Authors: Juan-Rodrigo Bastidas-Oyanedel[a,#], Akinleye Sowunmi[a], Jens Ejbye Schmidt[a,*]

Title: Valorization of paper and cardboard waste – determination of biomethane potential

Affiliations:
[a] Department of Chemical and Environmental Engineering, Khalifa University of Science and Technology, Masdar Institute, Masdar City, P.O. Box 54224, Abu Dhabi, United Arab Emirates

jbastidas@masdar.ac.ae, akinleye.sowunmi@yahoo.com, jschmidt@masdar.ac.ae

[#] Corresponding author during all stages of refereeing and publication
[*] Presenting author and post-publication corresponding author

Abstract

Purpose: Waste paper conversion to biomethane by anaerobic digestion appears as an alternative to landfilling, i.e. when the quality of waste paper does not match the requirements for recycling. The objective of the present work is to measure the biomethane potential (BMP) of three different types of waste paper: newspaper, cardboard, and office paper (A4), and to determine the effect of steam pretreatment on the BMP of these wastes.

Methods: The BMP tests were done in triplicates. Steam pretreatment was conducted at 120 °C for 30 minutes. Gompertz and modified-Gompertz models were used to estimate the maximum methane production rate (Rm).

Results: The maximum BMP obtained for the 3 wastes was in the range of 220-380 ml_CH_4/gVS. Steam pretreatment increased the BMP of newspaper by 270%, and 12% for cardboard and office paper. The statistical analysis showed that the modified-Gompertz model is simulates more accurately the experimental data than the Gompertz model.

Conclusions: The BMP of waste paper, and the steam pretreatment conditions resulted in close values to the maximum theoretical BMP for sugars (400 mL_CH_4/gVS). Perspectives are directed to reduce steam pretreatment costs by temperature and time modification minimizing reductions in the obtained BMP.

Keywords: Anaerobic digestion; steam pretreatment; biomethane potential; BMP; abattoir; slaughtering house

1 Introduction

Efficient waste paper recycling and/or reutilization has an environmental and economic role in a sustainable society [1]. The most extended process for the valorisation of waste paper is its recycling, incineration, and landfilling [2]. Waste paper conversion to biomethane by anaerobic digestion appears as an alternative to landfilling, i.e. when the quality of waste paper does not match the requirements for recycling. Landfilling or other waste disposal techniques signifies additional costs to waste management, in contrast anaerobic digestion add value/revenues to this waste stream, i.e. the production of bioenergy [3–5]. Also, anaerobic digestion is technologically mature, feasible and economically viable [4, 6]. Anaerobic digestion therefore comes as a solution to landfill of waste paper reduction and value generation.

Waste paper is considered to have a low biomethane potential (BMP), i.e. below 200 mL_CH4/gVS [7, 8]. The biomethane production from waste paper can be improved by hydrothermal steam pretreatment of the wastes [9, 10]. Under high temperature (above 100 °C) and pressure, water penetrates into the structure of recalcitrant biomass by hydrating its cellulose content, and removing part of lignin, and most of its hemicellulose content. This can increase the digestion reaction rate and improve the hydrolysis step [11–14].

The main objective of the present work is the determination and comparison of the BMP obtained from 3 different untreated and steam pretreated waste paper sources, i.e. newspaper, cardboard, and office paper (A4). Steam pretreatment was conducted at 120°C for 30 minutes. The maximum BMP expected is around 400 mL_CH4/gVS [15]., which corresponds to the maximum theoretical BMP using sugars, considering that paper is mainly consituted by carbohydrates polymers.

2 Materials and Methods

2.1 Material collection and characterization

The 3 collected waste paper consisted on: newspaper, cardboard and office paper (A4). The selected waste paper were collected from Masdar Institute paper recycling facilities, located in Abu Dhabi. The inoculum used for the biomethane potential experiments consisted on anaerobic sludge, collected from a domestic wastewater treatment plant in Abu Dhabi. The 3 selected waste paper and the anaerobic sludge were characterized. Total Solids (TS) and volatile solids (VS) were quantified as indicated in Standard Methods 2540D and E [16].

