Batch anaerobic digestion of banana waste - energy potential and modelling of methane production kinetics

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Abstract: Different fractions of banana (stalk, peel, and flesh) as well as the whole unpeeled banana were studied in a laboratory Biochemical Methane Potential (BMP) assay. After completion of 35-day digestion at 37 °C in 2L-reactors, specific methane yields reached 0.256, 0.322, 0.367 and 0.349 m ³kg VS (volatile solids) for stalk, peel, flesh, and unpeeled banana respectively. Considering the country of Uganda, East Africa, the collection of peels and stalks from banana production would yield a theoretical potential of about 60 GWh of electrical energy per year in biogas plants. In order to verify the suitability of banana fractions to the biogas process, their chemical composition was analyzed, and their methane production kinetics was estimated with exponential and logistic models. Banana peel was found to be easily degradable, and well suited for biogas production. Banana flesh had the fastest degradation rate of all banana fractions, and banana stalk had the slowest degradation rate, respectively. Methane production kinetics was fitted with first order and logistic models. The kinetics of methane production kinetics from banana stalk correlated well with exponential models, but did not with the logistic model. Methane production kinetics from banana peel did not correlate well with any model. Hence, the biochemistry of anaerobic processes may follow different patterns depending on substrate degradability, explaining the difficulty of finding a universal explanatory model of methane production kinetics in batch mode.

Keywords: biogas, anaerobic digestion, BMP assay, model, energy, methane, waste

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1 Introduction

1.1 Anaerobic digestion of banana waste

In 2012, Uganda produced 570 kt of bananas and 9200 kt of plantains, showing its importance as a staple food in the region (FAO, 2014). Per ton of bananas harvested about 0.1 t of rejected flesh and about 4 t of waste were produced (Abdullah et al., 2013). Furthermore, processing of banana to figs, flour and matooke also results in waste generation, comprising leaves, stalks and peels (Kalia et al., 2000). Improper disposal of banana waste can cause severe environmental nuisance through the release of noxious gases (Ilori et al., 2007). Biogas technology can address these issues by reducing the waste stream into landfills while generating energy (Koumanova and Saev, 2008). Gudo and Singarvelu (2014) reviewed the biogas potential from food waste, and found that the amount of waste generated during post harvest, distribution and processing of fruit and vegetables exceeds by far the amount of residues generated in the consumption stage.

Table 1 shows the methane production of banana fractions reported by different studies. Methane yields ranged between 223 and 336 L/kg volatile solids (VS) for banana peel, and between 188 and 334 L/kg VS for banana stalk, respectively, while banana flesh may reach almost 400 L/kg VS. Unfortunately many studies could not be included into this presentation because little

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information was available regarding either methane yields or assay conditions, or banana was applied in co-digestion with other substrates (Deivanai et al., 1995; Ilori et al., 2007; Inthapanya et al., 2013; Mandal and Mandal, 1997; Saha and Nagori, 2002; Sharma et al., **1.2 Modeling of batch anaerobic digestion** 1999; Viswanath et al., 1992; Zafar et al., 2014; Zainol et al., 2012). Based on literature results alone, it is difficult to establish a ranking of the digestibility of banana stalk, peel and flesh, and to evaluate their suitability to the biogas process.

generated at infinite time will be supposed to be equal to

Substrate	Process conditions	Methane yield	Reference	
Banana peel	Batch digestion 35 ℃	227 L/kg VS	Zheng et al, (2013)	
Banana peel	Batch digestion 21 d; 55 °C	289 L/kg VS	Buffiere et al, (2006)	
Banana peel (0.5 cm)	Batch digestion 35 d; 37 °C	294 L/kg VS	Tumutegyereize et al, (2011)	
Banana peel (different particle sizes, 0.1 - 3 cm)	Batch digestion 37 ℃	223-336 L/kg VS	Sharma et al, (1988)	
Banana peel (different varieties)	Batch digestion 100 d; 35 ℃	243-322 L/kg VS	Gunaseelan et al, (2004)	
Banana peel (chopped)	Continuous digestion 40 d; 37 °C	190 L/kg VS	Bardiya et al, (1996)	
Banana stalk (1 cm, air dried)	Batch digestion 40 d; 35 °C Inoculum:substrate ratio of 0.25 related to TS	~188 L/kg VS (control) 232 L/kg VS (Pretreated with 6% w/w NaOH)	Zhang et al, (2013)	
Banana stalk (1-2 cm)	Batch digestion 57 d; 37 ℃	196 L/kg VS	Kalia et al, (2000)	
Banana stalk	Continuous digestion 37-73 d; 37 °C OLR: 0.45-0.88 g VS/(L ×d)	192-334 L/kg VS	Elortegui et al, (1986)	
Banana waste (peduncle + green banana)	Fed batch digestion 70 d; 38 $^{\circ}$ C OLR: 0.6 g VS/(L × d)	398 L/kg VS	Clarke et al, (2008)	

 Table 1
 Methane yields of banana fractions reported in literature

Notes: TS: total solids, VS: volatile solids, FM: fresh mass, OLR: organic loading rate. °C: degrees Celsius (digestion temperature), d: days (retention time)

Models describing the kinetics of batch anaerobic digestion have been reviewed by researchers dealing with animal nutrition (Beuvink and Kogut, 1993; Fahey and Hussein, 1999; Mertens, 2005; Schofield et al., 1994), biogas production (Appels et al., 2008; Batstone, 2006; Gerber and Span, 2008; Lauwers et al., 2013; Lübken et al., 2010; Lyberatos and Skiadas, 1999; Pavlostathis and Giraldo-Gomez, 1991; Simeonov, 1999; Tomei et al., 2009; Vavilin et al., 2008; Yilmaz, 2003), and landfill gas production (Barlaz et al., 1990; Elagroudy and Warith, 2009; Hartz and Ham, 1982; Kamalan et al., 2011).

