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# KINETICS OF BIOGAS GENERATION FROM MICROBREWERIES ORGANIC WASTES

# CINÉTICA DE GENERACIÓN DE BIOGAS A PARTIR DE RESIDUOS ORGÁNICOS DE UNA MICROCERVECERÍA

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## ABSTRACT

The kinetics of methane generation was studied based on the anaerobic digestion of organic waste from a microbrewery. In particular, the effect of temperature and the concentration of total solids (TS) were analyzed through assays carried out in an anaerobic batch digester. The experiments were done using initial TS contents of 3%, 6%, and 10% at a digestion temperature of 30°C, and at temperatures of 20, 30, and 40°C with initial TS of 6%. The results indicated that temperature does not affect the total methane generated with 6% TS, but it does affect the initial speed of generation, which increases at higher temperatures. However, the concentration of TS affected both the total volume of methane generated, which increased at higher TS due to the greater availability of substrate, and the initial speed of generation, resulting in lower values with high TS concentrations, and indicating the inhibition of the reaction at high concentrations. Based on the experimental data, a kinetic model was applied that considers the availability of substrate as a limiting factor for biogas generation and assumes that the maximum methane generation is achieved immediately after the onset of each experiment. In addition, a model based on zero-order kinetics was developed for the first stage of the process in the case of 10% TS. The model was validated by comparing the theoretical and experimental values, resulting in a deviation of less than 20% in 73% of the cases, indicating that the model predicts satisfactorily the generation of methane under the conditions studied.

**Key words:** anaerobic digestion kinetics, brewery wastes.

## RESUMEN

Se estudió la cinética de generación de metano a partir de la digestión anaeróbica de residuos orgánicos de una microcervecería. En particular se analizó el efecto de la temperatura y concentración de sólidos totales (TS) en ensayos realizados en un digestor anaeróbico batch. Los experimentos fueron llevados a cabo con contenidos iniciales de TS de 3%, 6% y 10% a una temperatura de digestión de 30°C, y por otro lado a temperaturas de 20, 30 y 40°C con 6% de TS. Los resultados indicaron que la temperatura no incide en el metano total generado a un 6% de TS, pero sí afecta la velocidad inicial de generación, aumentando ésta a mayor temperatura. La concentración de TS incidió en el volumen total de metano generado, el que aumentó a mayores TS dada la mayor disponibilidad de sustrato y además en la velocidad inicial de generación, obteniéndose valores inferiores para altas concentraciones de TS, indicando inhibición de la reacción a altas concentraciones. A partir de

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**los datos experimentales se aplicó un modelo cinético que considera la disponibilidad de sustrato como factor limitante para la generación de biogás y supone que se logra máxima generación de metano inmediatamente después de iniciado cada experimento. Se desarrolló además un modelo basado en una cinética de orden 0 para la primera etapa del proceso para el caso de 10% de TS. El modelo fue validado comparando los valores teóricos con valores experimentales obteniéndose una desviación menor al 20% en un 73% de los casos, indicando que el modelo predice satisfactoriamente la generación de metano bajo las condiciones estudiadas.**

**Palabras clave:** cinética de digestión anaeróbica, residuos de cervecerías.

## INTRODUCTION

Breweries generate large amounts of waste water with high degradable organic loads (Zupančič et al., 2007), presenting typical Chemical Oxygen Demand (COD) values of 1200-3000 mg $L^{-1}$ and COD/Biochemical Oxygen Demand (BOD) ratios around 1.5 (Cronin and Lo, 1998; Leal et al., 1998). Thus, this waste can be treated effectively by anaerobic digestion.

On industrial scale, several effective conventional methods of anaerobic treatment of waste water are available to breweries. These methods range from fluidized bed bioreactors (Ochieng et al., 2002) to the most commonly used Upflow Anaerobic Sludge Bed (UASB) reactors (Yu and Gu, 1996; Cronin and Lo, 1998; Leal et al., 1998; Parawira et al., 2005). Most microbreweries with lower production volumes than industrial breweries use batch processes, which means interrupted processing of waste, and results in a huge amount of water with dissolved carbohydrates, ground malt, barley, yeast and hop. At the same time, various stages of beer making require energy and heat provided by electricity and the combustion of gas and wood. The recent earthquake in Chile caused a general failure of the different energy supplies in the affected regions. As these areas concentrate a large part of the country's agricultural production, economic losses were incurred. Clearly, industry needs to seek alternatives for autonomous generation of energy. The agroindustry has a great opportunity to move forward in this sense. Although it requires different forms of energy, it also generates important amounts of organic waste that can be revalued energetically, contributing partially to the industry's energetic autonomy and improving its environmental management.

One of the most attractive ways to recover energy from organic waste is by anaerobic digestion, which offers both economic and environmental advantages (Ergüder et al., 2001; Yu et al., 2002; Santosh et al., 2004; Bohn et al., 2007; Converti et al., 2009). Anaerobic digestion is a particularly attractive alternative for the energetic valorization of grain waste, especially barley. Given that barley is a raw material for beer making, it constitutes the main component of the solid phase of waste water. This cereal has a great potential to be converted into methane ($CH_4$) (Murphy and Power, 2009; Dinuccio et al., 2010). On the other hand, the chemical composition of brewers' spent grains varies according to barley variety, harvest time, malting and mashing conditions, and the quality and type of adjuncts added in the brewery process (Mussatto et al., 2006). Therefore, different biogas production from residues of industrial and microbreweries should be expected.

Anaerobic digestion consists of a series of multiple stages – hydrolysis or solubilization, acidogenesis, and methanogenesis, among others – each of which involves a series of biochemical reactions by microorganisms (Buzzini et al., 2006). In the first stage, the polymeric organic matter is hydrolyzed so that it will break down effectively. In the second stage, the acidogenic bacteria produce intermediaries, mainly volatile fatty acids. Finally, in the absence of oxygen, the metabolic processes of methanogenic organisms produce biogas (basically a mix of methane and carbon dioxide). In each of these stages, the rate of organic waste break down and generation of biogas depends on numerous factors, including temperature, pH, hydraulic retention time, as well as type and concentration of substrate (Komemoto et al., 2009).

Temperature is one of the most important parameters in anaerobic treatments, and its effect on the performance of anaerobic treatment systems has been studied exhaustively in recent years. Some studies reported that, under thermophilic conditions, high organic loads can be tolerated operating at low hydraulic retention times (HRT), as this generates a greater volume of biogas than under mesophilic and psychrophilic conditions (Kim et al., 2006; Şentürk et al., 2010). However, this requires the introduction of energy into the system, reducing global energy efficiency of the process and requiring a strict temperature control to avoid the accumulation of fatty acids, which would inhibit the methanogenesis (Yu et al., 2002). Consequently, the growing tendency is the use of mesophilic and even psychrophilic systems whose performance, in terms of efficiency of the removal of the organic load and potential for biogas generation, depends strongly on the speed of the processes involved during anaerobic digestion (Connaughton et al., 2006). Therefore, in order to select the design and operating conditions of the reactor, we must first understand the specific degradation kinetics of the substrate of interest.

The concentration of total solids in cellulose-rich wastes such as brewery waste water, with a high level of barley and malt, is another factor affecting how quickly the waste breaks down. In fact, the solubilization of cellulose has been shown to be the limiting stage in the digestion process (Jensen et al., 2009), a highly relevant aspect in terms of process efficiency. The hydrolysis of cellulose (considering its concentration) has been approximated using first-order models, being the cellulose availability the limiting factor of the process (Mouriño et al., 2001; O'Sullivan et al., 2006). The speed of solubilization differed widely between authors (Jensen et al., 2009). Different studies have shown that the speed of cellulose solubilization in experiments inoculated with rumen was significantly higher than in those inoculated with other sources of microorganisms due to the elevated enzymatic activity of the rumen (Hu et al., 2007; Zhao et al., 2009).

