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# Influence of chemical composition on biochemical methane potential of fruit and vegetable waste

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## ABSTRACT

This study investigates the influence of chemical composition on the biochemical methane potential (BMP) of twelve different batches of fruit and vegetable waste (FVW) with different compositions collected over one year. BMP ranged from 288 to 516 L<sub>N</sub> CH<sub>4</sub> kg VS<sup>-1</sup>, with significant statistical differences between means, which was explained by variations in the chemical composition over time. BMP was most strongly correlated to lipid content and high calorific values. Multiple linear regression was performed to develop statistical models to more rapidly predict methane potential. Models were analysed that considered chemical compounds and that considered only high calorific value as a single parameter. The best BMP prediction was obtained using the statistical model that included lipid, protein, cellulose, lignin, and high calorific value (HCV), with R<sup>2</sup> of 92.5%; lignin was negatively correlated to methane production. Because HCV and lipids are strongly correlated, and because HCV can be determined more rapidly than overall chemical composition, HCV may be useful for predicting BMP.

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## 1. Introduction

Fruit and vegetable waste (FVW) is an important category of waste that is produced in large amounts in wholesale markets and through other activities around the world (Sitorus et al., 2013; Viturtia et al., 1995). Approximately 1728 million tons of fruit and vegetables were produced worldwide in 2011; Brazil has a leading position in this market, as the third largest fruit producer in the world and the third largest vegetable producer in the Americas (FAO, 2014a).

According to the Food Wastage Footprint and Climate Change Report (FAO, 2014b), around 15% of fruit and 25% of vegetables are wasted at the bottom of the production chain. Traditionally, about 97% of Brazilian household and public waste, including FVW, enters landfills and dumping sites, while only 2% of waste

is recycled and 1% is composted; there is no registered data about energy recovery (IPEA, 2011).

FVW is characterized by high moisture content and rich biodegradable organic compounds, typically with solid content under 10%, and 85% corresponding to organic matter (Scano et al., 2014; Wang et al., 2014). These characteristics may contribute to negative issues in traditional solid waste disposal systems, such as greenhouse gas emissions and leachate discharge in landfills (Hartmann and Ahring, 2006). Along with these negative environmental impacts, the production of FVW increases market operating costs due to transport costs, sales losses, and disposal costs (Scano et al., 2014).

In contrast to this loss, anaerobic digestion (AD) can convert FVW into biogas, which can be used to produce energy while avoiding the aforementioned environmental issues (De Baere, 2006; Kafle et al., 2014). AD is a widely applied biochemical conversion process for the treatment of organic wastes such as manure, crop residues, and FVW (Appels et al., 2011). The scientific literature contains several studies on AD of FVW (Jiang et al., 2012; Lin et al., 2011; Sitorus et al., 2013; Wang et al., 2014), but

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only a few studies have been carried out using FVW as the only substrate. Moreover, few studies report the influence of organic matter composition on biochemical methane potential (BMP) over time.

A consequence of the increasing implementation of AD is the need to determine the ultimate methane potential of substrates, as this is a key parameter for implementation of AD processes (Angelidaki et al., 2009). One way to determine the properties of a given substrate for AD is to perform BMP assays on the substrate as well as macromolecular composition analysis to provide a good characterization of the substrate's organic features (Cabbai et al., 2013; Holliger et al., 2016; Raposo et al., 2011).

Organic matter can be fractionated into easily biodegradable compounds including carbohydrates, lipids, and proteins, and poorly biodegradable compounds such as lignocellulosic biopolymers (Triolo et al., 2012). Although characteristics such as solid content of FVW show little variation, the quality of organic matter must also be investigated, as methane productivity depends not only on the amount of volatile solids, but also on the nature of the organic compounds (Buffiere et al., 2006).

Unfortunately, BMP testing is very time consuming, as it is based on microbial processes (Lesteur et al., 2010; Strömberg et al., 2015). However, there is a relationship between methane yield and the type of organic matter found in substrate. Some studies have successfully found this relationship by building mathematical regression models that compare the organic matter and the amount of methane produced (Buffiere et al., 2006; Cu et al., 2015; Dandikas et al., 2014). However, none of them has used FVW as a single substrate.

The objective of this study was to determine the BMP of FVW and the relationship between methane production and the macromolecular composition of FVW using twelve different FVW mixtures sampled monthly over the course of one year in Brazil. Moreover, a statistical model was generated to predict BMP.