The present study analyzes the kinetics of cumulated methane production in batch anaerobic digestion. The primary objective is to estimate the ultimate methane yield at infinite time $(t \rightarrow \infty)$. This amount of methane

the total amount of degradable substrate available (S).

A first order model assumes that the rate (R_S) or velocity of reactant utilization (substrate) is proportional to the amount of reactant available in the medium:

$$R_{\rm s} = k \times S_{\rm t} \tag{1}$$

kFirst-order kinetics constant;

 \mathbf{S}_{t} : Amount of undegraded substrate remaining at time t (variable).

Integration along reaction time yields an exponential equation that gives the remaining (undegraded) substrate at time t (S_t) (Lopes et al., 2004):

$$S_t = S \times e^{-kt} \tag{2}$$

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S Total amount of degradable substrate;

k First-order kinetics constant;

t Time after experiment start-up.

Applying the kinetics of product formation to batch anaerobic digestion, the cumulated amount of methane generated at time t, (M_t) can be expressed as follows (Model A) (Ørskov and McDonald, 1979):

$$M_t = S \times \left(1 - e^{-kt}\right) \tag{3}$$

Model A is the most common model for the description of batch anaerobic digestion kinetics (Balat and Balat, 2009; Bilgili et al., 2009; Converti et al., 1999; El-Mashad, 2013; Gunaseelan, 2014; Jokela et al., 2005; Kafle et al., 2014; Owens and Chynoweth, 1993; Tong et al., 1990; Turick et al., 1991; Veeken and Hamelers, 1999; Veeken et al., 2000; Zaman, 2010; Zeng et al., 2010). This model assumes that substrate is converted into methane in a single-step reaction. However, from a biochemical point of view, anaerobic digestion is generally described as four subsequent steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Appels et al., 2008; Demirel and Scherer, 2008; Lyberatos and Skiadas, 1999; Muha et al., 2012; Shin and Song, 1995; Torre and Stephanppoulos, 1986). Furthermore, from a process engineering point of view, the biogas process may be simplified into two steps: an acidification step, comprising both hydrolysis and acidogenesis, which generates mainly volatile fatty acids (VFA) as reaction intermediates, and a methane production step, comprising both acetogenesis and methanogenesis, which generates methane as end product (Brulé et al., 2013; Hobson and Wheatley, 1993; Shin and Song, 1995; Weiland, 2001). Based on this concept, Shin and Song (1995) proposed a model accounting for a two-step process:

$$M_{t} = S \times \left(1 + \frac{k_{H} \times e^{-k_{VFA}t} - k_{VFA} \times e^{-k_{H}t}}{k_{VFA} - k_{H}}\right)$$
(4)

 $\mathbf{k}_{\mathbf{H}}$ First-order kinetics constant of substrate degradation;

 \mathbf{k}_{VFA} First-order kinetics constant of VFA degradation.

A competing approach is to assume that the reaction follows first-order kinetics (i.e. single reaction step), but that the substrate is divided into two fractions with different hydrolysis conversion velocities (Mertens, 2005; Schofield et al., 1994). Based on the latter approach, Rao et al. (2000), Kusch et al. (2008), and Luna del Risco et al. (2011) described methane production kinetics in batch anaerobic digestion with a model assuming the substrate to be divided into two pools, each following first-order kinetics:

$$M_{t} = S \times \left(1 - \alpha \times e^{-k_{F}t} - (1 - \alpha) \times e^{-k_{L}t}\right)$$
(5)

 α Ratio of rapidly degradable substrate to total degradable substrate;

 $\mathbf{k}_{\mathbf{F}}$ First-order kinetics constant for the degradation of rapidly degradable substrate;

 $\mathbf{k}_{\mathbf{L}}$ First-order kinetics constant for the degradation of slowly degradable substrate.

By combining previous models, Brulé et al. (2014) suggested a dual-pool two-step model (Model B) that assumes two distinct substrate pools (dual-pool), and two consecutive reaction steps in each compartment (two-step) as well:

$$M_{t} = S \times \left[\alpha \times \left(1 + \frac{k_{F} \times e^{-k_{VFA}t} - k_{VFA} \times e^{-k_{F}t}}{k_{VFA} - k_{F}} \right) + \left(1 - \alpha \right) \times \left(1 + \frac{k_{L} \times e^{-k_{VFA}t} - k_{VFA} \times e^{-k_{L}t}}{k_{VFA} - k_{L}} \right) \right]$$
(6)

The models described previously are derived from first-order reaction kinetics. Logistic models provide a different expression of reaction rates that is commonly applied to the simulation of population growth and of chemical autocatalysis reactions (Cramer, 2004). Kirubakaran et al. (2009) and Upadhyay et al. (2008) applied logistic models to the simulation of the biogas process. One of the simplest logistic models is Verhulst equation (Baca ër, 2011; Pearl and Slobodkin, 1976; Verhulst, 1847).

