Waste Management 72 (2018) 193–205

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Maize cob waste pre-treatments to enhance biogas production through co-anaerobic digestion with OFMSW

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ARTICLE INFO

Article history:
Received 26 June 2017
Revised 26 October 2017
Accepted 1 November 2017
Available online 21 November 2017

2010 MSC:
00-01
99-00

Keywords:
Anaerobic co-digestion
OFMSW
Maize cob wastes
Pre-treatments
Biogas

ABSTRACT

In the present work, the enhancement of biogas and methane yields through anaerobic co-digestion of the pre-hydrolised Organic Fraction of Municipal Solid Wastes (hOFMSW) and Maize Cob Wastes (MCW) in a lab-scale thermophilic anaerobic reactor was tested. In order to increase its biodegradability, MCW were submitted to an initial pre-treatment screening phase as follows: (i) microwave (MW) irradiation catalysed by NaOH, (ii) MW catalysed by glycerol in water and alkaline water solutions, (iii) MW catalysed by H_2O_2 with pH of 9.8 and (iv) chemical pre-treatment at room temperature catalysed by H_2O_2 with 4 h reaction time. The pre-treatments catatysed by H_2O_2 were performed with 2% MCW (wMCW/v alkaline water) at ratios of 0.125, 0.25, 0.5 and 1.0 (wH_2O_2/wMCW). The pre-treatment that presented the most favourable balance between sugars, lignin, cellulose and hemicellulose solubilisations, as well as low production of phenolic compound and furfural (inhibitors), was the chemical pre-treatment catalysed by H_2O_2, at room temperature, with a ratio of 0.5 wH_2O_2/wMCW (Pre1). This Pre1 was then optimised testing reaction times of 1, 2 and 3 days at a different pH (11.5) and MCW percentage (10% w/v). The optimised pre-treatment that presented the best results, considering the same criteria defined above, was the one carried out during 3 days, at pH 9.8 and 10% MCW w/v (Pre2).

The anaerobic reactor was initially fed with the hOFMSW obtained from the hydrolysis tank of an industrial AD plant. The hOFMSW was than co-digested with MCW submitted to the pre-treatment Pre1. In another assay, hOFMSW was co-digested with MCW submitted pre-treatment Pre 2. The co-digestion of hOFMSW + Pre1 increased the biogas yield by 38.9% and methane yield by 29.7%, when compared to the results obtained with hOFMSW alone. The co-digestion of hOFMSW + Pre2 increased biogas yield by 46.0% and CH_4 yield by 36.3%. In both cases, the methane content obtained in the biogas streams was above 66% v/v. These results show that pre-treatment with H_2O_2, at room temperature, is a promising low cost way to valorize MCW through co-digestion with hOFMSW.

1. Introduction

A correct management of organic wastes contributes to decrease GHG emissions and produce renewable energy (Dennehy et al., 2016). Anaerobic digestion (AD) offers the opportunity to valorise organic wastes by generating biogas, which is a renewable fuel suitable (i) for electricity and heat production, (ii) grid injection, or (iii) to be used as a fuel for transportation (Arizzi et al., 2016). These last two options require a biogas upgrading step to bio-methane (CH_4 > 97% v/v).

AD is a delicate microbiological process, whose efficiency and stability are affected by carbon (C) and nitrogen (N) availability in the substrate and by their balance (C:N ratio) (Kawai et al., 2014). A high C:N ratio is an evidence of lack of proteins or lack of their solubilisation, resulting in insufficient N to maintain

