Characterization of the anaerobic digestion of thermal pre-treated slaughterhouse waste by applying new IR techniques

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Abstract
In this work, thermal analysis and infrared spectrometry were used to explain the behaviour of two different pasteurized animal by-products with different protein/fat/carbohydrate composition. The presence of hardly degradable nitrogen containing components, identified by infrared spectrometry, and produced during Maillard reactions at pasteurization temperature, explained the different behaviour (methane rate and yield) under anaerobic conditions of pig and poultry wastes.

Keywords
Anaerobic digestion; FTIR; pasteurization; slaughterhouse waste; thermal analysis

INTRODUCTION

Different results about anaerobic digestion of thermal pre-treated slaughterhouse waste have been observed in literature. Hejnfelt and Angelidaki (2009) observed that a mixture of thermally pre-treated pig waste gave lower methane yields than untreated mixtures, while Edström et al. (2003) observed an improvement in methane yield after pre-treatment. Rodríguez-Abalde et al. (2011) attributed those differences to the effect of the pasteurization process on the composition of the treated slaughterhouse waste: after the pasteurization of a waste with a high carbohydrate and protein content, Maillard reaction products can be formed and a decrease of methane yield could be expected, while a pasteurized waste characterized by high fat and proteins concentrations and almost inexistent carbohydrate content let to an increase in methane yield and production rate, compared to the same untreated waste.

The determination of protein, fat and carbohydrate content, previous to anaerobic digestion, could help to predict the qualitative behaviour during anaerobic digestion. In this work, two helpful tools for characterizing waste organic matter, thermal analysis and Fourier transform infrared (FTIR) spectrometry, were used with untreated and pasteurized samples of animal by-products to study the anaerobic digestion process dependence on the chemical composition and degradation pattern.

MATERIALS AND METHODS

The selected animal by-products (ABP) were a poultry waste (wins, necks, internal organs and heads), named TI, and a piggery waste (mixture of internal and reproductive organs and fats), named TII, which were sampled in two slaughterhouse facilities located in Lleida and Barcelona (Spain), respectively. All fractions were minced (4 mm maximum particle size) and mixed. Pasteurization was applied with both mixtures at 70º and 60 minutes by triplicate with 500 g of waste in a high pressure and temperature reactor (Iberfluid Instruments, Spain). The pre-treated samples were named PTI for pasteurized poultry waste and PTII for pasteurized pig waste.

Obtained samples (TI, TII, PTI, PTII) were lyophilized in order to improve their homogeneity prior characterization. Total and volatile solids (TS, VS), pH, total and ammonia nitrogen (TN, TAN) and soluble chemical oxygen demand (CODs) of untreated and pre-treated wastes were measured according to Standard Methods (APHA, AWA, WEF, 2005). Total carbon and nitrogen were determined by elemental analysis (Leco Instruments, USA). The fat content was analyzed following Soxhlet method (Foss model Soxtec™ 2050, Denmark). Volatile fatty acids (VFA) and methane were determined by gas chromatography. The anaerobic biodegradability (AB) was determined according to Campos et al. (2008) in triplicate using 1 l flasks. The initial inoculum and substrate concentrations were 5 $gVSS \cdot l^{-1}$ and 5 $gCODt \cdot l^{-1}$, respectively. The flasks were continuously stirred (100 rpm) during incubation at 35ºC for 30 days.

The lyophilized samples TI, TII, PTI and PTII were ground with a ball mill (Retch 200MM) and submitted to thermal analysis (TA), using TA Instruments SDT2960 thermo-balance, with an applied heating rate of 10 $ºC \cdot min^{-1}$ (0-900 ºC) and a flow-rate of 100 $ml \cdot min^{-1}$ of synthetic air. Infrared spectrometry analysis was performed following Cuetos et al. (2009), using 2 mg of lyophilized milled samples, ground up with 200 mg KBr (FTIR grade) and homogenized in an agate mortar.

RESULTS AND DISCUSSION

Samples

The characteristics of raw ABP mixed substrates (TI and TII) are summarized in Table 1. The ash content, although small in both substrates, was higher in waste TI than in TII, due to the bone fraction of the poultry by-products. Both raw ABP materials were characterized by different fat, protein and carbohydrate ratio (F:P:C), related to initial COD_t content. The different organic fractions of TI waste were quite similar (33:33:34), while the fat fraction was the main component of waste TII, with a low amount of carbohydrates (82:13:4).