2.2 Biomethane potential

Biomethane potential (BMP) [17] was conducted on closed glass bottles with a working volume of 200 mL and a head-space of 400 mL. The bottles were incubated at 37 °C without agitation. All selected waste paper biomethane potentials, untreated and steam pretreated (see section 2.3), were performed in triplicates using a waste (feedstock) concentration of 5 g_VS/L, and a substrate to inoculum ratio of 1:1 (VS-based).

Inoculum blank, i.e. without substrate, was use to correct the biogas potential of the experiments by extracting the inoculum biomethane potential. For all the experiments, the inoculum was predigested for 2 days at 37 °C to reduce its indigenous biomethane potential.

After inoculation and previous to incubation, the glass bottles headspace was flushed with a gas mixture of 80% N_2 and 20% CO_2 to ensure anaerobic conditions and prevent pH change in the liquid phase. All experiments used an anaerobic media based on [18]. Biomethane was measured using a Gas Chromatograph (GC SRI Instrument, SRI 8610C with 3” Silica Gel column) equipped with Flame Ionization Detector (FID).

2.3 Thermal pretreatment

Thermal pretreatment was conducted at 120℃ for 30 minutes (see Appendix A for heating curve), in an autoclave. The pre-weighed substrates and anaerobic media (see section 2.2) were loaded to the glass bottles. The loaded glass bottles were closed and placed in the autoclave for the thermal pretreatment. Inoculation of the thermally pretreated wastes was done after cooling down (see section 2.2).

Under these conditions of temperature and time, the severity factor, log(Ro) has a value of 2.3. The severity factor was calculated according to Hendriks and Zeeman [19], and Overend and Chornet [20], considering the heating-up and cooling-down curves, together with the set-point temperature and treatment time. See Appendix A for the calculation of severity factor.

2.4 Biomethane potential data analysis

The kinetic data analysis of the biomethane potential experiments was performed using two mathematical models: Gompertz model [9], and a modified Gompertz model [21–24]. Both models were used to simulate the experimental biomethane production (mL_CH4/g_VS), to simulate the biomethane production rate (mL_CH4/(g_VS*day)), and to estimate the maximum biomethane production rate (mL_CH4/(g_VS*day)). The data analysis was conducted using Microsoft Excel®, and its solver tool. The Gompertz model is described in Equation 1, and the modified Gompertz model is described in Equation 2.

$$B = P\left(1 - exp\left(\frac{-Rm(t-\lambda)}{P}\right)\right) \qquad \text{(Equation 1)}$$

$$B = P \cdot exp\left(-exp\left(\frac{Rm \cdot e}{P}(\lambda - t) + 1\right)\right) \qquad \text{(Equation 2)}$$

where B is the methane production at time t (mL_CH4/g_VS), P is the maximum methane production (mL_CH4/g_VS), Rm is the maximum methane production rate (mL_CH4/(g_VS*day)), λ is the lag time (day), t is the time (day), and e corresponds to exp (1), equal to 2.7183. For each selected waste, the biomethane potential ratio between the thermally treated waste and the untreated waste, FN [9], was used for comparison between thermally treated and untreated biomethane potential.

3 Results and Discussions

3.1 Material characterization

Table 1 shows the material characterization results for the selected waste papers, and the inoculum (anaerobic sludge) used. Total solids (TS) and volatile solids (VS) values are expressed as percentage over the wet weight of the samples. The VS values are used for the calculation of biomethane potential.

