ENVIRONMENTAL AND SANITARY ENGINEERING

# Anaerobic digestion of food waste. Predicting of methane production by comparing kinetic models

INGENIERÍA AMBIENTAL Y SANITARIA

# Digestión anaerobia de residuos de alimentos. Predicción de la producción de metano mediante la comparación de modelos cinéticos

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**Abstract**

Anaerobic Digestion (AD) of food waste (FW) reduces risks to human health and environment, also increases the life of landfills, and mainly is an strategy to produce energy renewable as methane. Kinetic models can determine the influence of the factors that affect the process of AD and predicts more precisely methane production in order to prevent overestimation or underestimation, which may lead to the definition of real criteria to implement the technology. This study evaluated by means of Biochemical Methane Potential (BMP) assays, the AD of FW from a university restaurant using sludge from a UASB reactor in charge of treating municipal wastewater as inoculum. The factor evaluated was the influence of Substrate-Inoculum (S/I: 0.5, 1, 2 and 4 $gVS_{substrate} \cdot gVS_{inoculum}^{-1}$) ratio. For the prediction of methane were applied the kinetic models: Transfer Function, Logistics Function and Modified Gompertz models. It was found that the S/I ratio affect both, the efficiency of AD process and prediction of methane production, presenting the better results for S/I ratio below one. Within the kinetic models evaluated, the Logistic Function presented the best settings for predicting methane production and lag phase (R2> 0.9).

*Keywords: Anaerobic digestion, food waste, kinetic models, methane prediction.*

**Resumen**

La Digestión Anaerobia (DA) de los residuos de alimentos (RA), además de reducir los riesgos a la salud humana y el ambiente, permite aumentar la vida útil de los rellenos sanitarios y principalmente es una estrategia para la generación de un tipo de energía renovable como el metano. Los modelos cinéticos permiten determinar la influencia de los factores que afectan el proceso de DA y predecir de manera más precisa la producción de metano para evitar su sobreestimación o subestimación, que puede llevar a la definición de criterios reales para la implementación de la tecnología. Esta investigación evaluó, mediante ensayos de Potencial Bioquímico de Metano (PBM), la DA de RA provenientes de un restaurante universitario usando como inóculo lodo de un reactor UASB que trata aguas residuales municipales. El factor evaluado fue la influencia de la relación Sustrato-Inóculo (S/I: 0.5, 1, 2 y 4 $gSV_{sustrato} \cdot gSV_{inóculo}^{-1}$). Para la predicción de metano se aplicaron los modelos cinéticos de Función de Transferencia, Función Logística y el modelo Modificado de Gompertz. Se encontró que la relación S/I afectó tanto la eficiencia del proceso, como la predicción de la producción de metano, presentándose los mejores resultados en las relaciones inferiores a uno. Dentro de los modelos cinéticos evaluados, la función logística presentó los mejores ajustes para predecir la producción de metano y la fase de latencia ($R^2$> 0.9).

*Palabras claves: Digestión anaerobia, modelos cinéticos, predicción de metano, residuos de alimentos.*

## 1. Introduction

The final disposal of municipal solid waste (MSW) into landfills is the most applied worldwide strategy for its handling (Hoornweg et al., 2013). In Latin America, Europe and United States specifically, the fraction of MSW disposed into landfills represent approximately 73, 53 and 34%, respectively (TWB, 2012), which generates environmental impacts as: greenhouse gases-GHG, leachates, volatile organic compounds-VOC, among others. Additionally it causes environmental conflicts due to other issues such the devaluation of the surrounding land costs (Yang et al., 2014).

In developing countries, food waste (FW) represents over 60% of MSW (TWB, 2012; Oviedo et al., 2015). Currently, sustainable technologies such as composting and Anaerobic Digestion (AD) seek to reduce environmental impacts and human health effects, besides increasing the useful lifetime of landfills (Hartmann & Ahring, 2005) and provide added value to FW.