Table 1. Characterization of initial samples of poultry waste (TI) and piggery waste (TII). Nomenclature: (1) F-fat, P-protein and C-carbohydrate expressed in % of COD_t; (2) estimated value by elemental analysis; (3) estimated protein=$N_{org} \cdot 6.25\ g_{prot} \cdot g_{Norg}^{-1}$

Parameters	Units	TI (poultry)	TII (piggery)
TS (w/w)	%	30.7 ±0.4	50.7 ±0.4
VS (w/w)	%	26.6 ±0.6	48.9 ±0.1
F:P:C (1)	%:%:%	33:33:34	82:13:4
COD_t (2)	$g \cdot kg^{-1}$	653.49	1275.0
COD_s	$g \cdot kg^{-1}$	66.3 ±3.7	52.2 ±0.5
TN	$g \cdot kg^{-1}$	26.3 ±0.5	20.7 ±0.9
TAN	$g \cdot kg^{-1}$	2.1 ±0.1	1.4 ±0.0
Est. protein (3)	$g \cdot kg^{-1}$	151.3±3.6	120.9±5.7
Fat	$g \cdot kg^{-1}$	74.7 ±1.0	363.4 ±0.6

Anaerobic batch assays

Figure 1 shows methane evolutions during AB tests. The anaerobic biodegradability of untreated wastes TI and TII was 55.2 and 76.6% COD_t, respectively, while it was 61.8 and 94.3% COD_t for the pasteurized TI and TII, respectively. The non-biodegradable fraction decreased after the thermal pre-treatment: from 44.8% to 38.2% COD_t in TI and PTI, respectively, and from 23.4% to 5.3 % COD_t in TII and PTII, respectively. The pasteurization improved the methane production rate (MPR) in PTII (increase of 46.7% compared to TII methane rate), while this rate decreased 46.3%, related to untreated sample, in PTI.

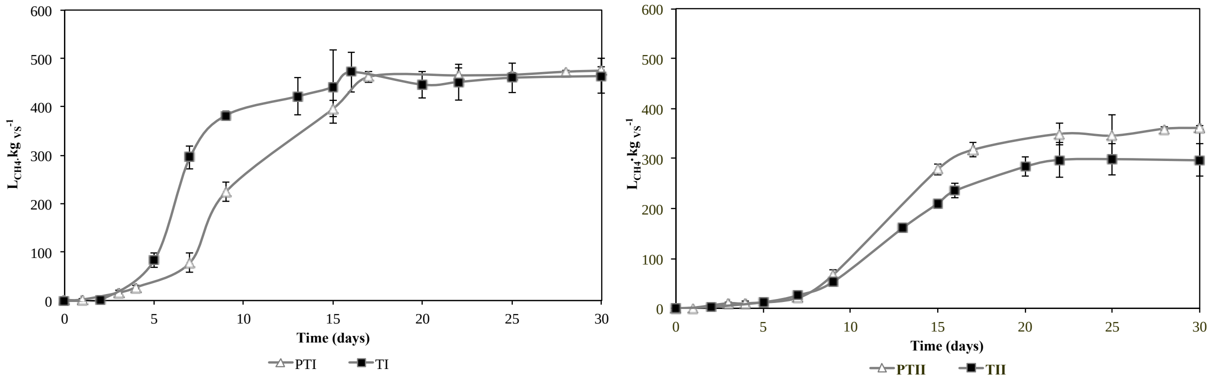

Figure 1. Methane evolution during the mesophilic anaerobic biodegradability assay of raw (TI, TII) and pre-treated (PTI, PTII) wastes.

Thermal analysis

Thermal analysis is characterized by a loss of water during dehydration taking place at temperatures between 10 and 800ºC. Thermograms obtained from the analyzed samples are shown if Figure 2. The pasteurization applied to TI (Fig.2a) allowed the degradation of complex materials, which may be observed by the lower temperature at which an intensive loss of mass is taking place in PTI. This sample was also characterized by two main organic fractions: a first part was thermally decomposed at temperatures below 400 ºC, with the peak centred around 200 ºC, indicating that readily degradable materials were generated with the pre-treatment, which may be anaerobically degraded earlier in the PTI than in TI, and a second fraction decomposed at higher temperatures with a reduction of mass around 400 ºC. However an increase of components centred close to 600 ºC, which are related to complex organic material containing nitrogen, was observed in PTI. In this sense, the lower biogas production obtained from PTI batch tests may be explained by the presence of these complex components.