Table 1: Total solids and volatile solids characterization for the selected waste papers

	(g/100g_wet_solid)	
	Total solids	Volatile solids
Newspaper	93 ± 0.1	80 ± 0.2
Cardboard	94 ± 0.1	86 ± 0.3
A4 paper	94 ± 0.1	79 ± 0.4
Anaerobic sludge	5 ± 0.4	3 ± 0.2

3.2 Biomethane potential

Figure 1 shows the cumulative biomethane kinetics for all the 3 selected waste papers, untreated and thermally treated. Figure 1 also shows the simulated biomethane production by Gompertz model and the modified Gompertz model for the respectively wastes. Note that the scales of the different plots in Figure 1 are different, in order to better present each waste's biomethane kinetics. The biomethane potential values of the three waste papers are in the range of what it has reported in literature [7, 8, 14].

Figure 2 presents the methane production rate kinetics for the 5 wastes, untreated and thermally treated, and the simulated results using Gompertz model and the modified Gompertz model. Figure 3 summarize the experimental determined biomethane potential for each untreated and thermally treated waste, the FN (ratio between thermally treated BMP over untreated BMP, see section 2.4) and the maximum biomethane production rates (Rm) for all waste determined by the Gompertz and modified Gompertz model.

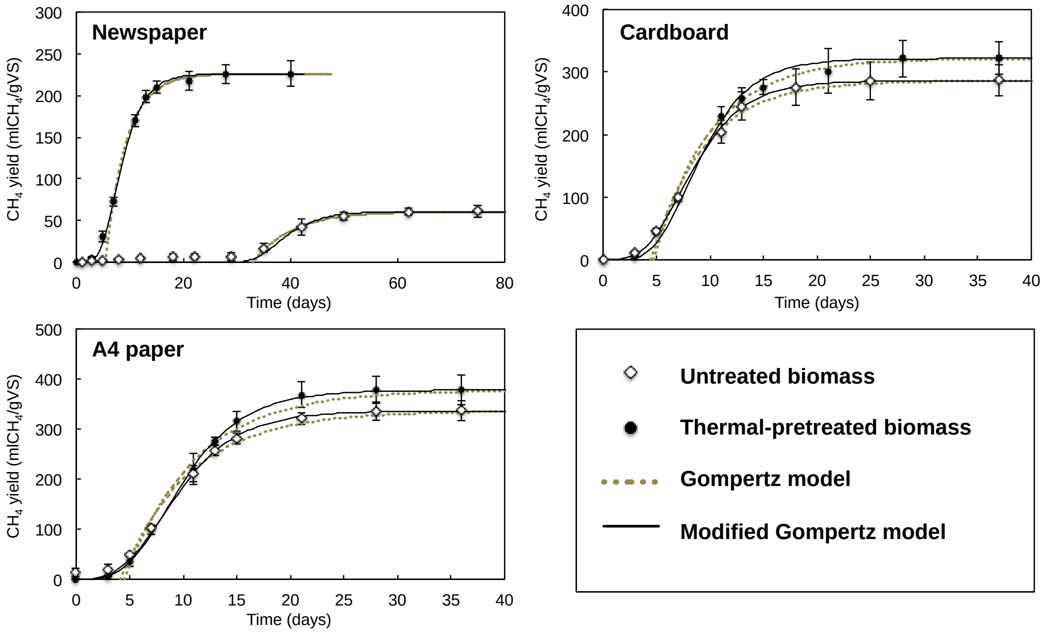

Figure 1: Cumulative biomethane kinetics for the selected untreated and steam pre-treated waste papers, and their simulation by Gompertz and modified-Gompertz models.

