Characterization of Particulate Substrates in Batch Reactors for Design and Modelling Purposes

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Abstract
An experimental protocol in batch reactor was designed for the measurement of the methane yield and of the kinetics of degradation of particulate substrates. This protocol requires successive batches to be carried out until the evolution of the biogas production is reproducible from one batch to the other. The developed protocol was applied to 18 particulate substrates in order to start a data base including the methane yield and the kinetics of degradation of the organic matter. The data were used for modelling the behaviour of a co-digestion reactor treating a mixture of 5 fruits and vegetables.

Keywords
Anaerobic digestion, Methane yield, Kinetics, batch.

INTRODUCTION

The measurement of the methane yield and of the kinetics of degradation of the organic matter of particulate substrates in batch reactors presents several advantages compared to the traditional BMP measurement method: (i) The measurement is made with acclimatized biomass as the experimental protocol in batch reactor requires to carry out successive batches until the biogas profiles from one batch to the other are similar. Indeed, experiences carried out in batch reactors have shown that the kinetic of the first batch is very often quite different from that of the other batches (Torrijos, 2009) and it is very important to take this into account for the measurement of the kinetics of degradation; (ii) The S_0/X_0 is much lower (0.04-0.08 g VS_{added}/g VSS) than that used in the classical BMP protocols (0.5-1 g VS_{added}/g VSS). This makes it possible to have rather short reaction times (< 7 days), making it possible to maintain the activity of the sludge from one batch to the other, and to be closer to the conditions used at industrial scale; (iii) The volume of biogas produced over time during the batches can be monitored online making it possible to measure accurately the kinetics of biogas production for each batch. As a result of both the number of batches and the low S_0/X_0, there is no lag phase in the final batch which is used to interpret the results.

MATERIALS AND METHODS

Substrates: The work presented in this paper focuses mainly on fruits and vegetable but the characterization of other kinds of substrates is currently ongoing and the first substrates have been included. The following 18 substrates have been studied: 5 fruits (peach, grape, mango, pineapple, banana), 7 vegetable (green cabbage, potato, carrot, lettuce, tomato, cauliflower, chayote) and 6 other substrates (oil cake from coconut oil production, micro-algae (*Scenedesmus sp.*), ground beef, coalfish, pork fat and grape marc).

Reactors: The experiments were carried out in four double-walled reactors of 6-L effective volume, maintained at 35 °C by a regulated water bath. Mixing in the reactors was done by a system of magnetic stirring. The biogas production was measured on-line by Milligascounter MGC-1 flow meters (Ritter gas meters) fitted with a 4-20 mA output. The "Modular SPC" software developed at the INRA laboratory was used to log gas output.

Inoculum: The reactors were seeded at a volatile suspended solids concentration (VSS) of around 12-14 g VSS/l with anaerobic sludge taken from an industrial-scale anaerobic UASB reactor treating the effluents from a sugar refinery. After seeding and before starting the addition of the waste, the reactors were fed 5 times with 5 mL of ethanol as sole source of carbon and energy to check the activity of the sludge.
Sampling and analysis: Gas composition was measured using a chromatograph Shimadzu GC 8 associated with an integrator Shimadzu GC 3A. The vector gas was argon. Other parameters were measured following Standard Methods.

RESULTS AND DISCUSSION

Design of a standard protocol in batch reactor

A standard protocol was designed for the operation of the batch reactors and used individually for 18 substrates for validation. Each reactor was fed with one of the substrates and operated in fed-batch mode for about 2 months, depending on batch length, with successive batches without withdrawal. The quantity of VS added at the beginning of each batch was 0.5 g/l for the first 3 batches and then 1 g of VS/l for the following 4 to 5 batches. The S_0/X_0 ratios were around 0.04 g VS_{added}/g $VSS_{reactor}$ and 0.08 g VS_{added}/g $VSS_{reactor}$ for the reactors fed with, respectively, 0.5 g VS/l and 1 g VS/l at the beginning of the batch. The volume of biogas produced over time was monitored online and logged every two minutes. Towards the end of the batches, the biogas production rate became very low and a specific method was developed to find out the time when the sludge was back to its endogenous activity, that is to say the time when it could be assumed that the reaction was over and the organic matter added was eliminated. In this aim, a "biogas activity curve" was plotted with time for each batch see figure 1. This curve is a kind of derivative with respect to the last available biogas flow rate measurement. The biogas production rate by endogenous respiration was measured in the few hours following the end of the reaction time. It was assumed that endogenous activity was constant all over the batch and biogas production by endogenous respiration was removed from the total volume of biogas produced.
Seven to eight batches were carried out for each substrate, depending on the behaviour of the batches. The criteria to stop the experiment with a given substrate is that at least 7 batches should have been carried out and the last 2 batches should have a very close biogas production profile with time. At the end of the experiment with a given substrate, that is to say for the last batch, the volume of biogas produced was collected into a bag to analyze its composition in order to measure the total volume of methane produced during the batch and to calculate the methane yield of the substrate. The average specific kinetic of degradation was calculated by dividing the quantity of substrate added (in VS) by the duration of the batch and by the volatile suspended solids (VSS) concentration in the reactor. This parameter was also measured when 80% of the total volume of biogas was produced. An example of results obtained with "peach" is presented in figure 1.