## 2. Material and methods

### 2.1. Substrate and analytical methods

Samples of FVW were collected monthly between September 2014 and August 2015 (12 in total) from a Municipal Central Supply (Foz do Iguaçu/Brazil) for determination of BMP. Samples consisted of stem, leaves, seeds and fruit bodies, which were homogenized immediately after collection by milling in an industrial blender (Polis LS-08); water was not added in order to maintain the original physical characteristics. Total solids (TS), volatile solids (VS) and pH were determined according to standard methods (APHA, 2005). To minimize the effect of sample aging and improve analytical precision, all samples were then dried at 60 °C, ground to a diameter smaller than 2 mm, and refrigerated at 4 °C until use. The drying and milling process does not significantly affect the ultimate methane potential, but it can improve the precision of tests (Raju et al., 2011; Triolo et al., 2012, 2014; Wahid et al., 2015).

Chemical composition and high calorific value (HCV) were determined from the dried sample. To express the chemical composition as solids content, and to determine the solids conditions of BMP tests, TS and VS were also determined from the dried sample. Lipid (LP) content and total Kjeldahl nitrogen (TKN) content were determined according to standard methods (APHA, 2005). Protein (PT) content was estimated by multiplying TKN by a factor of 6.25 (FAO, 2002), considering that ammonia nitrogen concentration is negligible.

Carbohydrates (CB) were estimated by the difference between 100 and the sum of the percentages of protein, lipid, lignin, water

and ash (FAO, 2002). Neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL) were measured to determine cellulose (CL), hemicellulose (HC), and lignin (LG) content according to Van Soest et al. (1991). Non-lignocellulosic carbohydrate (NLC) content was estimated by the difference between 100 and the sum of protein, lipid, water, ash, and lignocellulose (cellulose, hemicellulose, and lignin). A calorimeter pump was used to determine HCV (DIN 51900/00) of the dried samples.

### 2.2. BMP assay

The BMP was determined using a batch technique based on the guidelines proposed by VDI 4630 (2006). The system was composed of 39 glass reactors (200 mL each) coupled to graduated eudiometer tubes (300 mL). For each treatment (month of collection), three reactors were incubated with inoculum and substrate; three reactors containing only inoculum were used as control, for a total of 39 batch reactors. All tests were performed at the same time.

The inoculum was a mixture of two digestates and one organic waste – effluent from a biogas plant processing swine manure, effluent from a biogas plant processing cattle manure and a raw cattle manure, respectively – obtained from the mesophilic demonstration units of the International Centre for Renewable Energy – Biogas located in western Parana/Brazil. The mixture ratio was 1:0.5:0.5% (wt/wt%).

The inoculum was kept in a stainless steel reactor (working volume of 100 L) under continuous stirring at 60 rpm and the temperature was controlled at 37 °C. The inoculum was maintained by weekly feeding with a mixture of substrates with an organic loading rate (OLR) of 0.5 VS kg m<sup>-3</sup> d<sup>-1</sup> to keep it adapted and active. The feeding substrate was composed of powdered milk (25%), soy protein (10%), maize flour (20%), dry grass (25%), and vegetable oil (20%). The inoculum feeding procedure is a strategy of the International Centre for Renewable Energy – Biogas to maintain it in anaerobic mesophilic condition and acclimatized to several substrate compositions over time, as the availability of mesophilic biogas plants in Brazil is limited.

Three additional glass reactors were used to study the biological activity of the inoculum in a parallel test, using microcrystalline cellulose as the reference sample (Sigma-Aldrich, 20 µm diameter). After 10 days of batch AD, the biogas volume reached the minimum recommended by VDI 4630 (80% of the theoretical production of biogas, 740–750 mL<sub>N</sub> g VS<sup>-1</sup>), validating the effectiveness of the inoculum used in the tests.

AD tests were performed with 1 g VS substrate and 200 mL inoculum. All masses were recorded and the gas production related to the inoculum was subtracted for each reactor. Solids content was kept below the recommendations provided by VDI 4630 with TS under 10%, VS between 1.5% and 2.0%, and inoculum to substrate ratio (ISR) greater than 2 to prevent inhibitions during the experiment. Nitrogen gas was used to purge the air contained in the reactors. The batch experiment was maintained in a water bath at a controlled temperature of 37 °C for 32 days, at which point daily production represented less than 1% of the total accumulated produced gas. Digesters were agitated daily via manual shaking.

### 2.3. Methane content

The measured biogas was corrected to dried biogas at normal temperature and pressure conditions, and biogas yield was reported in normal litres per kilogram of volatile solids (L<sub>N</sub> kg VS<sup>-1</sup>) from Eqs. (1) and (2) at normal conditions:

$$V_0 = V \cdot \frac{(P_L - P_W) \cdot T_0}{P_0 \cdot T} \quad (1)$$

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