid fraction presents problems due to its high nitrogen and mineral content, high organic load and low C/N ratio. An alternative is the treatment of SM by hydrothermal carbonization (HTC) to obtain a carbonaceous solid, known as hydrochar. Hydrochar has a high C content, fixed carbon (FC) and higher heating value (HHV). This process, carried out under subcritical water conditions, does not require pre-drying the feedstock (Marin-Batista et al., 2020). The presence of water enhances the transfer of thermally less stable compounds, and facilitates the removal of N, S, solubilization of inorganic compounds in the process water, as well as eliminates pathogenic microorganisms, ensuring that HTC products are safe and free of harmful contaminants. The aim of this work is to study the optimal approach for the proper management of swine manure to obtain added-value products.

Materials and methods

The HTC runs were performed in a continuous reactor at pilot plant scale was developed collaboratively by the Chemical Engineering Department of Autonomous University of Madrid and Arquimea company (Arquimea, 2023). Two different swine manure were evaluated: i) the use of raw swine manure (SMr) without any pre-treatment or separation, and ii) the utilization of the solid fraction of swine manure (SMs) previously separated by centrifugation. The main characteristics of both swine manure are enlisted in the Table 1. The continuous HTC reactor, constructed from stainless steel with a 6 cm nominal radius and 200 cm length, employs a screw pump for substrate movement. It incorporates a stirring mechanism to prevent solid decantation and is segmented into five zones, including preheating and reaction sections. Temperature regulation is facilitated by external electrical resistance heaters and gate valves. The resulting wet hydrochar is collected in a cyclone vessel, while process water is directed to a storage tank. Experiments with crude SM or the solid fraction of SM mixed with tap water were carried out with a total solids content of 5%. Runs were performed at three different temperatures (210, 230 and 250 ºC) with a residence time of 45 min.

Results and discussion

The two types of SM showed significantly different characteristics (Table 1). The raw SM generally exhibited unfavorable properties for potential use as a biofuel, due to the low C content, HHV and high N, S and ash content. Separation of the solid fraction of the manure resulted in a lower ash content (~11 wt.%) compared to untreated raw swine manure (~21 wt.%). SSM showed a higher C content, up to 10 percentage points (p.p.) higher than RSM. However, the RSM showed a significant nutrient content, especially phosphorus (37.1 g kg^{-1}), which is around 6-fold higher than that of the SSM. Other nutrients, such as K, Ca and Mg, as well as heavy metals also followed the same trend.

Table 1. Main characteristics of raw swine manure (RSM) and the solid fraction of swine manure (SSM).

	FC (%)	VM (%)	Ash (%)	C (%)	N (%)	S (%)	H/C	O/C	HHV (MJ kg^{-1})
RSM	14.5 (0.2)	64.5 (0.3)	21.0 (0.2)	35.3 (0.3)	2.3 (0.1)	0.4 (0.0)	1.58	0.77	13.9 (0.2)
SSM	13.7 (0.2)	75.8 (0.1)	10.5 (0.1)	45.0 (0.4)	1.4 (0.0)	0.5 (0.0)	1.52	0.62	18.5 (0.2)
Mineral elements (g kg^{-1})	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Na**	**P**		
RSM	0.9 (0.1)	33.2 (1.2)	1.3 (0.1)	17.0 (0.4)	7.7 (0.2)	8.7 (0.2)	37.1 (0.2)		
SSM	0.5 (0.0)	15.4 (0.8)	1.0 (0.1)	4.0 (0.3)	2.5 (0.3)	1.4 (0.2)	6.7 (0.4)		

Table 2 shows the main characteristics of hydrochars from raw swine manure (RHC) and solid fraction of swine manure (SHC). After the hydrothermal process, a remarkable improvement in the characteristics of all hydrochars was observed, although there are some specific differences between both materials. One of the most significant changes was observed in the proximate analysis, where SHC showed a substantial increase in FC content (7 - 10 p.p.) and a significant decrease in ash (< 4 wt.%), while no significant changes were observed in MV content. RHC showed a decrease in FC content (11 - 12 wt.%) and an increase in MV content (71 - 76 wt.%), which is undesirable for their potential use as a biofuel, because could result in an incomplete combustion and flame instability (Sharma et al., 2020). The RHC reached a relatively low ash content (11 wt.%), which increased with increasing temperature (18 wt.%). SHC showed a higher C content up to 10 wt.% higher than SHC. The N and S content did not show significant changes, maintaining similar values to the initial SM.