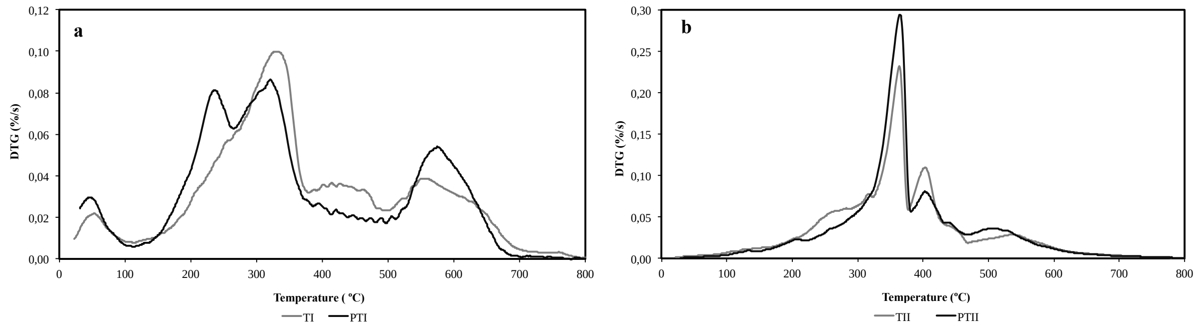

Figure 2. Evolution of the weight-loss profiles, determined by TG-DTG, of the initial (grey lines) and pre-treated wastes (black lines): (a) poultry wastes (TI and PTII); (b) piggery wastes (TII and PTII)

Thermograms obtained from TII and PTII samples are shown in Fig. 2b. The applied pre-treatment allowed a faster degradation of organic matter by increasing the content or readily degradable components, as the higher intensity of the peak centred on 350 ºC suggests. Regarding complex organic components, which were suffering thermal break up at high temperatures, it was observed a reduction of these constituents after the pasteurization since a lower intensity of peak at 400 ºC was observed for pre-treated sample PTII. Contrary to the previous case, the thermal pre-treatment was not associated to the intensive generation of complex nitrogen containing molecules. This behaviour may explain the increase in biogas production for the pre-treated sample PTII, although a small mass release at 600 ºC was observed for the pasteurized sample.

FTIR analysis

Spectra obtained from poultry wastes are presented in Figure 3a. The presence of nitrogen containing components, which was reported in the previous thermograms, is observed in the N-H stretching band around 3300 cm^{-1}, causing an asymmetry of the broad OH-band. The pre-treatment in TI caused an increase of signal registered at 1651 and 1541 cm^{-1} in the raw sample spectrum. These signals are ascribed to amide I (C=O vibration) and amide II (N-H bending), respectively. The recalcitrant nature of these components may have been responsible of the lower methane yield observed during the anaerobic digestion process and may be associated with the formation of compounds derived from Maillard reactions between proteins and carbohydrates, as may be inferred from the relative increase in the signal intensity in the region 1607-1463 cm^{-1} (Yaylayan and Kaminsky, 1998) with regard to 2924 and 2854 cm^{-1} signal. Su et al. (2010) also observed that the band at 1647 cm^{-1} indicates C=N stretching vibration that are attributed to Maillard reactions.

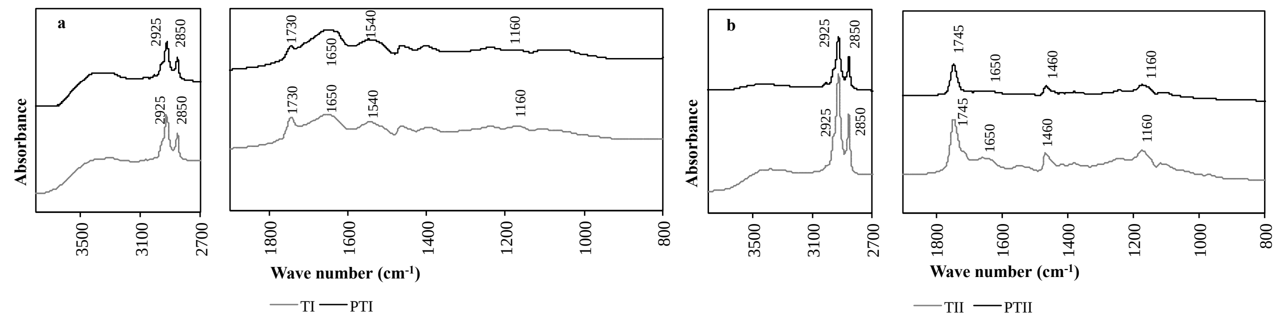

Figure 3. FTIR spectra for the initial (grey lines) and pre-treated wastes (black lines): (a) poultry wastes (TI and PTII); (b) piggery wastes (TII and PTII)

Spectra obtained from piggery wastes are shown in Figure 3b, where it can be observed that band at 1647 cm^{-1} decreased after thermal pre-treatment. As it was already reported from thermal analysis, nitrogen complex compounds are scarcely formed when applying thermal pre-treatment to TII, being now confirmed by stretching bands in FTIR spectra. These results could explain the higher increase in yields and methane production rate, respect to untreated, for pig than for poultry wastes.

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