According to Verhulst kinetics, the rate of methane production (R_M) can be expressed as follows (Tsoularis and Wallace, 2002):

$$R_{M} = r \times M_{t} \times \left(1 - \frac{M_{t}}{S}\right) \tag{7}$$

r Kinetics constant;

 \mathbf{M}_{t} Total amount of methane already generated at time t (variable);

S Saturation constant and total amount of substrate.

This expression shows that the reaction rate increases initially, and later decreases as the total amount of substrate (S) is applied as a constant of saturation. According to Kirubakaran et al. (2009), initially, reaction rates are low due to low bacterial activity at the beginning of the digestion period. Subsequently, the reaction rate increases due to the activation and multiplication of bacterial cells. Finally, the depletion of substrate causes reaction rates to collapse towards the end of the digestion period. This pattern is similar to autocatalytic kinetics.

Applying Verhulst equation, the cumulated amount of methane generated at time t, (M_t) can be expressed as follows (Tsoularis and Wallace, 2002):

$$M_{t} = \frac{S \times M_{0}}{(S - M_{0}) \times e^{-rt} + M_{0}}$$
(8)

 M_0 Amount of methane at t=0.

In order to be functional, Verhulst equation requires the initial amount of methane in the medium to be different from zero ($M_0 \neq 0$). This is not the case in batch anaerobic digestion assays. Nevertheless, this error is insignificant as the estimated value of M_0 is likely to be close to zero. Hence, this shortcoming of Verhulst equation will be ignored.

For convenience in building up a variable optimization method for the model, Verhulst equation can be simplified into the following expression (Model C) (Meyer, 1994; Wikipedia, 2014):

$$M_t = \frac{S}{w \times e^{-rt} + 1} \tag{9}$$

w Constant.

1.3 Objectives

This study has the following objectives:

 Estimate the amount of electrical energy that can be produced from anaerobic digestion of banana waste in Uganda;

(2). Perform batch anaerobic digestion assays at the laboratory to evaluate the suitability of banana waste fractions to the biogas process;

(3). Apply simple models to evaluate the kinetics of batch anaerobic digestion;

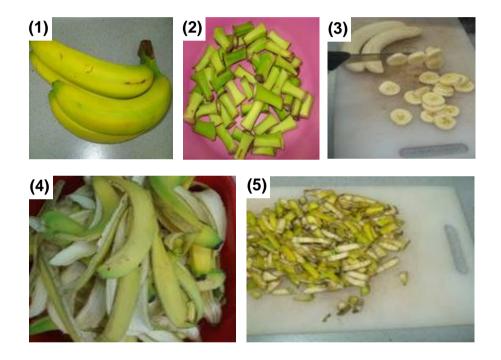
(4). As quality control, estimate the ultimate methane yields (at infinite time) with the models, and compare the results to values obtained experimentally in the anaerobic digestion assay to the end of the digestion period (35 days).

2 Materials and methods

2.1 Experimental design

Five substrates were tested for their methane production in a laboratory batch anaerobic digestion assay (Biochemical Methane Potential assay, BMP): hay (control and standard substrate), banana peel, banana stalk, banana flesh and unpeeled banana. Each variant was tested in four replicates using a laboratory apparatus comprising 24 reactors. At the beginning of the batch experiment, inoculum and substrate were added in a single step before closing the reactors. Reactors of the zero variant were fed with inoculum alone. The remaining reactors were fed with both inoculum and substrate.

Hay originated from permanent grassland, and was dried and ground to 1 mm fiber length for storage and conservation. Bananas (*Musa indica*) of Cavendish variety were purchased from a local whole sale market of Stuttgart (Germany) shortly before the experiment started. A sample of 100 bananas was separated into peel, stalk and flesh fractions. The banana fractions were weighed in order to determine their average proportion to the fresh mass of the whole, unpeeled banana. Subsequently, peel, stalk and flesh fractions as well as the unpeeled banana were chopped to a length of 5-10 mm, and mixed in buckets to generate a homogenous material (Figure 1). Inoculum was prepared at the State Institute of Agricultural Engineering and Bioenergy as described previously (Bolduan et al., 2011; Brul é 2014).



(1) unpeeled banana; (2) banana stalk; (3) banana flesh cut into slices; (4) banana peel; (5) banana peel cut into slices
 Figure 1 Processing of bananas

In order to calculate the amounts of substrate and inoculum to be fed into the reactors, the dry matter (total solids, TS) and organic matter (volatile solids, VS) of substrates and inoculum were determined as described previously (Brul & 2014; Brul é et al., 2013). The loading rate of the reactors was set at 12 g VS/L reactor volume. The loading corresponded to a inoculum:substrate ratio of 0.7 related to VS. As a comparison, the optimal inoculum:substrate VS ratio often recommended in the literature is ~ 2 (Angelidaki and Sanders, 2004; Fabbri et al., 2014; Kawai et al., 2014; Raposo et al., 2011; Shelton and Tiedje, 1984; VDI 4630, 2006). Table 2 shows total solids (TS) and volatile solids (VS) contents of the sole inoculum, and of the substrates (hay, banana peel, banana stalk, banana flesh, unpeeled banana), as well as the amounts fed into batch reactors.