Abbreviations: AC, Acetic Acid; AD, Anaerobic Digestion; co-AD, Anaerobic co-Digestion; BA, Butyric Acid; CA, Caffeic Acid; EA, Elemental Analysis; FA, Ferulic Acid; FoA, Formic Acid; HMF, Hydroxymethylfurfural; 5-HMF, 5-Hydroxymethylfurfural; hOFMSW, Pre-Hydrolysed Organic Fraction of Municipal Solid Waste; MCW, Maize Cob Waste; MSW, Municipal Solid Waste; MW, Microwave Irradiation; N-N4, Ammonium Nitrogen; OFMSW, Organic Fraction of Municipal Solid Wastes; OLR, Organic Load Rate; o-N, Organic Nitrogen; p-CA, p-Coumaric Acid; PA, Propionic Acid; SA, Syringinc Acid; sCOD, Soluble Chemical Oxygen Demand; tCOD, Total Chemical Oxygen Demand; TKN, Total Kjeldahl Nitrogen; TS, Total Solids; VA, Vanillin Acid; VnA, Vanillic Acid; VFA, Volatile Fatty Acids; VS, Volatile Solids.

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https://doi.org/10.1016/j.wasman.2017.11.004

biomass cells, whilst substrates characterized by a low C:N ratio can arise ammonia accumulation, which is toxic for methanogens (Jain et al., 2015). The optimal C:N ratio for AD has been shown to be in between 20 and 30 (Ponsá et al., 2011). Wang et al. (2012) reported 25 as the best C:N ratio. For this reason, the co-digestion of different organic wastes is considered one of the most successful strategies to optimise AD stability and efficiency as it is able to balance the C:N ratio (Shen et al., 2013; Zhang et al., 2013).

Two types of wastes, that can be submitted to AD, are the Organic Fraction of Municipal Solid Wastes (OFMSW) and Maize Cob Wastes (MCW). The world production of Municipal Solid Waste (MSW) is estimated to be 1300×10^6 t per year with a prevision trend of 2200×10^6 t in 2025; 46% of these wastes are readly biodegradable organics (Seadi et al., 2013).

The production of biogas from OFMSW through AD is a largely implemented technology at industrial scale to supply electricity and heat to cites (Mao et al., 2015). However OFMSW is not always characterised by the optimum C:N ratio because of their intrinsic composition in proteins, that reflects the high N content (Zarkadas et al., 2015).

On the other hand, maize is the most produced cereal in the world, with a production of 1.04×10^9 t in 2014 (URL1, 2015). Maize crop generates wastes that often exceed the organic-C needed for soil fertility, as well as the market capacity to absorb them as feedstock for full-scale production of biofuels (Liu et al., 2010) and chemicals (Gu et al., 2014). MCW are lignocellulosic biomass mainly composed of two types of fibers (cellulose and hemicellulose) and of a complex aromatic heteropolymer (lignin) (Su et al., 2014). Only cellulose and hemicellulose are fermentable after hydrolysis, while lignin, that has the structural role of cementing cellulose and hemicellulose micro-fibrils together, cannot be digested by bacteria (Zheng et al., 2014). This means that MCW have to be properly pre-treated before being submitted to AD, in order to remove lignin and to set free digestible carbohydrates from the substrate, possibly limiting as much as possible the formation of inhibitors. The presence of phenolic compounds derived from lignin decomposition and furfural and hydroxymethylfurfurals (HMF), produced by pentoses and hexoses degradation, can negatively affect AD (Hendriks and Zeeman, 2009). The main aim of this work is to test different thermochemical pre-treatments on MCW in order to assess their efficiency for biogas production during the co-digestion (co-AD) with hOFMSW. Pre-treatments with microwave irradiation (MW) catalysed by NaOH, glycerol and H_2O_2, and at room temperature catalysed by H_2O_2 have been tested.

This work contributes to the development of a new way to valorize MCW that, when left in the fields after harvesting, can lower the maize production yields due to their slow biodegradability in the soil.

2. Material and methods

2.1. Feedstock materials

For the laboratory assays, a pre-hydrolised OFMSW (hOFMSW) was used. This hOFMSW was collected from the hydrolysis tank of a Portuguese AD plant, located in Lisbon region. This AD plant processes OFMSW coming from canteens, restaurants and malls. The hOFMSW was stored at 4 °C in glass bottle until use. Samples of the hOFMSW have been collected with an adequate frequency to guarantee the freshness of the organic matter.