The complex substrate interactions, concentrations, and temperatures detailed above show how difficult it is to generalize and extrapolate results from specific case studies. Therefore, the objective of this work is to study the specific kinetics of the anaerobic digestion of a substrate of the organic waste typically generated by microbreweries, emphasizing the effects of temperature and substrate concentration. This was done to generate specific data on the rate of digestion for this type of waste, as this information would allow producers to make a better decision in terms of anaerobic energy recovery systems and their operating conditions.

## MATERIALS AND METHODS

### Substrate

Waste (pulp) from the maceration stage of the production process of a small scale beer plant was used as substrate. This waste contained water, barley, and malt. Chemical analyses of waste were performed to determine the elemental composition (C, N, P), contents of total solids (TS), volatile solids (VS), water, and ash. Latter analyses were done according to the standards 2540 B, 2540 E, NCh 841OF78, and NCh 842OF78, respectively (Greenberg et al., 1992). Table 1 provides substrate characteristics.

**Table 1. Composition of the substrate. Microbreweries organic wastes.**
**Tabla 1. Composición del sustrato. Residuos orgánicos de una microcervecería.**

| Parameter | % (w/w) |
|---|---|
| Carbon (C) | 47.57 |
| Nitrogen (N) | 3.08 |
| Phosphorus (P) | 0.28 |
| Water | 73.53 |
| Total solids (TS) | 26.47 |
| Volatile solids (VS) | 19.24 |
| Ash | 7.23 |

### Reactor

The reactor used for the anaerobic digestion of the waste generated by the small scale beer industry consisted of two 5-L anaerobic digesters (W8, Armfield Ltd., Ringwood, Hampshire, UK), as shown in Fig. 1. Both reactors had a capacity for sampling and gas collection, as well as 200 W warming blankets to keep the temperature constant at the desired levels according to experimental conditions.

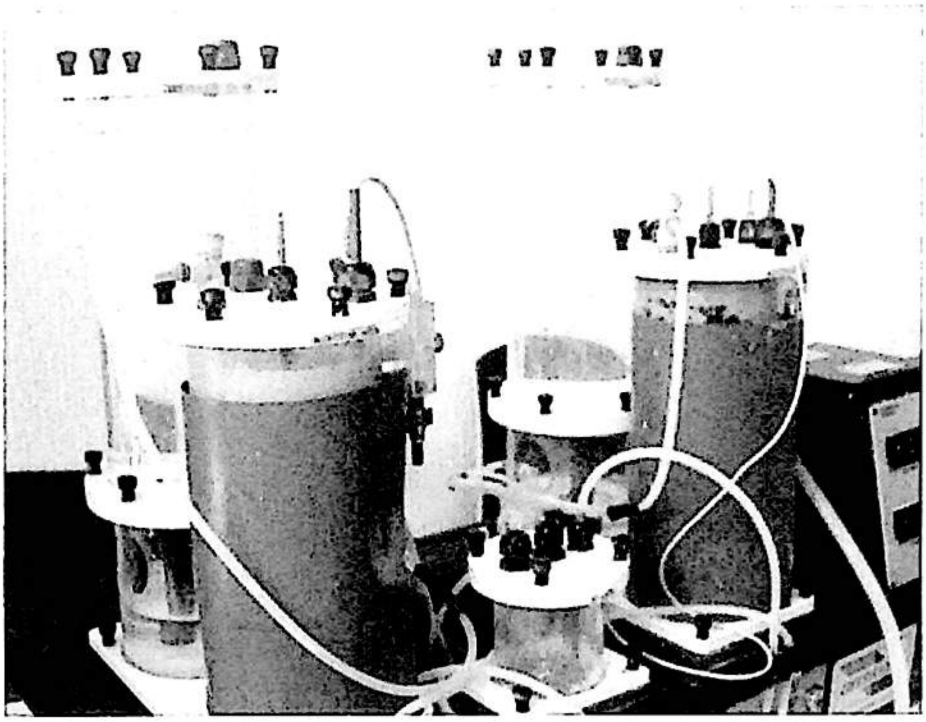


**Fig. 1. Anaerobic reactor. Biogas generation from microbrewery organic wastes.**
**Fig. 1. Reactor anaerobio. Generación de biogas de residuos orgánicos de una microcervecería.**

### Experimental procedure

Procedures used to determine the effect of temperature on the degradation of organic matter based on a TS concentration of 6% (w/w) at the onset of each experiment and temperatures of 20, 30, and 40°C. Those assays performed to study the effect of the concentration of total solids were done at a constant temperature (30°C) using initial TS contents of 3, 6, and 10% (w/w).

After being characterized, waste was mixed with water (100 g of waste with 200 mL of water) in a household blender for 20 s at the maximum speed in order to decrease the particle size and to increase their total surface area since decomposition occurs on the surface of organic matter (Hilkiah et al., 2008). Later, liquefied rumen was added in proportion to the amount of substrate (40% with respect to the total solids) and water was added until obtaining the desired percentage of TS in each set of experiments (3%, 6%, 10% w/w).

The prepared blend was incorporated into the reactor and stirred constantly. NaOH was added until reaching a pH of 7, which was fixed by adding a buffer solution of calcium carbonate ($CaCO_3$).

The experiment started by fixing the assay temperature (20, 30, 40°C) and determining the initial content of volatile solids.

During the experiments, pH and VS were measured every day at the same time. The volume of methane ($CH_4$) generated was recorded hourly for the first eight hours and then every six hours. The volume of methane generated in the process was measured using a collection recipient with volumetric calibration that operated by water displacement. This device had a liquid seal and constant load so pressure of the gas in the reactor remained constant throughout the entire assay. In order to remove carbon dioxide ($CO_2$), gases were washed with a solution of sodium hydroxide (NaOH) of 6N in a bottle that was connected between the reactor and the methane collector.

### Kinetic analysis

Given that operations were done in batch mode, the analysis was based on models that considered substrate availability as the limiting factor for biogas production. The ratio of $CH_4$ production to the concentration of biodegradable volatile solids (S) in the anaerobic process is given by Montalvo and Guerrero (2003):

$$\frac{B_0 - B}{B_0} = \frac{S}{S_0} \quad [1]$$

where $S_0$ is the initial concentration of substrate, $B_0$ is the total yield of methane (for an infinite time $\theta$), and B is the yield of methane for a particular time value ($m^3$ $CH_4$ $kg^{-1}$ of initial VS). This model describes the process of biogas generation once the maximum production of methane has been reached in the system. In this stage, we have:

$$-\frac{dS}{dt} = r_s \cdot S \qquad [2]$$

where $r_s$ is a kinetic constant ($h^{-1}$).

By combining and integrating equations 1 and 2, we get the following expression:

$$\frac{B_0 - B}{B_0} = e^{-r_s t} \qquad [3]$$

Based on the line that is obtained on the graph $\ln[(B_0-B)/B_0]$ versus t, we can determine the value of the kinetic constant $r_s$.

## RESULTS AND DISCUSSION

### Effect of the digestion temperature on methane generation

Fig. 2 shows the accumulation of methane as a function of time for a load of 6% total solids and digestion temperatures of 20, 30, and 40°C. As can be seen in all the cases, the accumulation of gas increased gradually with time until reaching an asymptotic value due to the lack of anaerobically biodegradable material at the end of the experiment. At all three temperatures, the volume of methane produced was near 7000 mL (Table 2), over periods of 48 to 72 hours, similar to that reported by other authors for a batch mode system (Siles et al., 2007). The methane generation in function of time for the first twelve hours of digestion (Fig. 3) shows that the initial rate of methane generation augmented along with the digestion temperature, with similar values for 30 and 40°C and lower values for 20°C. The slopes of these lines that represent the initial rate of methane generation are given in Table 2. The high biodegradation rate observed can be explained by considering the optimum conditions at a laboratory scale such as stirring, use of $CaCO_3$ buffer solution and the very active inoculum used, obtained from slaughter house the day when the experiment was carried out.