Variant -	TS and VS contents		Amount fed into batch reactors		
variant	TS, % (FM)	VS, % (DM)	Substrate, g (FM)	Inoculum, g (FM)	
Sole inoculum	1.87 ±0.02	41.13 ±4.63	-	1800	
Hay	92.34 ±0.07	91.92 ±0.75	25	1800	
Banana peel	9.70 ±0.08	86.29 ±0.16	258	1800	
Banana stalk	8.60 ±0.26	83.35 ±0.23	301	1800	
Banana flesh	22.38 ±0.24	92.98 ±0.75	96	1800	
Unpeeled banana	17.90 ±0.98	89.72 ±1.99	125	1800	

Table 2Total solids (TS) and volatile solids (VS) contents of the sole inoculum and of the substrates(hay, banana peel, banana stalk, banana flesh, unpeeled banana), and amounts fed into batch reactors

Notes: FM: fresh mass, DM: dry mass

2.2 Anaerobic digestion assay

The laboratory apparatus was composed of 24 reactors, each of 2 L capacity. The design and function of the apparatus have been described in previous works (Brul é, 2014; Mönch-Tegeder et al., 2014a; Mönch-Tegeder et al., 2013). The amounts of biogas generated were determined according to a volumetric

method: each reactor was connected to a gas outlet. Each gas outlet was connected to a 3.2 L-transparent cylinder (gasometer) for gas collection. The gasometer was diving onto a broader cylinder filled with a barrier solution (Figure 2). The composition of the barrier solution was taken from ISO 14853 (1997) as described by Müller et al. (2004).

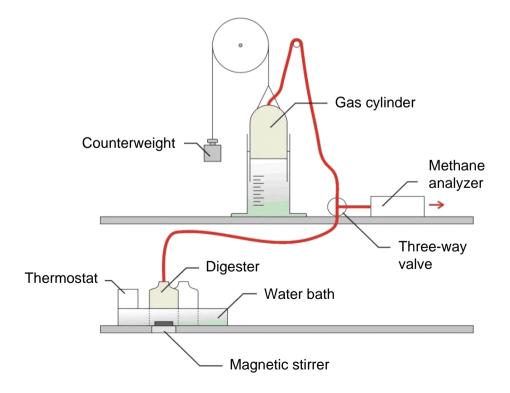


Figure 2 Design of the laboratory batch reactors (Source: Barthelme ß, 2008)

Anaerobic digestion was performed according to the German directive VDI 4630 (2006). At the start of the experiment, glass digesters were fed with the desired amounts of inoculum and substrate. Biogas produced by each reactor was guided into a separate gasometer. Gas measurement was performed as described in previous works (Brulé, 2014; Brulé et al., 2013; Mittweg et al., 2012). Gas and methane content measurement of each gasometer took place 13-14 times within the digestion period for the reactors filled with sample material, and only three times for the reactors filled with the sole inoculum, respectively. For this purpose, each gasometer was completely emptied and biogas was directed into a methane analyzer equipped with an infrared sensor for methane content measurement. Before and after each gas measurement phase, the methane analyzer was tested with ambient air as well as a standard gas containing ~60% v/v of CH₄ / ~40% v/v of CO₂, and calibrated if necessary.

Each reactor had a filling volume of about 1800 mL, and a headspace volume of only about 500 mL. Hence, the effect of initial air contamination on the assay was neglected, and inert gas sparging was not necessary to maintain anaerobic conditions in the reactor. In the course of anaerobic digestion, temperature was kept at 37 C with a water bath, and reactor contents were mixed for about 1 min every 15 min by magnetic stirrers (Figure 2). pH of the inoculum was within the range 7-8, which is favorable to anaerobic digestion. pH during the assay was not measured because the design of the equipment did not allow sampling after closing of the reactors.

The cumulated methane yield of dry gas at standard conditions (0 °C, 1013.25 hPa) was calculated according to VDI 4630 (2006). The cumulated methane production of the sole inoculum was correlated with a second-order polymeric curve. Applying this correlation, methane production of the inoculum was estimated for each reactor and subtracted from the total methane production (Brulé et al., 2013). Finally, methane yields were calculated in m^3/kg VS from the test

substrate as described in previous works (Bolduan et al., 2011; Brul é 2014).

2.3 Substrate composition

Substrate composition was analyzed at the State Institute for Agricultural Chemistry of the University of Hohenheim. Fibre analysis was based on the Van Soest method (Van Soest et al., 1991), which is widely used for fodder analyses. Analysis protocols were taken from German standards of VDLUFA method book (Naumann and Bassler, 1997).

2.4 Data fitting to the models

The three models (A, B, C) described in Introduction were fitted to the data series with Matlab® software, version 7.4.0 (R2007a). The Levenberg-Marquardt algorithm (Levenberg, 1944; Marquardt, 1963) was selected as a data fitting function. Arbitrary initial conditions were used to initiate the iteration process are specified in Table 3. As described in this table, optimization results of Model A were applied as initial conditions for Model B. As an example, the Matlab® code of the data series "banana flesh" is listed in the Appendix section. The Matlab® optimization function [lsqcurvefit] vas used. [Optimset] was kept at default values that have been specified in a previous paper (Brulé et al., 2014). The number of iterations required for the convergence of data to the models was always below 50. Furthermore, models always fulfilled the default optimization criteria: directional derivative along search direction less than [TolFun] and infinity-norm of gradient less than [10*(TolFun+TolX)], where the default value for both [TolFun] and [TolX] was 1×10^{-6} .