MCW was collected from a local farmer located in Coruche area, in Lisbon surroundings. The MCW was air-dried to a final moisture content of 13% w/w. The air-dried MCW was then ground into 2–4 mm particles by a Retsch SM 2000 mill. The ground MCW was then packed in closed plastic bins at 4 °C until use.

2.2. Feedstock characterisation

2.2.1. hOFMSW

The characterisation of hOFMSW included the following parameters: Total Solids (TS), Ashes and Volatile Solids (VS) (method 2540); total Chemical Oxygen Demand (tCOD) and soluble Chemical Oxygen Demand (sCOD) (method 5220 B) (APHA et al., 2005) Total Kjeldal Nitrogen (TKN) (method ISO 5663:1984), Ammonium Nitrogen (NH_4-N) (method ISO 5664:1984) and Organic Nitrogen (o-N) (TKN - NH_4-N); phosphorus (P) (method ISO 6878:2004); Elemental Analysis (EA); Volatile Fatty Acids (VFAs) as Acetic Acid (AA), Formic Acid (FA), Propionic Acid (PA) and Butyric Acid (BA). Each determination was performed in duplicate.

EA was performed on the dried hOFMSW (2 h at 105 ± 1 °C) in a Thermo Finnigan Elemental Analyzer - CE Instruments, model Flash EA 1112 (CHNS).

VFAs were analysed with a HPLC system (Dionex ICS3000, USA) equipped with Biorad Aminex 87H column, pre-column and UV detector at 210 nm. The eluent used was H_2SO_4 10 mN, with a flow rate of 0.6 ml/min, at 30 °C.

The characterisation of the hOFMSW is reported in Table 1.

TS (5.6%) and VS (4.5%) are relatively low, implying that the lab-scale digester had been operated under the liquid state anerobic digestion condition (L-AD). tCOD and sCOD are significantly higher than typical values found in literature for OFMSW (Cesaro et al., 2012; Cesaro and Belgiorno, 2013).

The C:N ratio of hOFMSW is 9.6 ± 0.3, which is considerably lower than the optimal value (25) for AD according to literature. This shows a low carbon contribution useful for cell structure maintenance (Wang et al., 2012). The ratio C:N:P in hOFMSW is 106:11:1. Again, this ratio presents unbalanced values of C relatively to the optimum C:N:P ratio for methane yield, which was reported in literature to be 200:5:1 (Lo et al., 2010).

In the absence of specific references in literature concerning the composition of hOFMSW, CHNS results obtained in dry basis (db) were compared to the average values found for OFMSW for 22 European and non-European countries (Campuzano and González-Martínez, 2016). C, N and S contents quantified in the present study were 12%, 86% and 613% higher, respectively, than the typical values pointed out for the other countries. This evidence and the high concentrations of tCOD and sCOD are probably due to the fact that the hOFMSW is mixed in the plant with anaerobic sludge pumped back before the hydrolysis take place. H does not show any significant variation in comparison to literature (6.93 w/w db *vs* 6.6% w/w db in the literature) (Campuzano and González-Martínez, 2016).

Table 1
Characterisation of the hOFMSW (average ± standard deviation).

Parameters	Units	Values
TS	% w/w	5.63 ± 0.45
VS	% w/w	4.55 ± 0.35
Ashes	% w/w	1.09 ± 0.11
tCOD	gO_2/L	87.7 ± 4.36
sCOD	gO_2/L	32.7 ± 1.88
P	g/L	0.49 ± 0.075
TKN	g/L	2.87 ± 0.66
NH_4-N	g/L	1.50 ± 0.09
o-N	g/L	1.37 ± 0.13
C	% w/w db	52.2 ± 7.66
N	% w/w db	5.41 ± 0.97
H	% w/w db	6.93 ± 0.96
S	% w/w db	1.84 ± 0.23

db: dry basis.