**Table 2.** Initial rate of methane production ($V_i$) and total production of methane ($B_0$). 6% of TS and a digestion temperature of 20, 30 and 40°C. Microbrewery organic wastes.

**Tabla 2.** Velocidad inicial de producción de metano ($V_i$) y la producción total de metano ($B_0$). 6% de TS y una temperatura de digestión de 20, 30 y 40°C. Residuos orgánicos de una microcervecería.

| Digestion temperature | TS | $V_i$ | $B_0$ |
|---|---|---|---|
| °C | % | mL $s^{-1}$ | mL |
| 20 | 6 | 301.2 | 7,109 |
| 30 | 6 | 417.4 | 7,080 |
| 40 | 6 | 428.5 | 7,464 |

TS: total solids

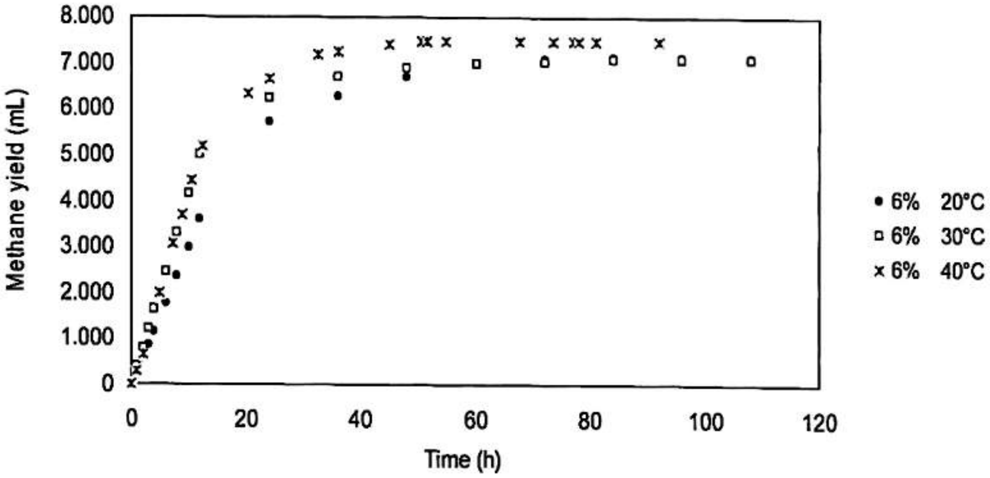


**Fig. 2.** Volume of gas produced over time for a feed of 6% of total solids and a temperature of digestion of 20, 30 and 40°C. Microbrewery organic wastes.

**Fig. 2.** Volumen de gas producido en el tiempo para una alimentación de 6% de sólidos totales y una temperatura de digestión de 20, 30 y 40°C. Residuos orgánicos de una microcervecería.

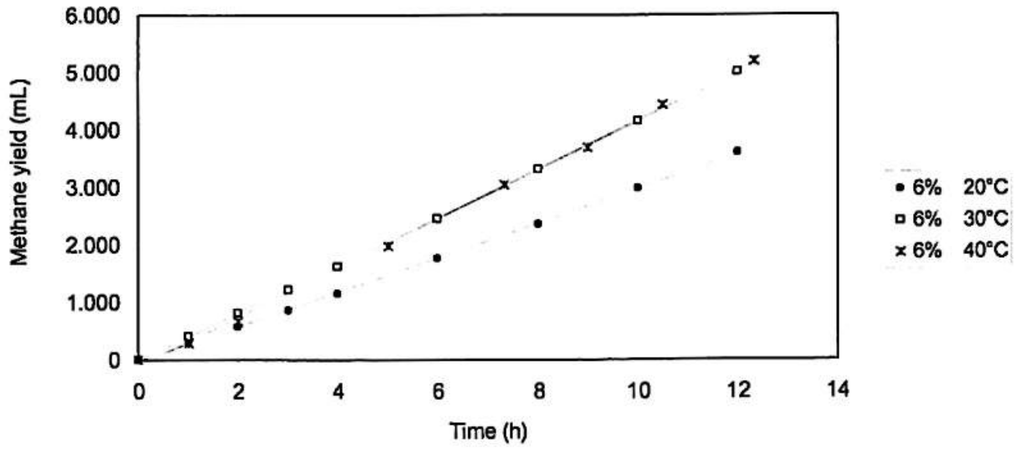


**Fig. 3. Volume of gas produced over time for a feed of 6% of total solids and a temperature of digestion of 20, 30 and 40°C during the first twelve hours. Microbrewery organic wastes.**

**Fig. 3. Volumen de gas producido en el tiempo para una alimentación de 6% de sólidos totales y una temperatura de digestión de 20, 30 y 40°C durante las primeras doce horas. Residuos orgánicos de una microcervecería.**

### Effect of the concentration of total solids on methane generation

Fig. 4 shows the accumulation of methane as a function of time for a digestion temperature of 30°C and loads of 3%, 6%, and 10% of total solids. As in the previous cases, the accumulation of biogas increased gradually with time until reaching an asymptotic value due to the lack of anaerobically biodegradable material. Moreover, the total volume of methane generated at the end of each experiment was greater as the concentration of total solids increased in the reactor, with values over 7000 mL for concentrations of 6% and 10% total solids, but with a total volume of less than 4800 mL in the case of 3% total solids due to the lower substrate availability (Table 3). Furthermore, the time required for the degradation of organic material also varied between 48 and 72 hours. The initial rate of methane generation was lower for a load of 10% total solids because the higher concentration of solids affected the process of mass transference between substrate and cells, and the solid material displaced active biomass, occupying an important part of the active volume of the reactor, and at the same time, incrementing the viscosity of the system and complicating correct mixing in the reactor (Klauss et al., 2007). These factors hindered, in this case, the supply of substrate to the microorganisms, decreasing gas production.

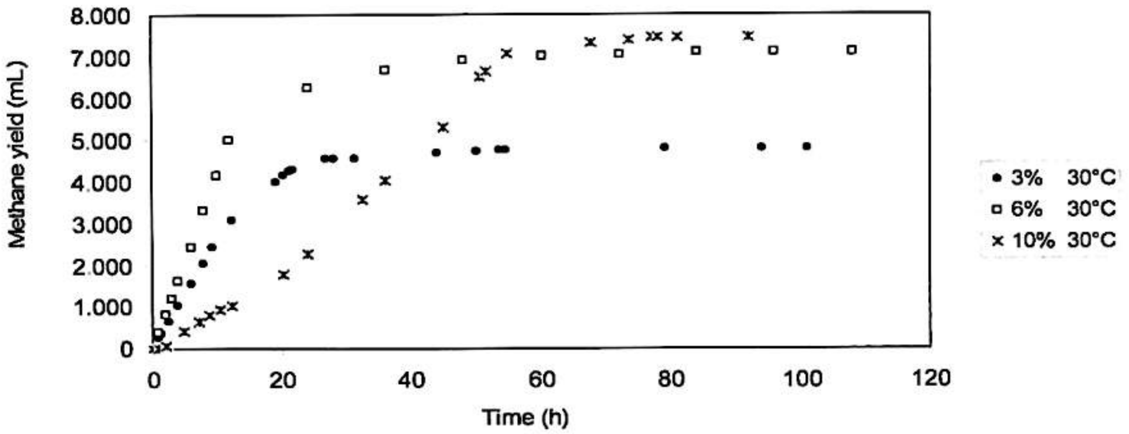


**Fig. 4. Volume of gas produced over time for a temperature of digestion of 30°C and a feed of 3, 6 and 10% of total solids. Microbrewery organic wastes.**

**Fig. 4. Volumen de gas producido en el tiempo para una temperatura de digestión de 30°C y una alimentación de 3, 6 y 10% de sólidos totales. Residuos orgánicos de una microcervecería.**

Graphs in Fig. 5 show the first twelve hours of methane generation in function of time and under the conditions mentioned before. The slopes of the lines representing the initial speed of methane generation are given in Table 3.