Table 3 Initial conditions for the iterations as definedin data fitting commands

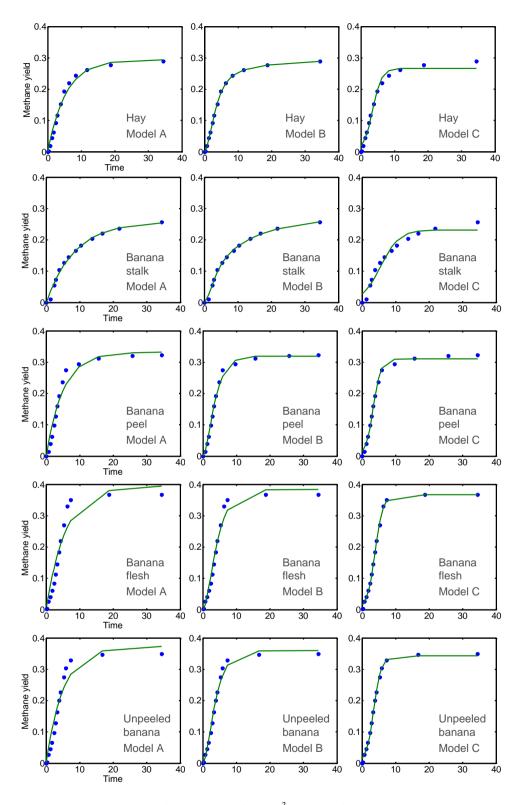
Model level	Model type	Constants				
A	First-order	\mathbf{S}_0	\mathbf{k}_0			
A	1 IISt-OLUEI	1	1			
В	Dual-pool	\mathbf{S}_0	α_0	k_{F0}	k_{L0}	$k_{\rm VFA}$
	two-step	S ^A	0.5	k A	$k^{A}/2$	k ^A $\times 2$
С	Verhulst	\mathbf{S}_0	\mathbf{W}_0	\mathbf{r}_0		
C	equation	1	2	1		

Notes: ^A Model constants obtained after completion of data fitting for Model A

3 Results

3.1 Validity range of the models

Figure 3 shows the experimental results fitted by Models A, B, and C, and Table 4 shows the estimated model constants after completion of the optimization process. The exponential models, Model A and Model B, were accurate only for hay and banana stalk. Model A is widely used for the estimation of rate constants and of the ultimate methane yield in batch anaerobic digestion assays (BMP assays). Although the level of correlation of Model A to real data of methane production kinetics is often poor, this model is very robust as it requires the estimation of only two constants, namely ultimate methane yield (S) and first-order constant (k). Alternately, Model B is less reliable as it requires the estimation of five model constants. For hay and banana stalk, two model constants were at the same level (kF \approx kVFA). Furthermore, for banana peel, banana flesh and the unpeeled banana, three model constants were at the same level ($kF \approx kL \approx kVFA$). The redundancy in Model B may indicate a poor convergence the experimental results, although variable to optimization was rated as successful by the software. The redundancy may also imply that Model B can be replaced with a simpler model, comprising fewer variables. The logistic model, Model C, was accurate only for banana flesh and for the unpeeled banana, the latter containing a high proportion of flesh. These are the most rapidly degradable substrates. Banana peel was in an intermediate situation between rapid biodegradation and slow biodegradation. Surprisingly, for banana peel no model could provide an accurate fitting of methane production kinetics.



Units: methane yield, m³/kg VS; Time, d Figure 3 Methane yields versus time of the substrates and fitted models

Model type	Substrate	Model correlation		Estimated model constants				
		\mathbb{R}^2	MAE	S	K			
	Hay	0.9887	0.0109	0.2943	0.1849			
First-order	Banana stalk	0.9902	0.0051	0.2591	0.1164			
(Model A)	Banana peel	0.9648	0.0196	0.3320	0.1989			
	Banana flesh	0.9371	0.0321	0.3958	0.1720			
	Unpeeled banana	0.9575	0.0250	0.3737	0.1939			
		\mathbf{R}^2	MAE	S	α	$k_{\rm F}$	$k_{\rm L}$	k_{VFA}
	Hay	0.9996	0.0014	0.2933	0.7834	0.5629	0.0790	0.5629
Dual-pool	Banana stalk	0.9969	0.0026	0.2698	0.3653	0.6096	0.0802	0.6097
two-step (Model B)	Banana peel	0.9948	0.0071	0.3195	0.6441	0.5076	0.5075	0.5077
	Banana flesh	0.9824	0.0146	0.3840	0.5930	0.4344	0.4343	0.4344
	Unpeeled banana	0.9921	0.0090	0.3596	0.7700	0.4838	0.4836	0.4838
		\mathbb{R}^2	MAE	S	W	R		
	Hay	0.9842	0.0114	0.2666	13.1060	0.7343		
Verhulst equation (Model C)	Banana stalk	0.9572	0.0147	0.2315	7.4103	0.3604		
	Banana peel	0.9943	0.0078	0.3105	19.6258	0.8873		
	Banana flesh	0.9977	0.0044	0.3669	25.5526	0.8314		
	Unpeeled banana	0.9966	0.0063	0.3431	21.6258	0.8712		

Table 4 Model constants and fitting accuracy

Notes: since data is nonlinear, the R^2 coefficient was gained from a linear correlation between measured and estimated values at each data point. MAE: Mean Absolute Error (Willmott and Matsuura, 2005).

3.2 Ultimate methane yields at infinite time

For each substrate, the models estimate the ultimate methane yield at infinite time, which is characterized by the variable S of the models. These values can be compared with the methane yields achieved to the end of the digestion period, i.e. after 35 days (Table 5). The methane yield achieved within the 35-day digestion period amounted to 94%-100% of the best estimates provided by the models for the ultimate methane yield. Hence, high levels of substrate degradation were reached in the assay, while moderate digestion duration of 35 days was applied. These results indicate very good digestion conditions.