Previous work on the effect of substrate-inoculum (S/I: $gVS_{substrate} \cdot gVS_{inoculum}^{-1}$) ratio in the Biochemical Methane Potential (BMP) assay has been limited (Raposo et al., 2006). The specific methane production rate increases at S/I of 0.5; but at higher ratios, it was found that this rate begins to decline although steadily. The S/I proposed by Owen et al. (1987) as a standard was approximately 1.0; however Raposo et al. (2006) and Parra et al. (2015) recommend defining the S/I ratio that increases methane production according to the substrate to be treated.

The biochemical and physicochemical processes that occurs in AD of FW are influenced by various factors, reason for which is recommended to study this process experimentally by performing the application of kinetic models (Aldin et al., 2011). Inadequate predicting of methane production can lead to erroneous conclusions as underestimation or overestimation of methane generation, whose impact may reduce the reliability and quality of outcomes to optimize the process and to increase the methane production (Gao et al., 2014).

Modeling is an important tool used to assess aspects of bioprocesses and optimization of biological systems. AD is a complex and non-linear bioprocess, and many different approaches have been used in the last two decades for modeling, identification of parameters and validation, with a great variability of results reported, even under the same operational and environmental conditions (Rivera et al., 2009).

The most used kinetic model in batch test is the first order model, since it lets to set the rate of degradation of the substrate in the AD, specifically the hydrolysis rate; however, this model can not evaluate some aspects of great importance during the startup and operation of batch anaerobic reactors (Angelidaki & Sanders, 2004; Trzcinski & Stuckey, 2012; Hidalgo & Martín, 2014). Therefore, the prediction of the behavior of biomass and its relationship with the AD byproducts, mainly methane production, have caused the need to apply other kinetic models that also evaluate another important features as the duration of the lag phase, which is an important parameter in AD and is associated with the acidogenic and acetogenic stages (Aldin et al., 2011).

Other models that have been applied in batch test are: the Transference Function, Logistic Function and Modified Gompertz. The Transference Function or reaction curve is used mainly for control purposes, which considers that any process might be analyzed as a system receiving inputs and generating outputs; Logistics Function assumes that methane production is proportional to the size of the microbial population and to the digestible substrate (Li et al., 2012) and the Modified Gompertz assumes that the rate of methane production is proportional to the microbial activity, but this proportionality decreases with the solids retention time -SRT , which can be interpreted as a loss of efficiency in the rate of substrate conversion over time (Donoso-Bravo et al., 2010).

Although Modified Gompertz Model is one of the most applied kinetic models in the study of factors that affect AD of FW, it presents several drawbacks that affect the prediction of methane production.

Authors such as Donoso-Bravo et al. (2010) found that this model tends to give slightly higher values without providing a biological explanation (negative lag phase) and Li et al. (2011) argue that this model can be altered when S/I ratio is greater than 0.7. However, the few reported studies evaluating kinetic models of AD of FW, may be due to part of them are based on the assumption that the FW are a readily biodegradable substrate and that any model can easily predict methane production under the influence of various factors at the same time.

This research aims to evaluate both, the incidence of S/I ratio on the AD of FW from a university restaurant, as well as the influence of the prediction of methane production by using different semi empirical models for the BMP assays.

## 2. Materials and methods

### 2.1 Substrate an inoculum

The FW raw samples were obtained from a restaurant at Universidad del Valle (Cali, Colombia) during 5 weeks (one sample was taken every week) and the physical categorization (mixture of fibers and minerals, carbohydrates, fruits citrus and semi-citrus and non-citrus fruits) was made according to revealed by Oviedo et al. (2014). The physicochemical characterization (pH (UNT), Moisture (%), Total Alkalinity-TA and Bicarbonate-BA (mgCaCO$_3$·L$^{-1}$), Volatile Fatty Acids-VFA´s (mg·L$^{-1}$), Total and Filtered Chemical Oxygen Demand-COD (mg O$_2$·L$^{-1}$), Biological Oxygen Demand-BOD$^5$ (mg O$_2$·L$^{-1}$), Total Solids –TS and Volatile-VS (mg·L$^{-1}$)) were performed according to procedures described in Standard Methods (APHA, 2005).