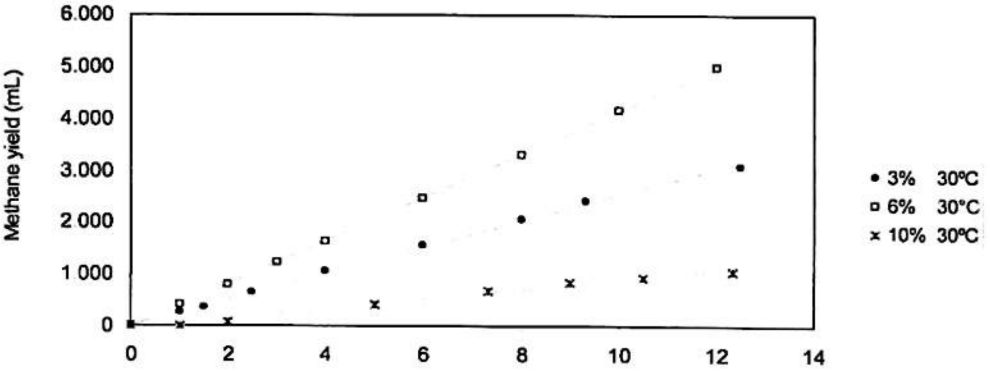


**Fig. 5.** **Volume of gas produced over time for a temperature of digestion of 30°C and a feed of 3, 6 and 10% of total solids during the first twelve hours. Microbrewery organic wastes.**

**Fig. 5.** **Volumen de gas producido en el tiempo para una temperatura de digestión de 30°C y una alimentación de 3, 6 y 10% de sólidos totales durante las primeras doce horas. Residuos orgánicos de una microcervecería.**

**Table 3.** **Initial rate of methane production ($V_i$) and total production of methane ($B_0$). Digestion temperature of 30°C and total solids (TS) of 3, 6 and 10%. Microbrewery organic wastes.**

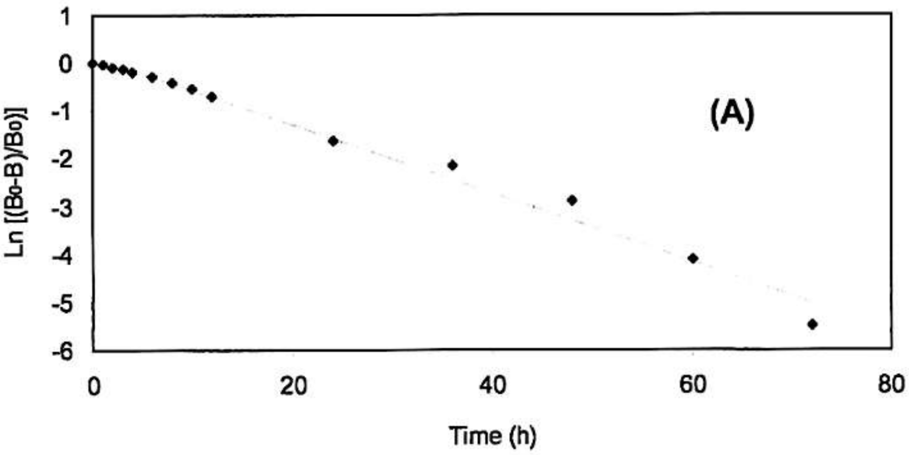
**Tabla 3.** **Velocidad inicial de producción de metano ($V_i$) y producción total de metano ($B_0$). Temperatura de digestión de 30°C y sólidos totales (TS) de 3, 6 y 10%. Residuos orgánicos de una microcervecería.**

| Digestion temperature | TS | $V_i$ | $B_0$ |
|---|---|---|---|
| °C | % | mL $s^{-1}$ | mL |
| 30 | 3 | 252.3 | 4,789 |
| 30 | 6 | 417.4 | 7,080 |
| 30 | 10 | 93.3 | 7,449 |

## Estimation of the kinetic constant for methane generation

Fig. 6A, 7A, 8A, 9A, and 10A show the graphs of $\ln((B_0\text{-}B)/B_0)$ in function of time for all the study conditions. These were used to determine experimentally the values of $B_0$, which correspond to the last value of each series of data in Fig. 2 and 4.

As mentioned before, this model describes the process once it has reached the maximum production of methane in the system. In this study, production peaked at the onset of each experiment due to inoculation, except for the experiment at a digestion temperature of 30°C and with 10% total solids, which reached its maximum methane production at 45 hours due to inhibition problems. Thus, in this particular case, the model was applied from 45 hours and a zero-order kinetic model ($dB/dt = k$) was used at the beginning of this experiment with a lineal behavior for methane generation. Initially substrate concentration is in excess, therefore substrate decrease (Eq. 2) does not depend upon substrate concentration, which gives place to a zero order kinetics. Later on substrate will be consumed; becoming limited thus changing to a first order kinetics.



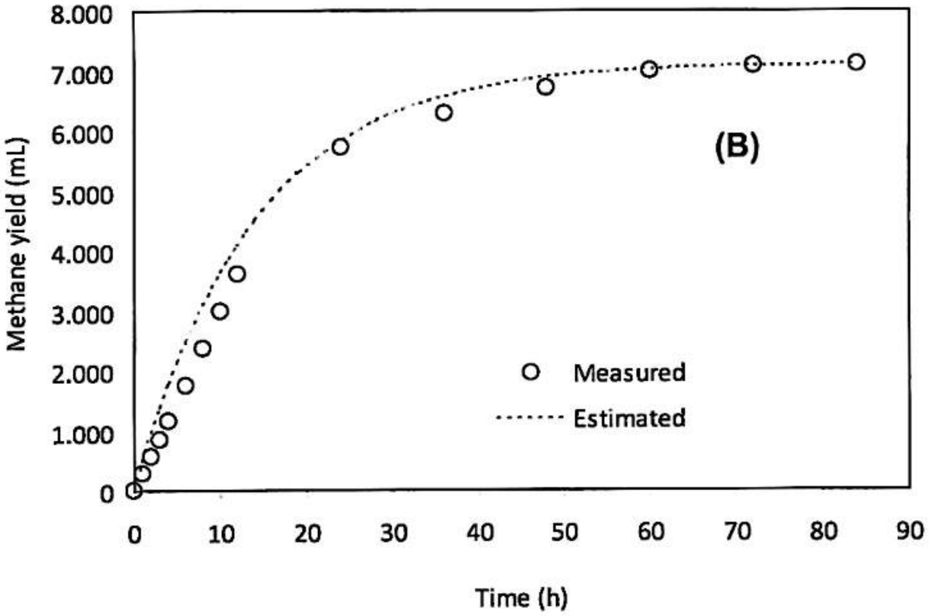


Fig. 6. (A) Graph of $\ln[(B_0-B)/B_0]$ as a function of time at a concentration of total solids of 6% and a temperature of digestion of 20°C. (B) Variation of the experimental (O) and theoretical values (dashed line) of the volume of gas produced by the reactor as a function of time for a concentration of total solids of 6% and a temperature of digestion of 20°C. Microbrewery organic wastes.

Fig. 6. (A) Gráfico de $\ln[(B_0-B)/B_0]$ en función del tiempo a una concentración de sólidos totales de 6% y una temperatura de digestión de 20°C. (B) Variación de los valores experimentales (O) y teóricos (línea punteada) del volumen de gas producido en el reactor en función del tiempo para una concentración de sólidos totales de 6% y una temperatura de digestión de 20°C. Residuos orgánicos de una microcervecería.