 Table 5 Measured values after 35 days of digestion and estimated values of the ultimate methane yield at infinite time

Substrate	Methane Content 1 , % (v/v)	Measured methane yield after 35 days, m ³ /kg VS	Methane yield from Model A at infinite time, m ³ /kg VS	Methane yield from Model B at infinite time, m ³ /kg VS	Methane yield from Model C at infinite time, m ³ /kg VS
Нау	54.2 ± 0.2	0.288 ± 0.005	0.294	0.293 ²	0.267
Banana stalk	57.8 ± 1.0	0.256 ± 0.007	0.259	0.270 ²	0.232
Banana peel	53.9 ± 0.9	0.322 ± 0.011	0.332	0.320	0.311
Banana flesh	49.6 ± 0.6	0.367 ± 0.007	0.396	0.384	0.367 ²
Unpeeled banana	49.4 ± 0.3	0.349 ± 0.005	0.374	0.360	0.343 ²

Notes: Measured values as averages $(n=4) \pm SD$.¹ measured methane content in the total amount of biogas produced from the substrate till the end of the digestion period (35 days)² Very good correlation of the model with experimental data of methane production kinetics (see Figure 3)

3.3 Energy potential of banana waste

Table 6 shows the theoretical energy potential from banana waste for the East African country of Uganda in 2012. Collecting all peels from the banana produced in Uganda would yield 56.72 GWh_{el}/a of electrical energy. Converted into power, this corresponds to a constant

supply of 6.5 MW_{el} (assuming continuous operation of biogas plants i.e. 8766 h/a). The calculation is based on the assumption that residues from all banana produced in Uganda can be recovered.

Banana fraction	Share in the fresh mass of the banana, % w/w FW	Ugandan production, kt FW/a	Ugandan production, kt VS/a	Measured methane yield, m ³ /kg VS	Amount of methane produced, Mm ³ /a	Electrical energy, GWh/a
Unpeeled banana	100	570	91.54	0.349	31.948	-
Banana stalk	2.6	14.62	1.06	0.256	0.268	2.67
Banana peel	37.1	211.11	17.70	0.322	5.690	56.72
Banana flesh	60.3	344.27	71.52	0.367	26.292	-

 Table 6
 Energy potential of biogas production from banana waste

Notes: a: annum (year); calculations are based on the assumptions that 100% of the banana stalk and peel can be collected and used in biogas plants, with cogeneration units with an electric efficiency of 35%, based on a LHV value of methane of 9.968 kWh/m^3 (Cerbe et al., 2008)

4 Discussion

4.1 Biodegradability of the substrates

Tong et al. (1990) and Buffiere et al. (2006) found an inverse relationship between fibre content, i.e. lignin and cellulose content, and substrate biodegradation in the biogas process. The kinetics constants of Model A (k) and Model C (w, r) increased while lignin and cellulose contents of the substrates decreased (comparing Table 4 with Figure 4). Hence the relationship between fibre content and biodegradation of substrates was validated. Furthermore, lower fibre contents and faster degradation rates of the substrates were linked to higher contents in non-structural carbohydrates (NSC, also named NFE, non-fibrous extract, cf. Figure 4). This observation confirmed the findings of Mauky et al. (2015), who noticed that substrates containing high shares of NSC were degraded more rapidly.

Banana peel was easily degradable, with model kinetics constants (k, w, r) almost as high as banana flesh and the whole, unpeeled banana (Table 4). This pattern may be related to the presence of a high share of NSC in banana peel, amounting to 48% of VS, as shown in Figure 4.

Due to its low fibre content, banana peel can probably be used at a high share in the substrate mix of full-scale biogas reactors. Banana stalk is less degradable, but according to the dual-pool two-step model (Model B), banana stalk may still contain an easily degradable fraction that accounts for about 37% of its total methane generation (i.e. α =0.3653, cf. Table 4). Banana flesh and the unpeeled banana, which were degraded at the fastest rates, contained very high shares of NSC amounting to 91% and 81% of VS, respectively.

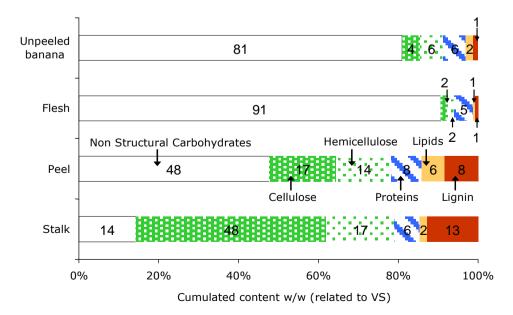


Figure 4 Chemical composition of the banana fractions and of the unpeeled banana

4.2 Kinetics of batch anaerobic digestion

Microbiologists and researchers in the biogas field have suggested empirical models such as the modified Gomperz equation, as well as the Chapman-Richards model, to evaluate batch anaerobic digestion (Altaş, 2009; Chapman, 1961; Li et al., 2013; Mähnert, 2007; Mähnert et al., 2002; Mu et al., 2007; Richards, 1959; Zwietering et al., 1990). Donoso-Bravo et al. (2010) compared different models for the evaluation of batch digestion of sewage sludge. Strömberg et al. (2015) compared first order, Monod and Gomperz models with different substrates and concluded that modelling can be used for estimating the final methane yield and reducing the duration of batch anaerobic digestion assays.

