## Nutrient and energy recovery from chicken meat and bones meal by hydrothermal treatment and anaerobic digestion

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Chicken meat and bones meal (C-MBM) is the most generated meat-derived food waste in the world. The main characteristics (79.0 g N/kg, 26.8 g P/kg and 5 g K/kg, 66.5 g total solids (TS)/kg, 56.9 g volatile solids (VS)/kg, total chemical oxygen demand (TCOD) of 260.9 mg  $O_2/g_{TS}$ , and a moisture content of 67 %) of a C-MBM collected from a local food management plant (Madrid, Spain), appear interesting for valorization by hydrothermal carbonization (HTC) combined with anaerobic digestion (AD) to recover both nutrients and energy. Usually, the main product of HTC is a carbonaceous solid, called hydrochar (HC), with properties suitable for use as biofuel. In addition, a process water (PW) is generated, which contains organic compounds and inorganic salts; and a minor gaseous stream, consisting mainly of  $CO_2$  [1]. Depending on the operating conditions (pH, temperature and residence time) the release of nutrients, mainly phosphorus and nitrogen, mostly to the process water is possible, which can be recovered by chemical precipitation in the form of struvite [2]. After nutrient recovery, the process water contains a high content of organic compounds, which can be valorized through AD to obtain biogas as an additional energy source. The overall goal of this study is the recovery of nutrients from the PW obtained in the hydrothermal treatment of C-MBM and the energy valorization of both HC and PW, free of nutrients, via combustion and AD, respectively.

The raw C-MBM was diluted with deionized water to obtain a feedstock with a 10 wt.% solid content. Thermochemical experiments were carried out in a ZipperClave stirred pressure vessel (4 L) at temperatures in the range of 170 - 230 °C for 1 h. In addition, an acid-mediated hydrothermal treatment was performed using 0.5 M HCl to promote nutrient solubilization in the process water. After the reaction, the reactor was cooled to room temperature and the slurry was separated by vacuum filtration. Depending on the experimental conditions, reaction medium consisted of a mixture of carbonaceous solid (hydrochar) and process water or a bio-oil-in-water emulsion.. The hydrochar (HC-T, being T referred to temperature) and bio-oil (BiO-T) were dried at 105 °C for 24 h and process water (PW-T-A, being A referred to acidic reactions) was filtered using a glass microfiber filter (0.45  $\mu$ m).

The elemental (C, N, S, and H) and proximate (moisture, ash, volatile matter and fixed carbon) composition of HC and BiO was determined. In addition, the behaviour of hydrochar as solid fuel was studied (combustion temperatures, activation energy, comprehensive combustion index, ignitability index). For the process water, total N (TN), total P (TP) and total K (TK) concentration was measured, as well as the content of nitrite, nitrate, ammonium and ortho-phosphate, together with the main metallic ions were measured. After hydrothermal tests, P, Mg and ammonium present in the process water were precipitated in form of struvite at pH 9, using Mg(OH)<sub>2</sub> as reagent. The structure of struvite was determined by X-ray diffraction. Soluble chemical oxygen demand (SCOD) (60-80 g O<sub>2</sub>/L), TS (58-75 g TS/kg) and VS (47-56 g VS/kg) were determined in the process water (nutrient-free), before being treated by AD. A granular anaerobic sludge from an industrial digester treating brewery wastewater under mesophilic conditions was used as AD inoculum. AD tests were carried out in 120 mL glass serum vials, using an initial inoculum concentration of 15 g VS/L and an inoculum-to-substrate ratio of 2 on a VS basis. During the AD process, biogas volume and composition (H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>), pH, alkalinity, SCOD, ammonia nitrogen (N-NH<sub>4</sub><sup>+</sup>) and volatile fatty acids (VFA) were determined.

The distribution of N, P and K in the HTC products is shown in Table 1. The fate of P along the hydrothermal treatment in absence of acid was linked to the hydrochar, mainly due to the formation of precipitable phosphatometallic complexes [3]. An increase in the reaction temperature favoured the release of N (from the hydrolysis of proteins and amino acids), N-NH<sub>4</sub><sup>+</sup> and K (mainly in form of soluble salts) directly to process water (practically all the initial N and K, at 230 °C). The acidic treatment, at temperatures of 170 and 200 °C, was favourable for the extraction of P in the process water, in the form of orthophosphate, obtaining up to 30% more solubilized P than in the 230 °C experiment. The fate of N and K was mostly in the process water. It should be noted that a bio-oil mainly formed by volatile compounds was obtained, which provides a severe increase in higher heating value (data not shown). The C enrichment (close to 75%) of the bio-oils and the low N (< 0.5%), S (< 0.1%) and ash (< 0.3%) content make BiO-170 and BiO-200 suitable for blending with anthropogenic coal as a combustion booster [4].

Table 1. Nutrient distribution in the products obtained after hydrothermal tretament (g/kg<sub>C·MBM</sub>, d.b.)

Sample	Ν	Р	Κ	Sample	Ν	$N-NH_4^+$	Р	Κ
HC-170	7.2	23.8	0.1	PW-170	71.8	8.1	2.2	5.0
HC-200	4.4	22.8	0.3	PW-200	74.6	16.0	2.9	4.8
HC-230	0.5	22.6	0.2	PW-230	78.5	18.0	3.0	5.0
BiO-170	0.0	1.4	0.0	PW-170-A	79.5	13.4	25.4	5.1
BiO-200	0.3	1.2	0.1	PW-200-A	79.2	18.7	25.6	5.1
BiO-230	0.1	9.1	0.0	PW-230-A	79.4	23.4	17.7	5.0

Nutrients concentration in the PW-170-A (3.0 g P-PO<sub>4</sub>/L, 0.11 g Mg<sup>2+</sup>/L and 1.5 g N-NH<sub>4</sub><sup>+</sup>/L) and PW-200-A (3.0 g P-PO<sub>4</sub>/L, 0.12 g Mg<sup>2+</sup>/L and 2.3 g N-NH<sub>4</sub><sup>+</sup>/L) were measured, in order to adequate the effluent to a 1:3:1 P-PO<sub>4</sub>:Mg:N-NH<sub>4</sub><sup>+</sup> molar ratio to be precipitated in form of struvite. On this way, only Mg<sup>2+</sup> addition was necessary, and Mg(OH)<sub>2</sub> salt was used to achieve it. To favour the struvite precipitation, 6M NaOH solution was added to keep pH 9. After stirring for 20 min, the solid formed was separated and dried. The X-ray diffraction of these precipitates showed crystalline peaks corresponded to pure struvite ones. Composition of struvite showed a high content in P (126-132 g P/kg) and Mg (80-100 g Mg/kg), with no relevant presence on other metals.

After struvite precipitation, the nutrient-free PW-170-A and PW-200-A process waters were subjected to anaerobic digestion (AD-170-A and AD-200-A). Figure 1 shows the time course of specific methane production during the AD tests. Methane production from AD-170 and AD-200 resulted in 300 and 235 mL CH<sub>4</sub> STP/g COD, with COD removal of 32% and 72%, respectively. Similar values of the kinetic constant (0.048 and 0.050 d<sup>-1</sup>, respectively were obtained by fitting the experimental results to a first-order equation.



Fig. 1. Specific methane production during AD of PW-170-A and PW-200-A. Symbols and lines represent experimental values and those obtained by kinetic fitting, respectively.

According to the obtained results, hydrothermal carbonization of C-MBM integrated to the anaerobic digestion of the resulting process water seems to be an interesting valorization process for material (struvite generation) and energy (combustion of bio-oil and biogas) recovery.

## References

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