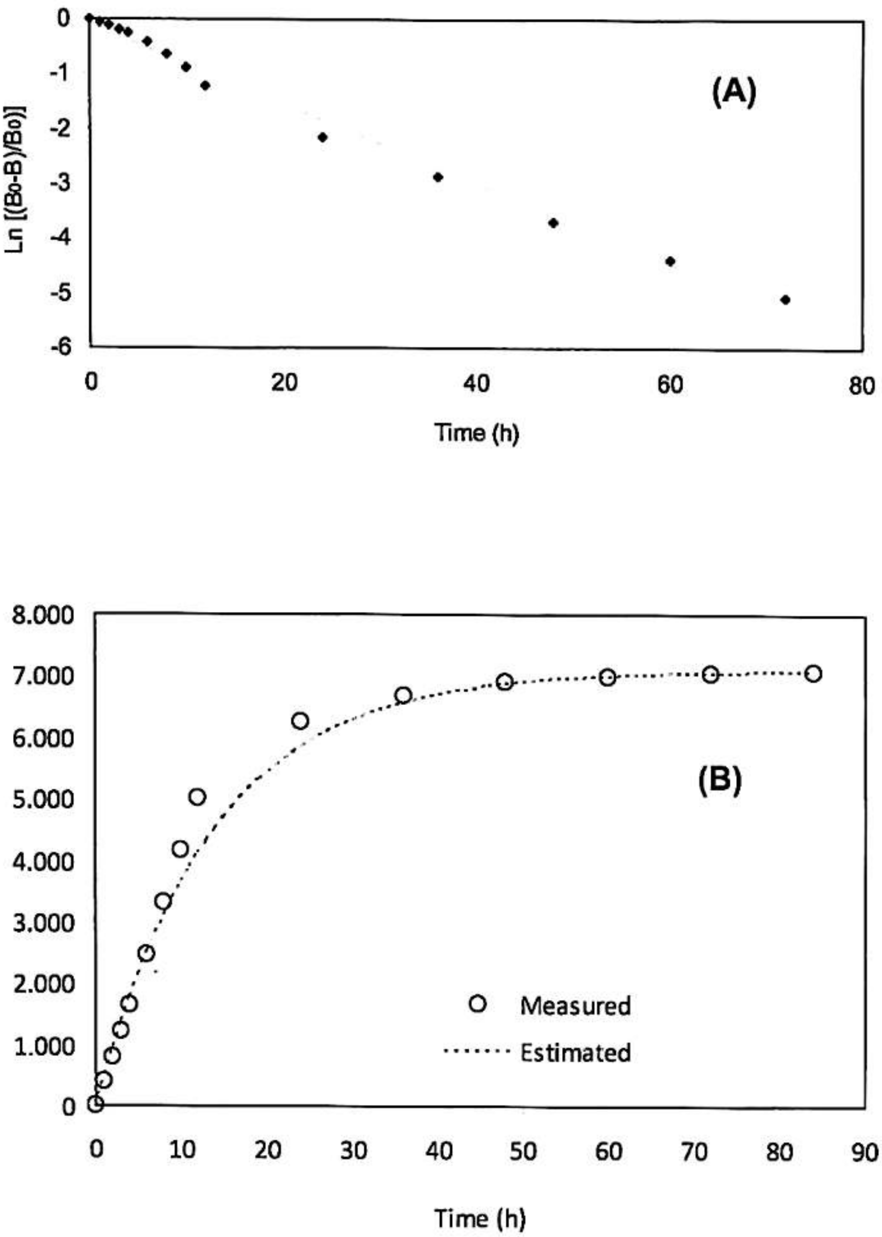


**Fig. 7. (A) Graph of ln[($B_0$-B)/$B_0$] as a function of time at a concentration of total solids of 6% and a temperature of digestion of 30°C. (B) Variation of the experimental (O) and theoretical values (dashed line) of the volume of gas produced by the reactor as a function of time for a concentration of total solids of 6% and a temperature of digestion of 30°C. Microbrewery organic wastes.**

**Fig. 7. (A) Gráfico de ln[($B_0$-B)/$B_0$] en función del tiempo a una concentración de sólidos totales de 6% y una temperatura de digestión de 30°C. (B) Variación de los valores experimentales (O) y teóricos (línea punteada) del volumen de gas producido en el reactor en función del tiempo para una concentración de sólidos totales de 6% y una temperatura de digestión de 30°C. Residuos orgánicos de una microcervecería.**

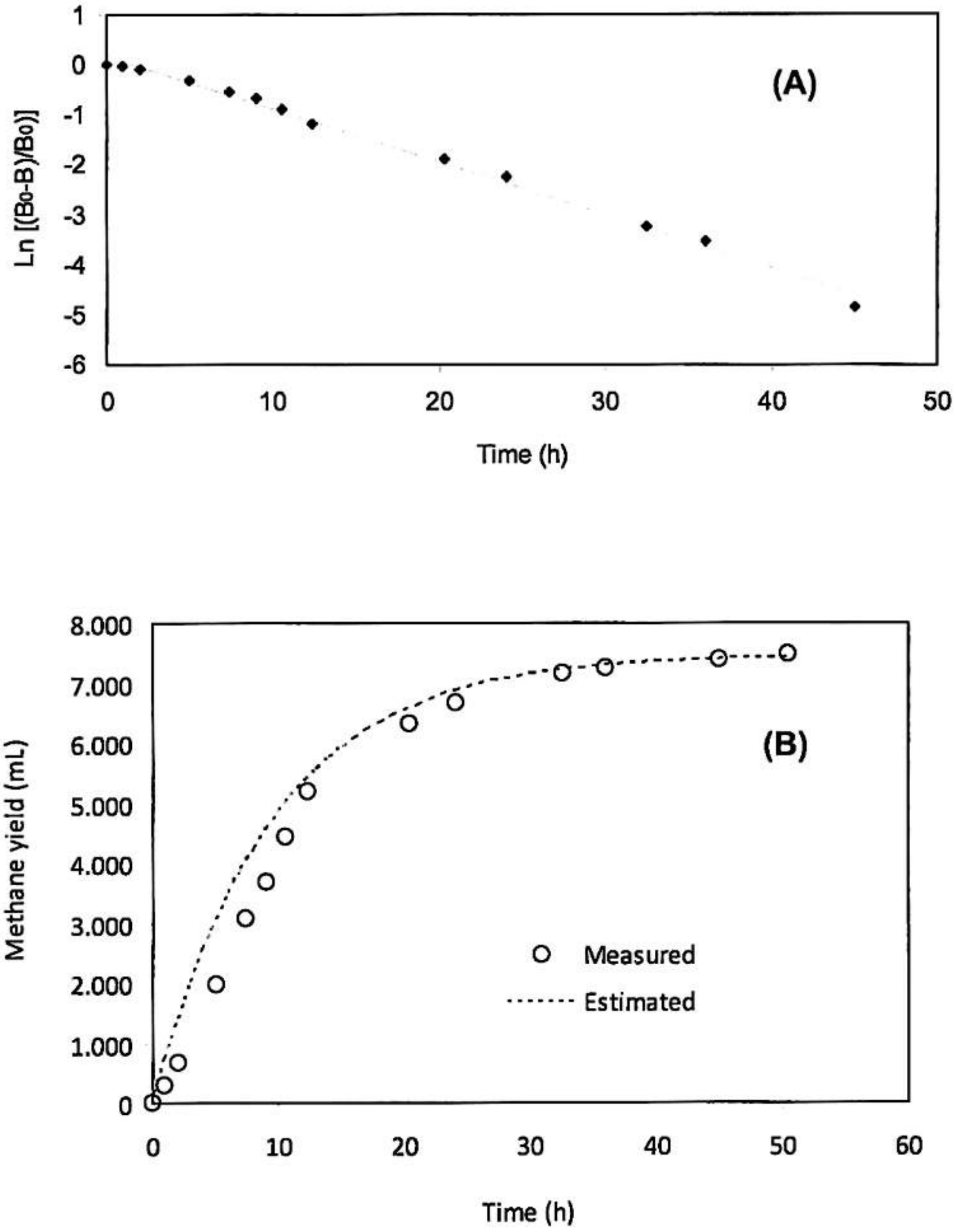


Fig. 8. (A) Graph of ln[($B_0$-B)/$B_0$] as a function of time at a concentration of total solids of 6% and a temperature of digestion of 40°C. (B) Variation of the experimental (O) and theoretical values (dashed line) of the volume of gas produced by the reactor as a function of time for a concentration of total solids of 6% and a temperature of digestion of 40°C. Microbrewery organic wastes.