Prior to characterization of FW and the BMP assays, the inert material and slow-degrading material (plastic) were removed as recommended by Mukherjee et al. (2008). Afterwards, a shredding process was implemented with a Waring Commercial blender during one minute at a speed of 15800 rpm (standard speed) as suggested by Sharma et al. (1988).

The inoculum was obtained from a UASB reactor of a municipal wastewater treatment plant

(WWTP), which was characterized in terms of pH, TA, BA, VFA´s, TS and VS. In addition, specific methanogenic activity-SMA (gCOD·gVS-1·d-1) tests were carried out. The FW samples and inoculum were maintained at a temperature below 4°C throughout periods of less than seven days before starting of tests. The results of the physicochemical characteristics of the substrate and inoculum samples were processed by descriptive statistics analysis.

### 2.2 BMP assays

The quantification of biogas was performed by using the manometric method using an Oxitop® system at 35 °C, which is a pressure-monitoring instrument that consists of a 250 mL reactor with a measurement device that is inserted on the mouth of the reactor with a control that uses an infrared interface for data transfer (Pabón et al., 2012). The tests were performed in a WTW TS 606-G/2-I incubator with intermittent manual agitation for a period of 21 days (Aquino et al., 2007). Based on the recommendations of Aquino et al. (2007), the working volume of the reactors was 200 mL, a free space of 50 mL was left with the aim of store the biogas produced. The volume of methane at standard conditions-SC (T= 273 K and P= 1 atm) was determined by applying the equations suggested by Giménez et al. (2012), where the ratio of dissolved methane was considered. The pH was 7.0 UNT conditioned with a solution of NaHCO$_3$ (4%). The nutrient solution used was the recommended by Angelidaki & Sanders (2004). The S/I ratios evaluated were 0.5, 1, 2 and 4 gVS$_{substrate}$·gVS$_{inoculum}$$^{-1}$ respectively, maintaining 1.5 gVS·L$^{-1}$ as a fixed concentration of the inoculum. The experiments were performed in duplicate (n=2) including a control (distilled water with inoculum) for the determination of endogenous methane production.

### 2.3 Kinetics models

In order to determine the effect of S/I ratio on the BMP assay, an analysis of variance (ANOVA) and Tukey's test at $p<0.05$ were applied using the software R (i386 3.0.2).

From the experimental data, parameters such as methane volume in time ($V_{CH4\,(t)}$) for each S/I ratio, the duration of the lag phase ($\lambda$) (hours), the maximum methane production ($P_{max}$) (mL) and

the maximum rate of methane production ( $R_{max}$ ) ( $mL \cdot h^{-1}$ ) were determined by using three kinetic models as displayed in Table 1. For each fitted model, corresponding measures of goodness of fit, coefficient of determination ($R^2$) and the Mean Square Error (MSE) were obtained, then it was used the software Minitab 16 to identified the best fit model that maximizes the coefficient $R^2$ and minimizes the MSE.

**Table 1.** *Kinetic models used.*

| Model | Equation |
|---|---|
| Transfer Function (TF) | $V_{CH4}(t) = P_{max}\left[1 - exp\left[\dfrac{-R_{max\,(t-\lambda)}}{P_{max}}\right]\right]$ |
| Logistic Function (LF) | $V_{CH4}(t) = \dfrac{P_{max}}{1 + exp\left[\dfrac{4R_{max}(\lambda - t)}{P_{max}} + 2\right]}$ |
| Modified Gompertz (MG) | $V_{CH4}(t) = P_{max}\,exp\left[-exp\left(\dfrac{R_{max}exp\,(1)}{P_{max}}(\lambda - t) + 1\right)\right]$ |

*Source: Adapted from Donoso-Bravo et al. (2010).*

## 3. Results and discussion

### 3.1 Characterization substrate and inoculum

The FW presented the following physical composition: 39% fibers and mineral mix (carrot peels, banana, pumpkin, tomato, cucumber and eggs, among others), 33% carbohydrates (banana peels, potato and so on), 15% citrus fruit and semi-citrus (lemon, orange, tangerine, passion fruit, pineapple, guava, grape, and lime) and 13% non-citrus fruits (mango, banana, watermelon, papaya, and apple). These characteristics are similar to those found by other authors like Oviedo et al. (2014) and Alibardi & Cossu (2015). Table 2 presents the results of the physicochemical characterization of substrate and inoculum.