Measurement of the Methane Yield and of the degradation kinetics of different substrates

The average specific reaction kinetics were evaluated at two different times. The fist one at the end of the reaction phase when the sludge was only at endogenous respiration and the second one when 80 % of the reaction was completed. The results of the methane yield and of the kinetics at 80 % of the reaction are reported at figure 2 for all the substrates studied.

For fruits and vegetables the methane yields were all between 230 and 360 ml CH4/g VS. However, the range of specific degradation kinetics was quite large with values in the range 0,03-0,1 g VS/gVSS.d. Fish and meat had close both methane yields and kinetics. Pork fat had a very high methane yield linked to its high fat content. Grape marc had the highest degradation rate probably because it contains an easily biodegradable fraction (ethanol mainly).

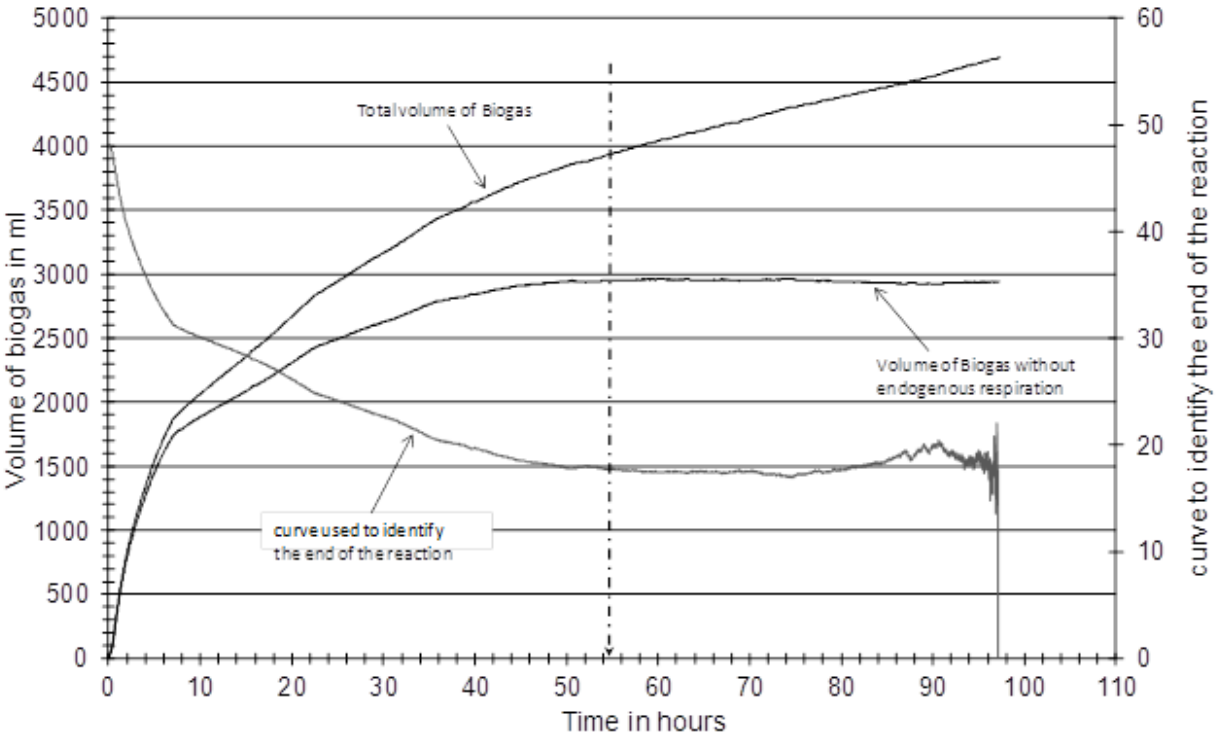

Figure 1: Evolution over time of the volume of biogas produced, of the volume of biogas without endogenous respiration and of the curve used to identify the end of the reaction (biogas activity curve).