Fig. 8. (A) Gráfico de ln[($B_0$-B)/$B_0$] en función del tiempo a una concentración de sólidos totales de 6% y una temperatura de digestión de 40°C. (B) Variación de los valores experimentales (O) y teóricos (línea punteada) del volumen de gas producido en el reactor en función del tiempo para una concentración de sólidos totales de 6% y una temperatura de digestión de 40°C. Residuos orgánicos de una microcervecería.

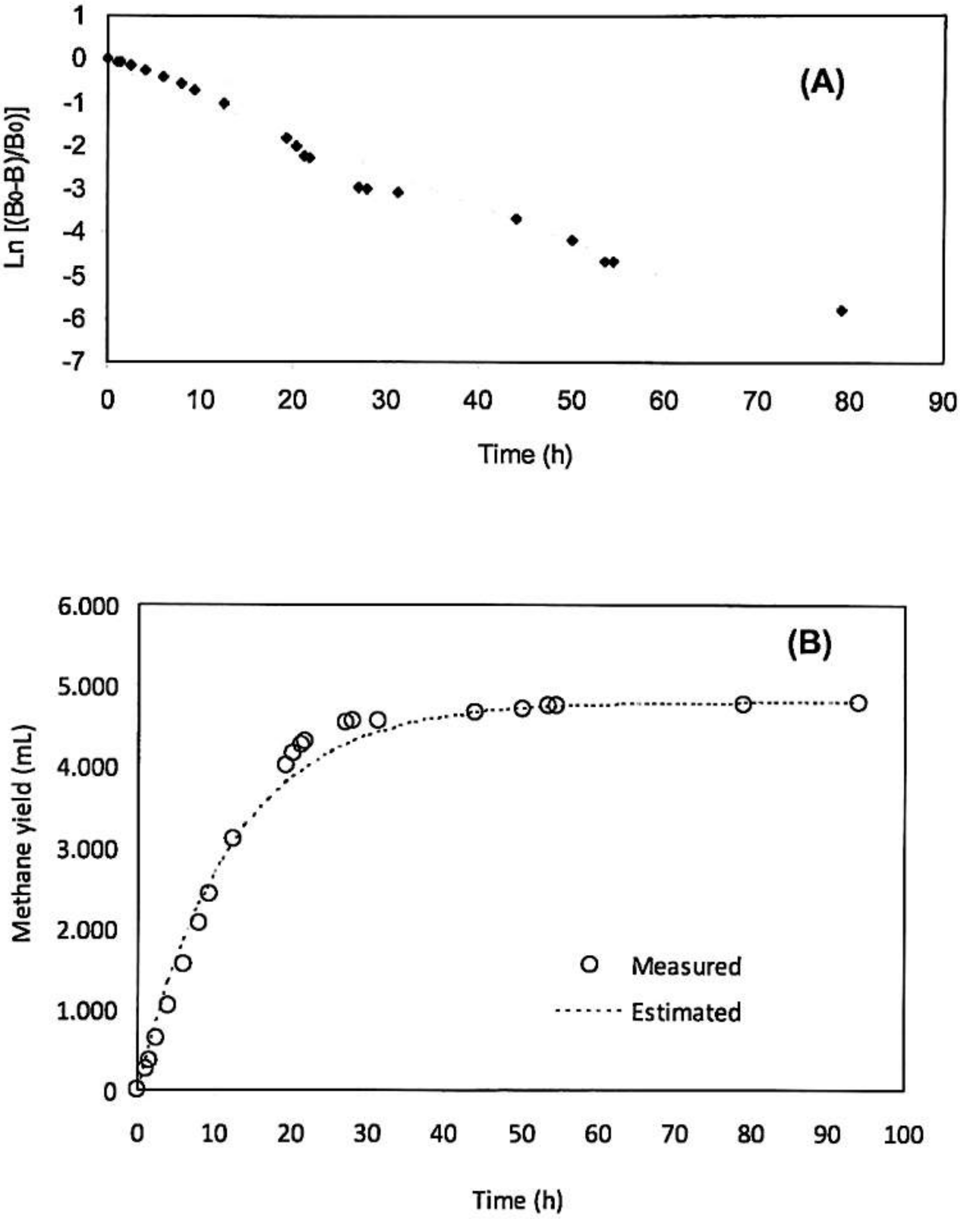


**Fig. 9.** (A) Graph of $\ln[(B_0\text{-}B)/B_0]$ as a function of time at a concentration of total solids of 3% and a temperature of digestion of 30°C. (B) Variation of the experimental (O) and theoretical values (dashed line) of the volume of gas produced by the reactor as a function of time for a concentration of total solids of 3% and a temperature of digestion of 30°C. Microbrewery organic wastes.

**Fig. 9.** (A) Gráfico de $\ln[(B_0\text{-}B)/B_0]$ en función del tiempo a una concentración de sólidos totales de 3% y una temperatura de digestión de 30°C. (B) Variación de los valores experimentales (O) y teóricos (línea punteada) del volumen de gas producido en el reactor en función del tiempo para una concentración de sólidos totales de 3% y una temperatura de digestión de 30°C. Residuos orgánicos de una microcervecería.