This paper focused only on a few models that are based on a theoretical background for the interpretation of the methane production rate. However, the models studied in this experiment were valid only under specific conditions, and there was no universal model that would match with methane production kinetics of all substrates. Furthermore, while being efficient in data fitting as well as the estimation of ultimate methane yields for slowly degradable substrates, Model B is redundant and can be probably be simplified under these particular assay conditions. However, we could not yet identify a simplified model that reaches similar accuracy, and further research is necessary.

According to the exponential models, which are based on first-order kinetics, methane production at a given time is directly proportional to the amount of substrate available in the medium. Alternately, according to the autocatalysis model, methane production is initially low, then reaches a maximum due to bacterial activation, and finally decreases due to scarcity and/or reduced biodegradability of substrate. Contrary to first-order kinetics models, the autocatalysis model takes into consideration an increase in bacterial activity in the course of the batch assay. This typical characteristic may explain why the autocatalysis model is well suited to rapidly degradable substrates. Alternately, considering slowly degradable substrates, bacterial development during the batch assay has little impact, and first-order kinetic models are more appropriate. Hence, the exponential models may be suited to slowly degradable, lignocellulosic substrates whereas logistic models may be suited to rapidly degradable substrates. Further experiments would be required to confirm this hypothesis.

4.3 Energy production from banana waste

Clarke et al. (2008) estimated that a stream of 1 t/d (fresh mass) of banana waste can be converted into 7.5 kW_{el} (i.e. kW of electrical power). The results of our study validated that ratio: we found that 1 t/d of banana stalk can yield 7.6 kW_{el}, while 1 t/d of banana peel can yield 11.19 kW_{el} (assuming constant supply).

According to our laboratory results, banana peel can be considered an easily degradable substrate that is particularly suitable to biogas production. The use of all peels and stalks from the banana cultivated in Uganda into biogas plants could yield about 60 GWhel of electrical energy per year (cf. Table 6), or a continuous supply of ~6.5 MW_{el} . In comparison, Tock et al. (2010) calculated a potential power of 190-270 MW_{el} of biogas production from banana residue for the country of Malaysia. However, the estimate of these authors may include the valorization of other waste streams such as overripe banana and banana peduncles. These figures represent the maximum energy potential. Taking for granted that a 100% use of the banana wastes is not a realistic assumption, the numbers can be adjusted according to the percentage of waste collected for biogas production. Plantain production has not been considered in this work. Plantain accounts for a high share of local food consumption (FAO, 2014), so that the use of plantain peels would probably yield a high energy potential.

About 19% of the energy gained via anaerobic digestion of the whole banana can be produced by the waste fractions of the banana (cf. Table 6): stalk and peel. Banana flesh should be fed into biogas plants only in the

case of unpalatable, overripe banana. If the biogas technology can be implemented close to banana production sites, excess heat from the cogeneration engine may be used in a drier for efficient production of dried banana, hereby limiting waste production and increasing food security. Alternately, in Uganda and other African countries, biogas can be used directly for heating and cooking, replacing firewood and reducing deforestation (Menya et al., 2013). Furthermore, if the biogas process is run properly, the digested effluent, which is compost-like, odorless, and free of pathogens, can be used as an efficient organic fertilizer in the fields for food production (Lukehurst et al., 2010). Hence, biogas production from organic waste can have a positive impact on food security, contrary to food-competitive bioenergy sources such as sugarcane bioethanol and palm oil (Nzila et al., 2010; Sabiiti, 2011).

4.4 Suitability of banana waste for anaerobic digestion

Banana waste should not be digested alone, but in combination with other waste streams of fruits and vegetables such as plantain. Gudo and Singarvelu (2014) found that post-harvest, distribution and processing generate more waste than the final consumption of fruit and vegetables. Hence, farms and companies dealing with products in the agricultural sector must be involved in waste collection schemes.

Mono-digestion of fruit and vegetable waste may not be advisable due to nutrient unbalance and trace metals deficiency, both hampering the development of anaerobic bacteria. Nutrient-rich co-substrates such as livestock dejections are best suited to provide stable and efficient digestion conditions (Lemmer et al., 2010; Preißler et al., 2007a; Preißler et al., 2007b; Vintiloiu et al., 2012; Weiland, 2006; Weiland, 2010). Furthermore, mechanical particle size reduction in full-scale biogas plants should be performed to the same extent as in this laboratory experiment to prevent the accumulation of floating layers as well as difficulties in mixing/pumping of reactor contents (Bolduan et al., 2011; Izumi et al., 2010; Mönch-Tegeder et al., 2014a; Mönch-Tegeder et al., 2014b; Schimpf, 2014; Sharma et al., 1988). Hence, special consideration should be given to processes for mechanical particle size reduction of banana residue as well as to the addition of nutrient-rich co-substrates, such as livestock dejections.

5 Conclusions

The methodologies presented in this article can assist in the estimation of the energy potential of biogas production from organic waste streams. These methodologies must be further developed by researchers, in order to raise awareness about the potential of biogas technology for developing countries, and try to gain institutional support (Sabiiti, 2011).

This study shows that banana waste can be degraded easily in the biogas process. Furthermore, mechanical pre-treatment of the substrate is recommended to ensure high conversion rates. Particularly, the peel fraction can be degraded very easily and therefore is a very good candidate for biogas production.