**Table 2**. *Physicochemical characterization of FW and inoculum.*

| Parameter | FW[*n] | Inoculum [*n] |
|---|---|---|
| pH (UNT) | 5.1±0.04 | 7.4±0.2 |
| Moisture (%) | 86.7±3.7 | - |
| TA($mgCaCO_3 \cdot L^{-1}$) | 4212.8±5.2 | 2461.4±378.2 |
| BA($mgCaCO_3 \cdot L^{-1}$) | - | 1277±279.9 |
| VFA($mg \cdot L^{-1}$) | 24611.4±12.7 | 873±104.1 |
| $COD_{total}$($mg \cdot L^{-1}$) | 125812.3±479.1 | - |
| $COD_{filtered}$($mg \cdot L^{-1}$) | 38187.1±140.6 | - |
| $BOD_5$($mg \cdot L^{-1}$) | 113346.6±495.6 | - |
| VS($mg \cdot L^{-1}$) | 93256.7±147.5 | 36783.8±2116 |
| TS($mg \cdot L^{-1}$) | 110735.7±242.1 | 53964±1603.7 |
| VS/TS | 0.8 | 0.7 |
| SMA**($gCOD \cdot gVS^{-1} \cdot d^{-1}$) | - | 0.012 |

*\* n: number of samples (5); \*\*Solution VFA´s: (Acetic: Propionic: Butyric: 73:23:4 %) .*

The obtained values for pH, moisture, TA, BA and VFAs of the FW listed in Table 2 correspond to normal values for acidified wastes and are similar to the findings obtained by other authors, such as Pesta (2007) and Zupančič & Roš (2012). The low pH values are related to the high contents of moisture (due to the high amount of raw food wastes), which favors the production of VFAs and decreasing bicarbonate alkalinity, hence an alkaline solution with enough buffer capacity should be used in order to neutralize the acidity during AD of FW (Abdulkarim & Abdullahi, 2010).

All the organic matter indicators of the FW showed high values due to its physical categorization (Oviedo et al., 2014; Parra et al., 2015). Additionally, the $COD_{filtered}/COD_{total}$ ratio (0.30) showed high quantities of particulate material that can affect the stage of hydrolysis of the organic matter (Parra et al., 2015).

Regarding inoculum, it presented typical values of anaerobic sludge from municipal WWTP since pH, TA and BA are indicative of good buffer capacity which favors anaerobic digestion (Torres et al., 2009). The VS/TS ratio indicated a greater presence of active biomass, which can be associated with the UASB reactors that allow greater contact between biomass and substrate, enabling more stable microbial consortia compared to conventional reactors and sludge digesters (Álvarez et al., 2006). The SMA was low and typical of anaerobic reactors that treat municipal wastewater (Quintero, 2011).

### 3.2 Influence of the substrate ratios on methane production

In the Figure 1 the results of BMP for each S/I ratio evaluated is presented.
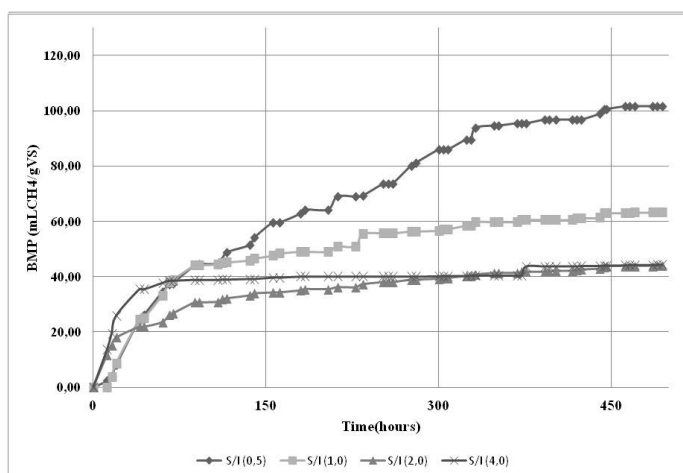


*Figure 1. BMP for each S/I ratio assessed.*

According to the results of ANOVA ($p < 0.05$), there are statistically significant differences among the S/I ratios evaluated, being the best S/I ratios below 1, which is in accordance to the findings reported by Raposo et al. (2006), who stated that when organic load increases in the AD of the FW, inhibitory effects may occur due to accumulation of inhibitory substances such as VFA´s. In addition, the optimum range of S/I ratios is similar to that reported by authors as Hidalgo & Martín (2014).