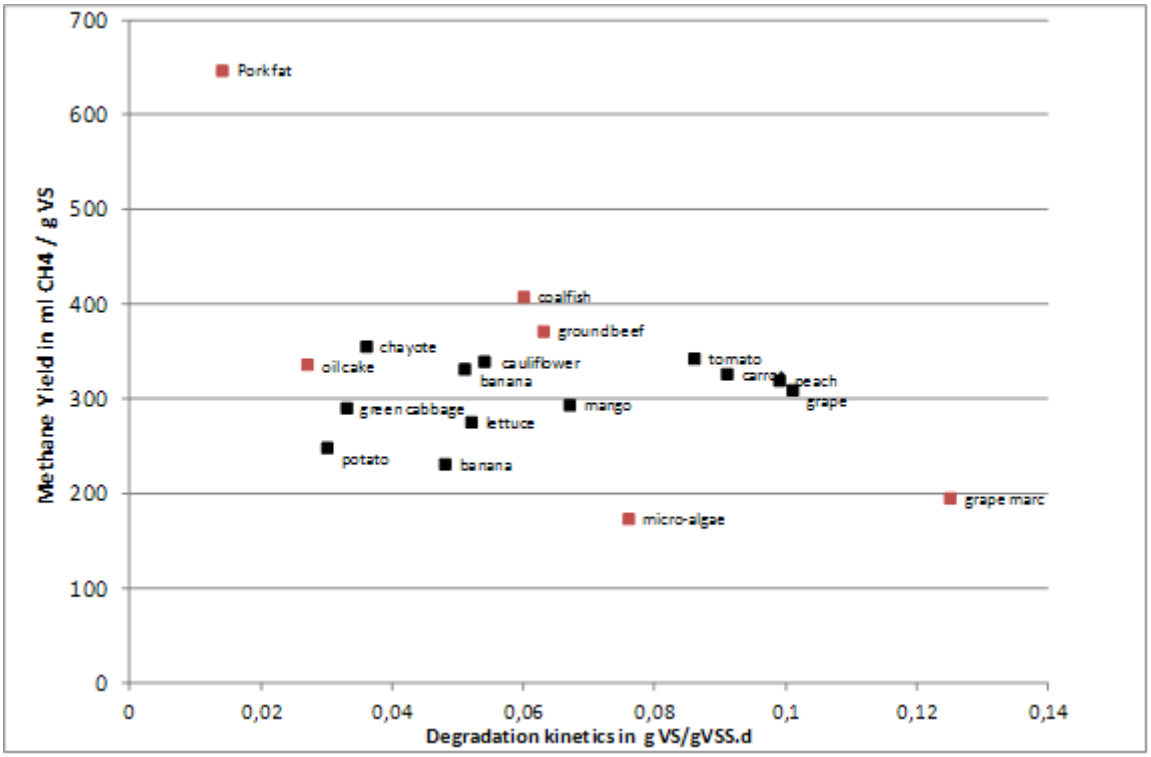

Figure 2: Methane yield and degradation kinetics for the 18 substrates studied.

Modeling of the data

The data obtained during this work were used for two purposes:

- The first objective was to make a classification of the different substrates based on their degradation kinetics, by the modeling of the biogas production curves. In this aim, the organic matter of the substrates was divided into compartments according to the degradation kinetics of these compartments (e.g. rapidly or slowly biodegradable) and according to the order of the reactions (first order or zero order). This first step involves the identification of a low number of parameters that are the initial fractions of slowly and readily biodegradable matter as well as the kinetics parameters associated to the models. It gives both an initial guess for a more accurate modeling of the system described herebelow and input data for a simple classification of the substrates under interest. This work is currently being done and will be presented at the conference.

- A methodology, using an ADM1-based AcoD model (*Anaerobic Digestion Model No.1*, ADM1 (Batstone et al., 2002), Garcia-Gen et al., 2013a), was developed to calculate kinetic parameters of disintegration and hydrolysis, readily and slowly biodegradable fractions, and inert fractions of particulate substrates from the results in batch reactors. For validation, a reactor treating a mixture of five fruits and vegetables (lettuce, potato, apple, carrot and banana) was run for 15 weeks in a continuous operation. The process was simulated with the AcoD model in order to validate the model for solid wastes. Parameters obtained from batch assays were used and ADM1 parameters remained constant. The results of this second part of modelling will be presented in details by Garcia-Gen et al., 2013b.

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