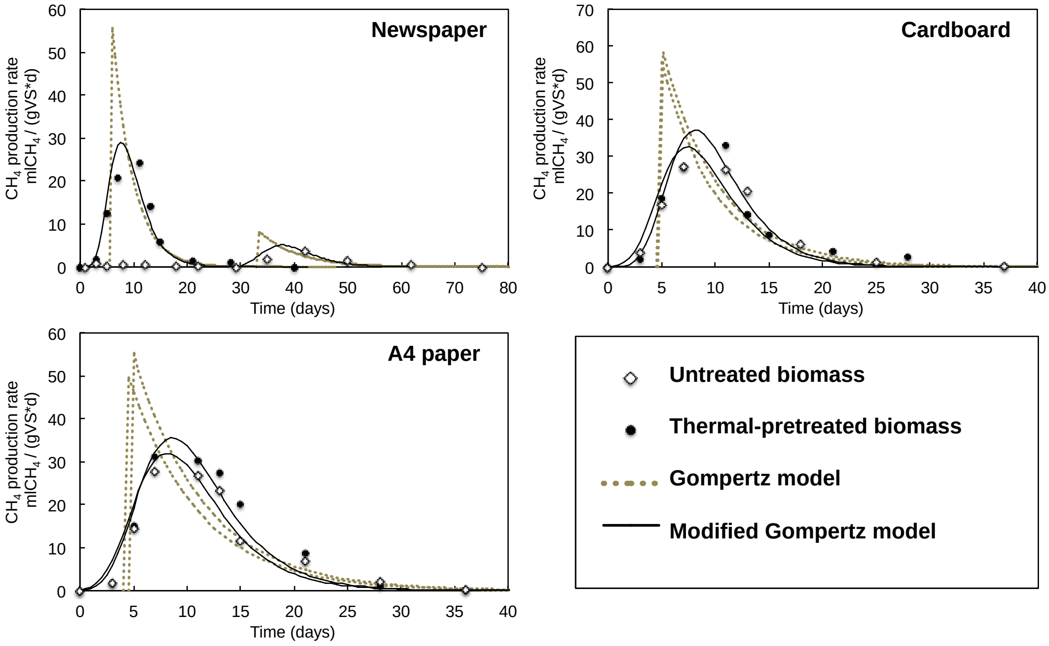

Figure 2: Methane production rate kinetics for the selected untreated and steam pretreated waste papers, and their simulation by Gompertz and modified-Gompertz models.