The low values of BMP achieved differ from those found by authors like Elbeshbishy et al. (2012), who found methane yields above 660 mLCH4·gVS-1, due to probably to the source of the inoculum used in their study (municipal WWTP with separated sewer systems), unlike the present study where collection networks are combined sewage which generated a negative dilution effect.

About the kinetic performance, Figure 2 and Table 3 show the methane prediction and the kinetic parameters attained by using kinetic models.
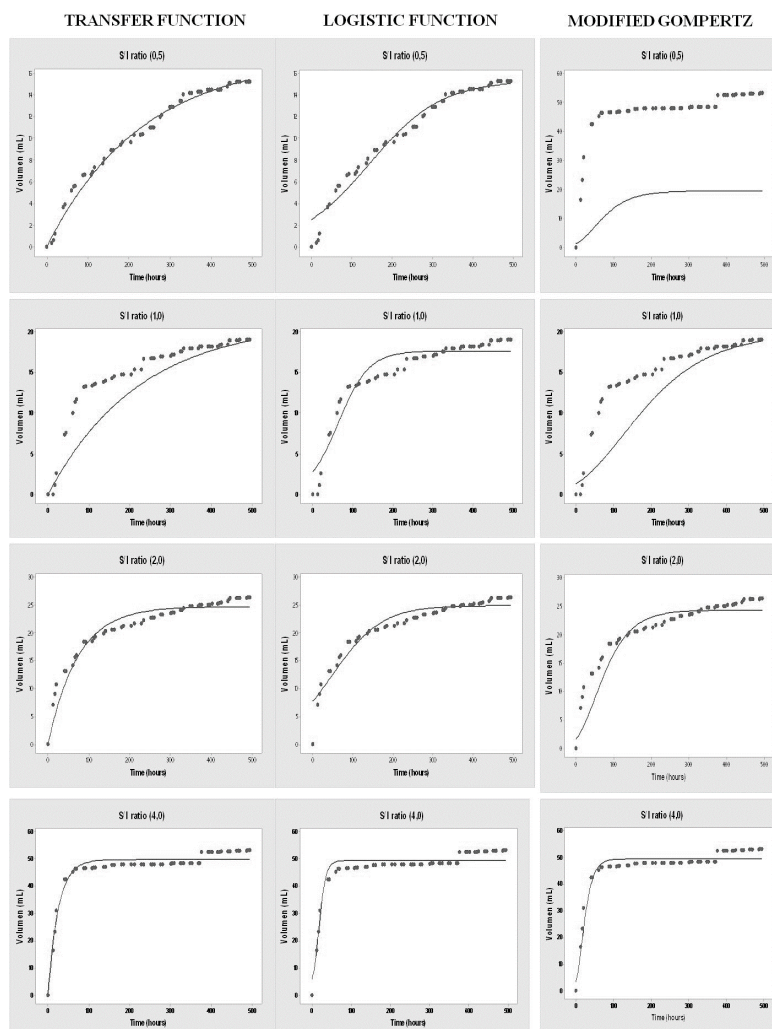
**Figure 2.** *Methane production predictions for each S/I ratio with each kinetic model evaluated.*