One of the most significant changes was observed in the HHV value, being significantly higher (20 - 21 MJ kg^{-1}) in the SHC compared to the RHC (~ 17 MJ kg^{-1}). The hydrochar mass yield (Y_{HC}) was similar in both cases, except at the highest temperature tested, where there is a disparity of 12 p.p., with the RHC showing a higher mass yield. It is important to note that the hydrocarbon derived crude MS has a higher percentage of ash, so when ash-free mass yield is considered, the separated MS shows a higher mass yield than the crude MS. Although both substrates show improvements compared to the initial substrates, it is necessary to compare these hydrocarbons with ISO 17225-8, which establishes criteria for the use of solid biofuels from biomass densified by thermochemical treatment, such as HHV > 17 MJ kg^{-1}, VM < 75 wt.%, N < 3 wt.%, S < 0.5 wt.%, and ash < 10 wt.%.

Table 2. Main characteristics of hydrochars from raw swine manure (RHC) and solid fraction of swine manure (SHC).

	RHC-210	**RHC-230**	**RHC-250**	**SHC-210**	**SHC-230**	**SHC-250**
Y_{HC} (%)	50.9 (1.0)	46.9 (0.4)	36.2 (1.2)	52.4 (2.4)	46.2 (1.9)	22.7 (0.6)
FC (%)	12.4 (0.2)	11.3 (0.0)	11.1 (0.2)	21.2 (0.4)	22.2 (0.3)	23.5 (0.4)
VM (%)	76.3 (0.2)	71.7 (0.6)	71.3 (0.3)	75.0 (0.4)	73.8 (0.2)	72.6 (0.2)
Ash (%)	11.3 (0.2)	17.0 (0.4)	17.6 (0.2)	3.7 (0.1)	3.9 (0.2)	3.9 (0.2)
C (%)	40.8 (0.6)	41.4 (0.5)	41.6 (0.7)	50.4 (0.3)	51.5 (0.6)	51.7 (0.5)
N (%)	2.0 (0.0)	2.2 (0.0)	2.2 (0.1)	1.6 (0.3)	1.4 (0.1)	1.2 (0.1)
S (%)	0.4 (0.0)	0.3 (0.0)	0.5 (0.0)	0.4 (0.0)	0.2 (0.0)	0.4 (0.0)
H/C	1.60	1.56	1.54	1.35	1.32	1.34
O/C	0.74	0.61	0.59	0.57	0.54	0.54
HHV (MJ kg^{-1})	16.5 (0.4)	17.2 (0.4)	17.4 (0.1)	20.3 (0.3)	20.7 (0.3)	20.9 (0.2)
E_{yield} (%)	60.5 (0.5)	58.1 (0.9)	45.4 (0.5)	57.5 (0.2)	51.7 (0.2)	25.6 (0.4)

Conclusions

Hydrothermal carbonization of swine manure allowed a significant improvement in the properties of hydrochar as a biofuel, which was evident by an increase in C content, HHV and energy densification. However, from an integrated manure management perspective on a pig farm, treatment of raw swine manure proved to be a more efficient strategy, allowing management of both the solid and liquid fractions. Although hydrochar derived from separated swine manure shows improvements compared to raw swine manure, mixing separated swine manure with water is not an environmentally friendly strategy. This highlights the efficiency of hydrothermal carbonization as a tool to transform an organic waste into a carbonaceous solid with properties suitable for use as a industrial biofuel.

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