Due to low amounts of waste generated, the potential of energy production of banana residue in the biogas process is rather low, but if other streams, such as plantain waste can also be used, the energy potential for tropical African countries can be high. In this regard, the whole processing chain should be taken into account while implementing waste collection schemes, since high amounts of waste are produced during harvest, post-harvest, and processing of fruit and vegetables (Gudo and Singarvelu, 2014).

As suggested in previous studies (Bruléet al., 2014; Strömberg et al., 2015), modeling can be used to evaluate and improve batch BMP assays. However, methane production kinetics follows different patterns depending on substrate characteristics. The slowly degradable banana fraction (stalk) followed first-order kinetics (exponential models). Alternately, rapidly degradable banana fractions (flesh and whole unpeeled banana) followed autocatalysis (logistic model). Hence, the biochemistry of microbial conversion may react in different ways depending on substrate degradation rate. Since models of batch anaerobic digestion are a simplification of complex biochemical pathways, only the most influential parameters are selected and retained in the models. Hence, designing a simple universal model is a difficult task. Instead of relying on one single universal model, an alternative option is to select the most appropriate model depending on both substrate characteristics and assay conditions.

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APPENDIX

Matlab® command lines, exemplified through the data series of Banana flesh

% Program works since Matlab Version 7.4.0
(R2007a)
% Optional display settings
clc; format compact; format short;
set(0,'DefaultFigureWindowStyle','normal');

% Entering data series: t= time - y= methane yield t=[0.15 0.32 0.74 1.32 1.90 2.36 2.86 3.36 3.86 4.36 5.36 6.36 7.36 18.74 34.47]; y=[0.0018 0.0026 0.0259 0.0399 0.0601 0.0834 0.1123 0.1447 0.1837 0.2190 0.2694 0.3295 0.3505 0.3670 0.3669];

% Selecting Levenberg-Marquardt algorithm for iterations and enabling display options = optimset('LargeScale','off','LevenbergMarquar dt','on','Display','on');

% First order kinetics model
F = @(a,xdata)a(1)*(1 - exp(-a(2)*xdata)); a0 =
[1 1];
[a] = lsqcurvefit(F,a0,t,y,[],[],options);

% Two-pool two-step reaction model

```
G
@(b,xdata)b(1)*(b(2)*(1+(b(3)*exp(-b(5)*xdata
)-b(5)*exp(-b(3)*xdata))...
/(b(5)-b(3)) + (1-b(2)) * (1+(b(4)) * exp(-b(5)) * xda
ta) -b(5) *exp(-b(4) *xdata))/...
(b(5)-b(4)));
b0 = [a(1) \ 0.5 \ a(2) \ a(2)/2 \ a(2)*2];
[b] = lsqcurvefit(G,b0,t,y,[],[],options);
% Verhulst equation
H = Q(c, xdata) c(1) . / (1+c(2) * exp(-c(3) * xdata));
c0 = [1 \ 2 \ 1];
[c] = lsqcurvefit(H, c0, t, y, [], [], options);
%Displaying constants of all models in the
command window
disp('Model A. First order kinetics model');
disp('
        S
                    k'); disp(a)
disp('Model B. Two-pool two-step
                                      reaction
model');
disp('
           S
                      alpha
                                   kF
                                             kL
kVFA'); disp(b)
disp('Model C. Verhulst')
disp('
          S
                   kΑ
                            kB'); disp(c)
% Plotting models curves and residuals
set(0, 'DefaultFigureWindowStyle', 'normal',...
'DefaultLineLinewidth',2.5, 'DefaultAxesFontSi
ze',18,'DefaultLineMarkerSize',25,...
'defaultaxeslinewidth',2.5,'defaultpatchlinew
idth',2.5);
set(figure, 'Units',
                                 'Normalized',
'OuterPosition', [0 0 1 1]);
                       plot(t,y,'.',t,F(a,t));
subplot(2,3,1);
title('Model A. 1st order'); xlabel('Time');
ylabel ('Methane yield')
                       plot(t,y,'.',t,G(b,t));
subplot(2,3,2);
title('Model B. 2-pool 2-step');
subplot(2,3,3);
                       plot(t,y,'.',t,H(c,t));
title('Model C. Verhulst');
subplot(2,3,4);
                             plot(t, F(a, t) - y);
title('Residuals
                    A');
                            set(gca, 'Ylim',
[-0.1; 0.1])
subplot(2,3,5);
                             plot(t,G(b,t)-y);
title('Residuals
                    B');
                                       'Ylim',
                            set(gca,
[-0.1; 0.1])
subplot(2,3,6);
                             plot(t, H(c, t) - y);
title('Residuals
                    C');
                            set(gca,
                                      'Ylim',
[-0.1; 0.1])
cf = corrcoef(F(a,t),y); disp('R2 model A');
disp(cf(2)^2);
cg = corrcoef(G(b,t),y); disp('R2 model B');
disp(cg(2)^2);
ch = corrcoef(H(c,t),y); disp('R2 model C');
disp(ch(2)^2);
ef = y-F(a,t); aef = abs(ef); maef = mean(aef);
disp('MAE model A'); disp(maef);
eg = y-G(b,t); aeg = abs(eg); maeg = mean(aeg);
disp('MAE model B'); disp(maeg);
eh = y-H(c,t); aeh = abs(eh); maeh = mean(aeh);
disp('MAE model C'); disp(maeh)
```

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