***Table 3.*** *Results of kinetic models applied to each S/I ratio.*

| M | S/I | $\lambda$ (h) | $CI_{95\%}$ | $P_{max}$(mL) | $CI_{95\%}$ | $R_{max}$ (mL· h⁻¹) | $CI_{95\%}$ | $R^2$ | MSE |
|---|---|---|---|---|---|---|---|---|---|
| | 0.5 | 0.0 | N.I | 17.5 | N.I | 0.1 | N.I | 0.99 | 0.3 |
| TF | 1.0 | 0.0 | N.I | 21.2 | N.I | 0.1 | N.I | 0.98 | 8.2 |
| | 2.0 | 0.0 | N.I | 24.8 | N.I | 0.3 | N.I | 0.93 | 2.3 |
| | 4.0 | 0.0 | N.I | 49.8 | N.I | 2.0 | N.I | 0.94 | 5.2 |
| | 0.5 | 143.9 | (130.8;158.6) | 15.3 | (14.7;16) | 0.1 | (0;0.1) | 0.97 | 0.7 |
| LF | 1.0 | 63.8 | (54.7;74) | 17.6 | (17.;18.2) | 0.1 | (0.1;0.2) | 0.92 | 2.1 |
| | 2.0 | 49 | (39.3;58.4) | 24.9 | (24.2;25.7) | 0.1 | (0.09;0.1) | 0.93 | 2.4 |
| | 4.0 | 17.8 | (15.4;21) | 49.3 | (48.5;50.1) | 1.5 | (1;2.7) | 0.92 | 7.2 |
| | 0.5 | 0.0 | N.I | 19.5 | N.I | 0.14 | N.I | 0.41 | 1019.6 |
| MG | 1.0 | 0.0 | N.I | 19.8 | N.I | 0.1 | N.I | 0.17 | 13.9 |
| | 2.0 | 0.0 | N.I | 24.4 | N.I | 0.2 | N.I | 0.41 | 5.7 |
| | 4.0 | 0.0 | N.I | 49.6 | N.I | 1.2 | N.I | 0.93 | 7.3 |

*M: Model; CI: Confidence interval; N.I: No interval*

Table 3 presented the best results obtained regarding the fitting procedure (maximizing $R^2$ and minimizing MSE) attained with the Logistic Function (LF) model for all S/I ratio evaluated (See Figure 2). The values of lag phase duration were shorter in S/I ratios below 1, since these presented the higher $R^2$ and the lower MSE. Despite the fact that the S/I ratio of 4 achieved an $R^2$ greater than 0.9 and a lag phase of 17.8 hours, the high MSE value indicates a high variability causing that the prediction of methane as well as biochemical phenomena in the AD of the FW are possibly not reliable and may not be extrapolated to conditions of reactors at pilot and real scale.

Although Transference Function (TF) model obtained an $R^2 > 0.9$, the results of certain parameters as lag phase indicated that this model is not appropriate to predict methane production. These results are different from those obtained by Deepanraj et al. (2015) who found that the MG model is suitable for determining the lag phase with respect to LF model for the duration of the process of AD of FW. However, Donoso-Bravo et al. (2010) and Gao et al. (2014) during their investigations with organic wastes found that the best model for predicting methane was the TF when making a comparison to MG.

This phenomenon was also observed by Li et al. (2011) who found that lag phase was basically negligible ($\lambda = 0$) in all of the cases, which from a biological perspective is invalid, since it would break the assumption that microbial consortia were formed by spontaneous generation and thereby these models would not be suitable to predict methane production.

These results suggest that although the kinetic models tested have benefits in terms of predicting methane production and in turn allow enabling a connection with the behaviour of the biomass, it is necessary to incorporate other type of dynamic models that predicts not only the methane production but also the generation or transformation of other substances or operational variables (removal of COD, ammonia nitrogen, alkalinity, VFA's, amongst other parameters) (Liotta et al., 2015).

Models as the ADM1 can be a reliable option in order to evaluate AD and the formation of other substances during the batch process.

## 4. Conclusions

The substrate-inoculum (S/I) ratio affects the AD of FW. At an S/I ratio below 1, a better production of methane was presented, which means that S/I ratio affect the modelling process. Therefore is highlighted the importance to apply kinetic models for prediction of methane production during BMP assays.

On this study, the Logistic Function was the model with best fit compared to Modified Gompertz and Transfer Function models, in terms of prediction of methane production and lag phase, which can be affected by factors such as the ratio S/I. Therefore, it is necessary to evaluate other more robust models to understand more clearly the phenomena that occur in the anaerobic digestion.

## 5. Acknowledgements

## 6. References

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