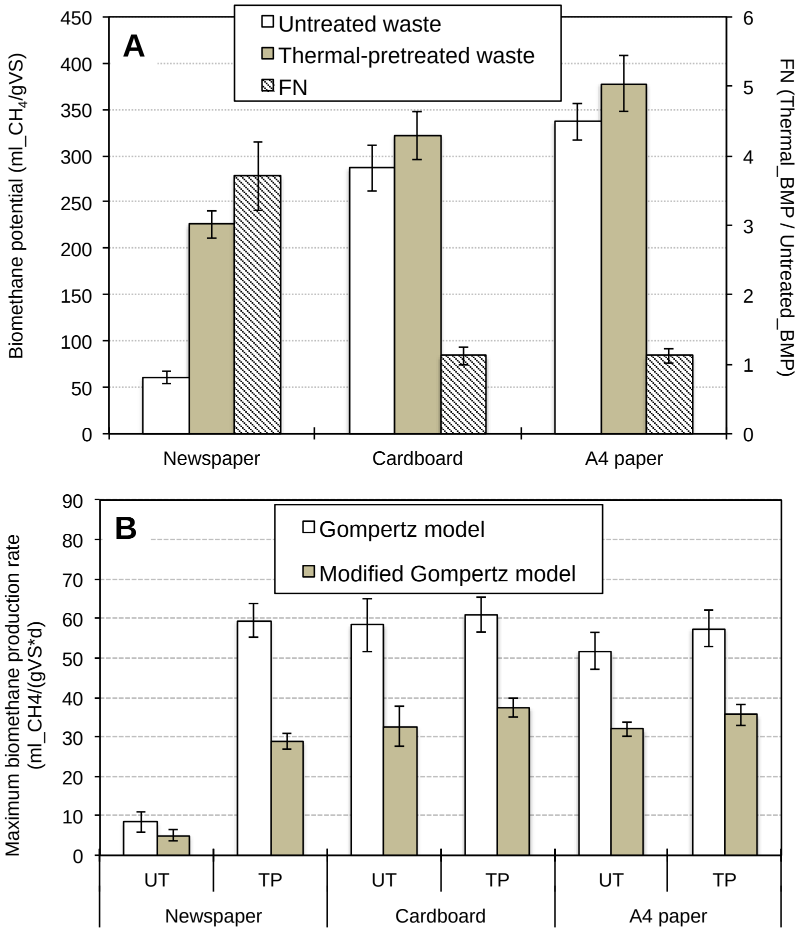

Figure 3: **A**, summary of biomethane potential (BMP) for the selected untreated (UT) and thermally steam pretreated (TP) waste papers, BMP ratio between thermally steam pretreated over untreated wastes, FN. **B**, maximum biomethane production rates (Rm) estimated by the Gompertz and modified-Gompertz models.

Under the tested conditions, the BMP (Figures 1 and 3A) of the untreated newspaper waste was 60 ml_CH_4/g_VS, and cardboard and office paper (A4) were 290 and 340 ml_CH_4/g_VS, respectively. The steam pretreatment resulted in an increase of the BMP for the different waste papers. The highest increase was obtained for stream pretreated newspaper, 270% increase, (FN 3.7), when compared with the untreated newspaper BMP, i.e. from 60 to 225 mL_CH_4/gVS (Figure 3A). The steam pretreatment BMP increase was not significant, 12% (FN 1.12) for cardboard and office paper (A4). Also the untreated and pretreated BMP for each of these two waste papers (Figure 3A) are statistically similar, i.e. 290 ± 25 and 320 ± 26 mL_CH_4/gVS for untreated and pretreated cardboard, respectively, and 340 ± 20 and 380 ± 30 mL_CH_4/gVS for untreated and pretreated office paper (A4), respectively.

The obtained BMP values in this study are comparable with the values obtained in the literature. Walter et al. [14] obtained a BMP of 331 mL_CH_4/gVS from steam pretreated (121 °C, 20 minutes) pulp residues from industrial paper waste production. This signified only a 2% increase when compared to the untreated pulp residue (BMP 323 mL_CH$_4$/gVS).

The present work results highlight the fact that the valorization of non-recyclable waste paper is possible. This will not only prevent the useless emissions of green house gases, i.e. from landfilling of this kind of wastes, but it has the potential to create revenues, instead of only costs, from the utilization of biomethane for heat and power generation [3, 5]. Another attractive way to generate revenues from this kind of wastes is the production of organic acids and biohydrogen by dark fermentation [25–27]. If an organic waste is methanizable, it also can be processed by dark fermentation. Market prices for organic acids are in the range of 400-2,500 USD/tonne [4, 25, 28] versus 0.05-0.12 USD/tonne of natural gas (biogas can be further processed to have similar characteristics to natural gas) [28], making dark fermentation process a more attractive option for the treatment of organic wastes.

The Gompertz and modified-Gompertz estimated maximum biomethane production rates (Rm) are different (Figure 3B). In general, for the same data set, Gompertz model estimates higher Rm values than the modified Gompertz model. The modified Gompertz model simulated data seems closer to the experimental data (Figures 1 and 2) than the Gompertz model. This is clearer when comparing both simulated and experimental data in Figure 2. Table 2 presents a coefficient of determination (R^2) analysis for both Gompertz and modified Gompertz simulated data respect to the experimental data, for the cumulative biomethane production (Figure 1) and for the biomethane production rate (Figure 2). Based on the calculated coefficient of determination, the modified Gompertz model seems to provide a better simulation for the cumulative biomethane production and the biomethane production rate. Anyhow, more sophisticated modeling attempts have been done by other authors [29, 30], as well as advanced statistical analysis [31].