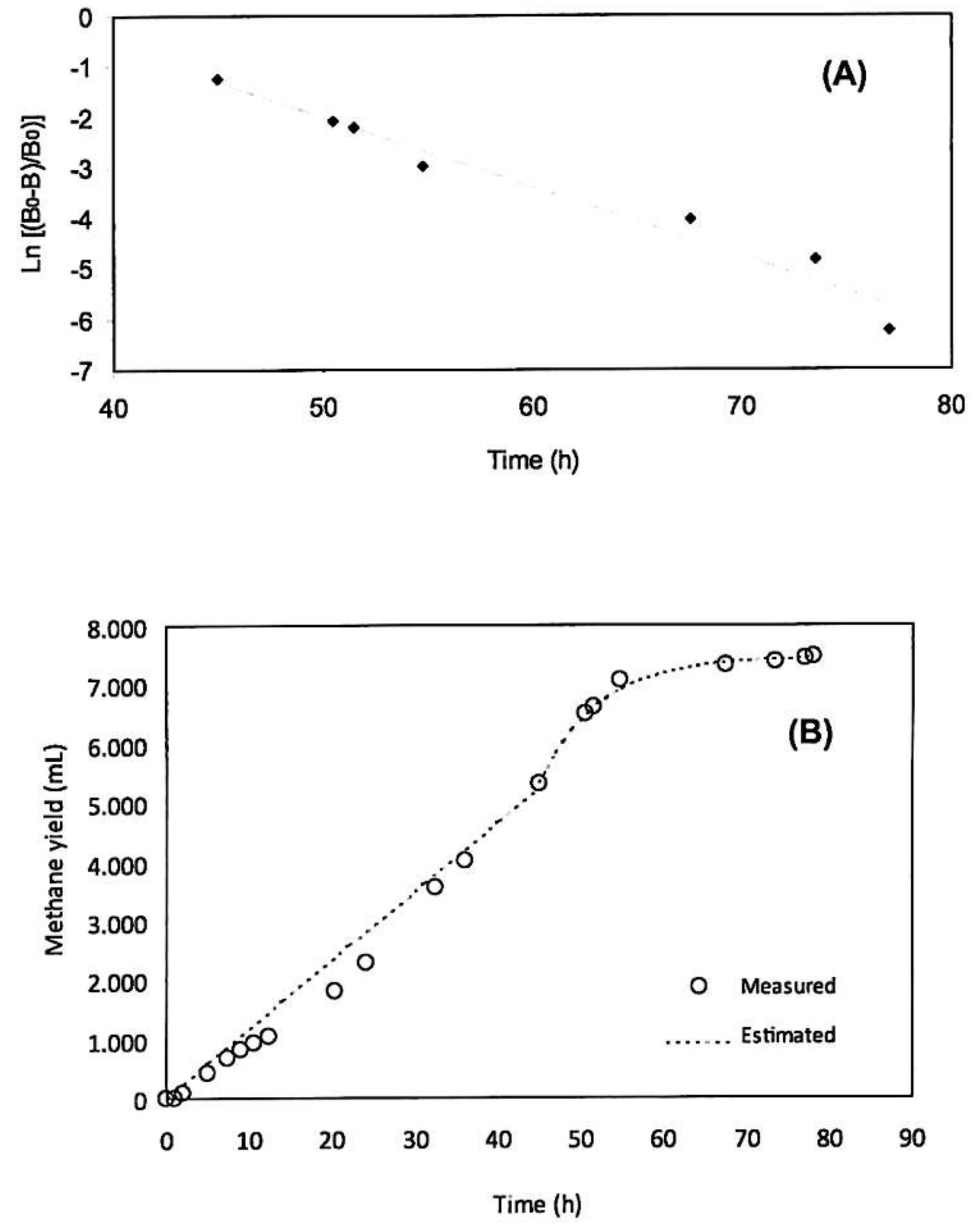


Fig. 10. (A) Graph of ln[$(B_0$-B)/$B_0$] as a function of time at a concentration of total solids of 10% and a temperature of digestion of 30°C. (B) Variation of the experimental (O) and theoretical values (dashed line) of the volume of gas produced by the reactor as a function of time for a concentration of total solids of 10% and a temperature of digestion of 30°C. Microbrewery organic wastes.

Fig. 10. (A) Gráfico de ln[$(B_0$-B)/$B_0$] en función del tiempo a una concentración de sólidos totales de 10% y una temperatura de digestión de 30°C. (B) Variación de los valores experimentales (O) y teóricos (línea punteada) del volumen de gas producido en el reactor en función del tiempo para una concentración de sólidos totales de 10% y una temperatura de digestión de 30°C. Residuos orgánicos de una microcervecería.

The value of $r_s$ was determined from the graph $\ln[(B_0-B)/B_0)]$ versus time t. This value corresponds to the slope of the straight line for each studied condition. Table 4 presents the results of this analysis. For a TS content of 6%, the kinetic constant ($r_s$) increased along with the digestion temperature, and reached its highest value at 40°C, followed by 30°C; the $r_s$ reached its lowest value at 20°C. For the experiments using a digestion temperature of 30°C, the $r_s$ was lower with 6% TS and higher with 3% TS, although the final production of methane in this last case was considerably lower. With respect to the assay at 30°C and 10% TS, the $r_s$ value was larger than the previous ones, but this result is only valid 45 hours after assay start. From the start of the assay at 30°C and 6% TS to 45 hours after, a zero-order kinetic was observed with a constant k for methane generation of 116.3 mL per hour.

**Table 4. Total yield of methane ($B_0$) and kinetic constant ($r_s$) for each of the experimental conditions, and the kinetic constant (k) for a temperature of 30°C and a content of TS of 10%. Microbrewery organic wastes.**

**Tabla 4. Rendimiento total de metano ($B_0$) y la constante cinética ($r_s$) para cada una de las condiciones experimentales, y la constante cinética (k) para una temperatura de 30°C y un contenido de TS de 10%. Residuos orgánicos de una microcervecería.**

| Temperature of digestion | TS | $B_0$ | $r_s$ | k |
|---|---|---|---|---|
| °C | % | mL | $h^{-1}$ | mL $h^{-1}$ |
| 20 | 6 | 7,109 | 0.0715 | |
| 30 | 6 | 7,080 | 0.0727 | |
| 40 | 6 | 7,464 | 0.1056 | |
| 30 | 3 | 4,789 | 0.0814 | |
| 30 | 10 | 7,449 | 0.1375* | 116.3** |

* Time of digestion more than 45 hours.

** Time of digestion less than 45 hours.

The graphs in Fig. 6B, 7B, 8B, 9B, and 10B show the values of gas generation versus digestion time obtained experimentally and those estimated using the model. Fig. 10B contains a graph of the two models developed for this particular case as well as experimental data.

## Validation of the kinetic model

Graphs in Fig. 6B, 7B, 8B, 9B, and 10B compare the values of the generation of gas versus digestion time from experimental data with those estimated by modelling. These results in a good correlation with small deviations in all cases. Thus, the validity of the proposed model that gives an adequate description of methane production under experimental conditions has been demonstrated.

In Fig. 11, experimental values of methane generation are compared with the theoretical values from the model. This figure also includes the 10% and 20% error bands. Most of the data fall within the 20% range, which means that the deviation between the measured values and those estimated by the model was less than 20% in most cases. In fact, for 70% of the data, the deviation was less than 20%, and for 59% of the data was less than 10%. This implies that the proposed model is able to predict methane generation appropriately and that the kinetic parameters obtained effectively represent the activity of the reactor for brewery waste under studied conditions.

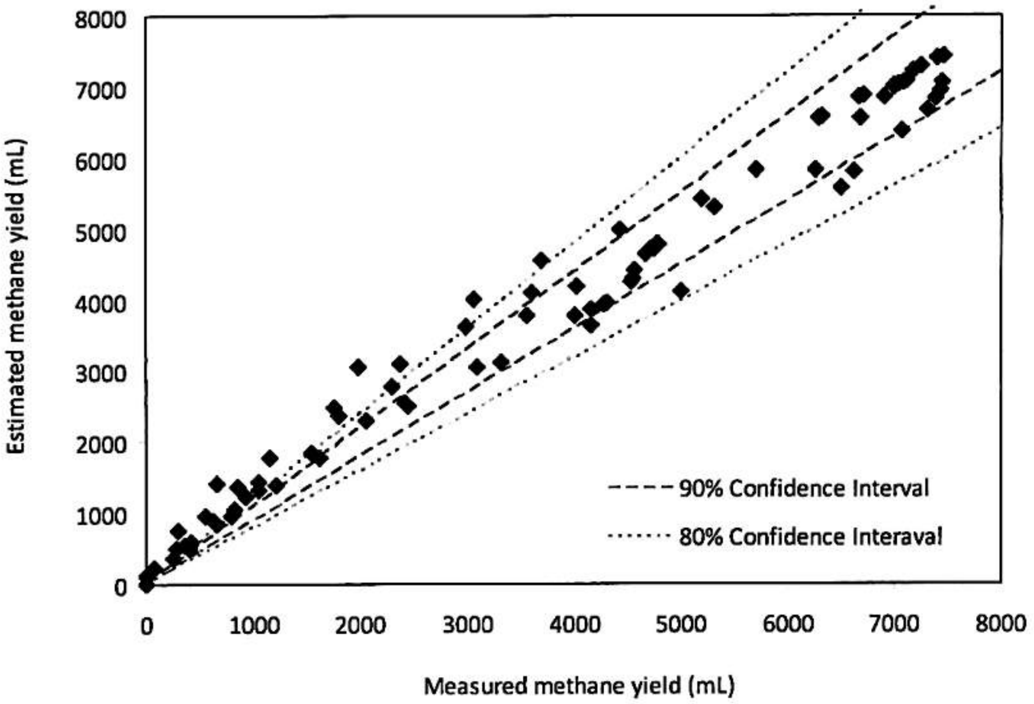


**Fig. 11. Comparison between the experimental values of methane production and the theoretical values from the model. Microbrewery organic wastes.**

**Fig. 11. Comparación entre los valores experimentales de producción de metano y los valores teóricos del modelo. Residuos orgánicos de una microcervecería.**

## CONCLUSIONS

Under the experimental conditions of this study, the digestion temperature (ranging from 20 to 40°C) does not influence the total amount of methane generated for a concentration of total solids of 6%, but it does affect the initial rate of methane generation, which is higher as the digestion temperature increases. Thus, when designing real-scale reactors, it would be best to maintain these near mesophilic conditions (over 30°C) in order to obtain lower residence times, that in turn results in smaller-sized equipment and lower associated costs.

On the other hand, the initial concentration of total solids does affect the total volume of methane generated, which increases with higher concentrations of total solids in the reactor due to the greater substrate availability. Nonetheless, the initial speed of methane generation recorded its highest value for a concentration of 6% and its lowest value for a load of 10% total solids, which means inhibition at high concentration of total solids. In agreement with the observations derived from the assays using constant organic loads, we conclude that there is a recommendable limit in terms of the concentration of total solids (herein, 6%) in order to obtain an optimal real-scale reactor design from a technical and economic point of view.

By combining the two previous conclusions, and based on the results derived from this study, we determined that the recommendable ranges of operation are temperatures near the low thermophilic zone (~30°C) with an initial concentration less than 10% total solids (w/w).

A model was applied to describe methane generation in a batch system from solid beer waste that considers substrate availability to be the limiting factor for the generation of biogas, assuming that the system achieves the maximum production of methane immediately after the onset of each experiment. It was just necessary to develop a different model for the first stage of the process in the case of 10% total solids, for which we assumed zero-order kinetics.

The model was validated by comparing the theoretical values for methane generation obtained from the curves with the corresponding experimental values, which gives a deviation less than 20% in 70% of the cases and, consequently, validates the mathematical model. Thus, the proposed model can be used to predict methane generation from brewery waste under the studied conditions, and provides key information for the design and selection of real-scale reactors.

## LITERATURE CITED

Bohn, I., L. Bjornsson, and B. Mattiasson 2007. Effect of temperature decrease on the microbial population and process performance of a mesophilic anaerobic reactor. Environ. Tech. 28:943-952.

Buzzini, A.P., I.K. Sakamoto, M.B. Varesche, and E.C. Pires. 2006. Evaluation of the microbial diversity in an UASB reactor treating wastewater from an unbleached pulp plant. Process Biochem. 41:168-176.

Connaughton, S., G. Collins, and V. O'Flaherty. 2006. Psychrophilic and mesophilic anaerobic digestion of brewery effluent: A comparative study. Water Res. 40:2503-2510.

Converti, A., R.P.S. Oliveira, B.R. Torres, A. Lodi, and M. Zilli. 2009. Biogas production and valorization by means of a two-step biological process. Bioresource Technology 100:5771-5776.

Cronin C., and K.V. Lo. 1998. Anaerobic treatment of brewery wastewater using UASB reactor seeded with activated sludge. Bioresource Technology 64:33-38.

Dinuccio, E., P. Balsari, F. Gioelli, and S. Menardo. 2010. Evaluation of the biogas productivity potential of some italian agro-industrial biomasses. Bioresource Technology 101:3780-3783.

Ergüder T.H., U. Tezel, E. Güven, and G.N. Demirer. 2001. Anaerobic biotransformation and methane generation potential of cheese whey in batch and UASB reactors. Waste Manag. 21:643-650.

Greenberg, A.E., L.S. Clesceri, and A.D. Eaton. 1992. Standard methods for the examination of water and wastewater. American Public Health Association, American Water Works Association and Water Environment Federation, 18th ed., APHA, Washington DC, USA.

Hilkiah A., M.J. Ayotamuno, C.L. Eze, S.O.T. Ogaji, and S.D. Probert. 2008. Designs of anaerobic digesters for producing biogas from municipal solid-waste. Appl. Energy 85:430-438.

Hu, Z.H., H.Q. Yu, Z.B.Yue, H. Harada, and Y.Y. Li. 2007. Kinetic analysis of anaerobic digestion of cattail by rumen microbes in a modified UASB reactor. Biochem. Eng. J. 37:219-225.

Jensen, P.D., M.T. Hardin, and W.P. Clarke. 2009. Effect of biomass concentration and inoculum source on the rate of anaerobic cellulose solubilisation. Bioresource Tecnology 100:5219-5225.

Kim J.K., B.R. Oh, Y.N. Chun, and S.W. Kim. 2006. Effects of temperature and hydraulic retention time on anaerobic digestion of food waste. J. Biosci. Bioeng. 102:328-332.

Klauss, M., E. Stetiford, and J. Matthes. 2007. Effect of particle size on composting: Literature review. Biovag/Leeds University, Leeds, UK.

Komemoto, K., Y.G. Lim, N. Nagao, Y. Onoue, C. Niwa, and T. Toda. 2009. Effect of temperature on VFA's and biogas production in anaerobic solubilization of food waste. Waste Manag. 29:2950-2955.

Leal, K., E. Chacin, E. Behling, E. Gutierrez, N. Fernandez, and C.F. Foster. 1998. A mesophilic digestion of brewery wastewater an unheated anaerobic fliter. Bioresource Technology 65:51-55.

Montalvo, S., y L. Guerrero. 2003. Tratamiento anaerobio de residuos. Producción de biogás. Universidad Técnica Federico Santa María, Valparaíso, Chile.

Mouriño, F., R. Akkarawongsa, and P.J. Weimer. 2001. Initial pH as a determinant of cellulose digestion rate by mixed ruminal microorganism in vitro. J. Dairy Sci. 84:848-859.

Murphy, J.D., and N. Power. 2009. Technical and economic analysis of biogas production in Ireland utilising three different crop rotations. Appl. Energy 86:25-36.

Mussatto, S.I., G. Dragone, and I.C. Roberto. 2006. Brewers' spent grain: generation, characteristics and potential applications. J. Cereal Sci. 43:1-14.

Ochieng, A., T. Ogada, W. Sisenda, and P. Wambua. 2002. Brewery wastewater treatment in a fluidised bed bioreactor. J. Hazardous Mater. 90:311-321.

O'Sullivan, C.A., P.C. Burrell, W.P. Clarke, and L.L. Blackall. 2006. Comparison of cellulose solubilisation rates in rumen and landfill leachate inoculated reactors. Bioresource Technology 97:2356-2363.

Parawira, W., I. Kudita, M.G. Nyandoroh, and R. Zvauya. 2005. A study of industrial treatment of opaque beer brewery wastewater in a tropical climate using a full-scale UASB reactor seeded with activated sludge. Process Biochem. 40:593-599.

Santosh, Y. T.R. Sreekrishnan, S. Kohli, and V. Rana. 2004. Enhancement of biogas production from solid substrates using different techniques. A review. Bioresource Technology 95:1-10.

Şentürk, E., M. Ince, and G. Onkal Engin. 2010. Kinetic evaluation and performance of a mesophilic anaerobic contact reactor treating medium-strength food-processing wastewater. Bioresource Technology 101:3970-3977.

Siles, J.A., M.A. Martín, A. Chica, and R. Borja. 2007.

Kinetic modelling of the anaerobic digestion of wastewater derived from the pressing of orange rind produced in orange juice manufacturing. Chem. Eng. J. 140:145-156.

Yu, H., and G. Gu, 1996. Biomethanation of brewery wastewater using an anaerobic upflow blanket filter. Journal of Cleaner Production 4:219-223.

Yu, H.Q., H.H.P. Fang, and G.W. Gu. 2002. Comparative performance of mesophilic and thermophilic acidogenic upflow reactors. Process Biochem. 38:447-454.

Zhao, B.H., Z.B. Gue, B.J. Ni, Y. Mu, H.Q. Yu, and H. Harada. 2009. Modeling anaerobic digestion of aquatic plants by rumen cultures: Cattail as an example. Water Res. 43:2047-2055.

Zupančič, G.D., M. Straziscar, and M. Ros. 2007. Treatment of brewery slurry in themophilic anaerobic sequencing batch reactor. Bioresource Technology 98:2714-2722.