Table 2: Coefficient of determination (R2) analysis for the experimental data and the Gompertz and modified Gompertz models

		R2 Cumulative biomethane production		R2 Biomethane production rate	
		Gompertz	Modified-Gompertz	Gompertz	Modified-Gompertz
Untreated	Newspaper	0.9959	0.9913	0.4089	0.7401
	Cardboard	0.9882	0.9994	0.4512	0.8550
	A4 paper	0.9940	0.9994	0.4709	0.9104
Steam pretreated	Newspaper	0.9972	0.9991	0.5416	0.8486
	Cardboard	0.9896	0.9964	0.4905	0.9176
	A4 paper	0.9895	0.9994	0.4069	0.9350

4 Conclusions

The present work focus waste paper biomethane potential (BMP) experimental determination. 3 waste papers were selected: newspaper, cardboard and office paper (A4). BMP was determined individually for each of the wastes. Thermal steam pretreatment of the 3 wastes, at 120 °C for 30 minutes, was performed to determine the extent of BMP improvement. Steam pretreatment resulted in a BMP increase of 270%, for newspaper waste, compared to the untreated waste. For the other two waste papers the steam pretreatment did not resulted in a significant BMP increase. Anyhow, the BMP results are close to the maximum theoretical BMP for carbohydrates, i.e. 400 mL_CH_4/gVS. The experimental results were analyzed by Gompertz model and modified Gompertz model. The analysis showed that the modified Gompertz model simulate in a more accurate extent the experimental data.

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Appendix A - Heating curve, and calculation of severity factor log(Ro)

Figure A.1 presents the heating curve of the thermal pretreatment, i.e. set point temperature of 120 °C for 30 minutes.

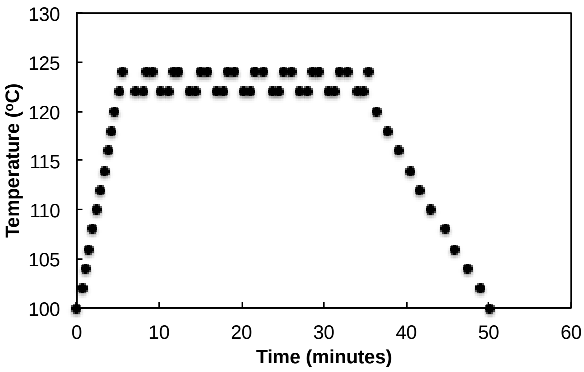

Figure A.1: Experimental temperature profile for the hydrothermal treatment of abattoir animal waste.

The experimental heating temperature profile for the hydrothermal treatment is used to create the Pt profile as in Figure A.2. As in section 2.4, the severity factor, log(Ro) is function of the integral of t*Pt. This has been solved by numerical integration, using the experimental discrete points.

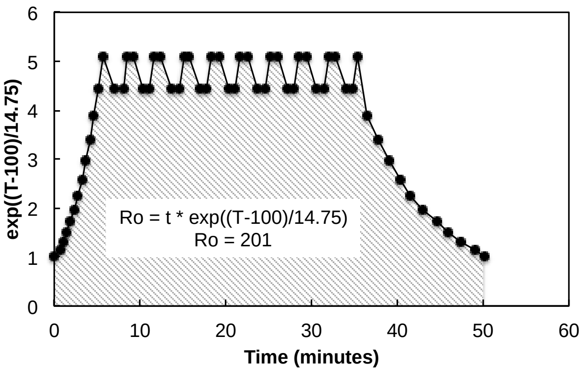

Figure A.2: Plotting of experimental Pt, and numerical integration of Ro.

log(Ro) was calculated according to Hendriks and Zeeman (2009), where Ro is the combined effect of steam temperature (over 100 °C) and time, described by Overend and Chornet (1987) by equations A.1 to A.3.

$$Pt = e^{\frac{T-100}{14.75}} \qquad \text{(equation A.1)}$$

$$Ro = \int t \cdot Pt \, dt \qquad \text{(equation A.2)}$$

$$Ro = \sum (t_{i+1} - t_i)\left(Pt_i + \left|\frac{Pt_{i+1} - Pt_i}{2}\right|\right) \qquad \text{(equation A.3)}$$