On-line titrimetric sensor for the control of VFA and/or alkalinity in anaerobic digestion processes treating industrial vinasses

J.C. Bouvier, J.P. Steyer, J.P. Delgenes.

Laboratoire de Biotechnologie de l'Environnement, Institut National de la Recherche Agronomique. Avenue des Etangs, 11100 Narbonne - France.

ABSTRACT

This paper describes the principle and the technical details of a cheap titrimetric sensor for the measurements of total and partial alkalinity and the estimation of bicarbonate and volatile fatty acids concentrations in anaerobic digestion processes. The on-line operation of the sensor connected to a 1 m$^3$ upflow fixed bed reactor treating raw industrial wine vinasses has been shown to be reliable over a five year period of daily use with one measurement every half hour. In addition, this sensor requires a very low maintenance effort while providing very useful information for the on-line control of the process.

KEYWORDS

On-line titrimetric sensor, alkalinity, volatile fatty acids, closed-loop control, anaerobic digestion.

INTRODUCTION

Among all the available processes, anaerobic digestion is of particular interest for the treatment of wastewater highly concentrated with carbon: high capacity to degrade slowly biodegradable substrates at high concentrations, very low sludge production, low energy requirements and possibility for energy recovery through methane combustion… However, despite their large interests, many industrials are still reluctant to use anaerobic digestion processes in practice, probably because of the counterpart of their efficiency: they can become unstable under some circumstances. Indeed, disturbances like variations of the process operating conditions can lead to a destabilisation of the process due to accumulation of intermediate toxic compounds (e.g. volatile fatty acids that have an inhibitory effect on the methanogenesis step) resulting in possible biomass washout. Several weeks to several months are then necessary for the reactor to recover (see for example Steyer et al., 2001). During this period, no treatment can be performed by the unit. It is therefore a great challenge for instrumentation and control sciences to make this process more reliable and usable at industrial scale. The first and key step is to be able to follow dynamically the key process variables (i.e., using on-line sensors with a sampling period small enough).

This paper goes in that direction describing our five year experience in using an on-line self-made titrimetric sensor for the measurement of total and partial alkalinity and the estimation of volatile fatty acids and bicarbonate concentrations. The paper is organised as follows. First, principle and technical details of the titrimetric sensor are briefly presented. The anaerobic digestion process and wastewater used are then shortly described before detailing the on-line results obtained. Finally, some perspective and conclusions are drawn from this experience.

PRINCIPLES OF THE TITRIMETRIC SENSOR

If the mid-point used to determine partial alkalinity (PA) in a titration curve is usually chosen at pH 5.75 to minimise the influence of volatile fatty acids (VFAs) (see for example Jenkins et al., 1983), the choice of the end-point for the determination of the total alkalinity (TA) is subject to changes. In some cases, a value of 4.5 is chosen (mainly when a coloured indicator as methylorange is used – APHA, 1985) but other authors prefer 4.7 using the Gram method (Loewenthal et al., 1989; Loewenthal et al., 1991), 4.3 (Ripley et al., 1986), 4.0 (McCarthy, 1964), 3.3 (DiLallo and Albertson, 1961) or even 2.2 with then a back titration (Powel and Archer, 1989).

Several methods also exist to determine VFAs concentration from a titration curve and most of them assume that VFAs are mainly composed of acetic acid. Indeed, acetic acid is the main acid produced by anaerobic digestion and other acids have close $pK_a$ (i.e., 4.75 for acetic acid, 4.87 for propionic acid and 4.81 for butyric acid).
A two-point method (i.e., pH 5.1 and 3.5) can be chosen as Anderson and Yang (1992) or Feitkenhauer et al. (2002) but other authors prefer to use four (Moosbrugger et al., 1993a; 1993b) or five (Moosbrugger et al., 1993c; 1993d) pH values, one on each side of the pKa (i.e., pH 6.7 and 5.9 for the bicarbonate and pH 5.2 and 4.3 for the VFAs). The five-point method has been lately improved to avoid systematic error with pH measurements (Lahav and Loewenthal, 2000).

Some authors are also in favour of a least square linear regression on n points in order to differentiate between the VFAs (Bisogni, 1994; Bisogni et al., 1998) while others like (Wang et al., 1998) model the kinetic of pH to calculate VFAs concentrations from a non linear regression using added volumes of acid and base.

Few comparative studies between the different methods can be found in the literature. For example, (Buchauer, 1998) evaluated the method developed by Kapp (Kapp, 1992) and the one developed by Moosbrugger (Moosbrugger et al., 1993c). These methods were found very similar in terms of precision but the Kapp method was easier to implement to determine the VFAs concentration between 0 and 3500 mg/l. Indeed, this method only requires to know the total alkalinity at pH 4.3 (then, less than 1 % of bicarbonate is converted in carbon dioxide) and the volume of acid added to lower the pH from 5 to 4 (V<sub>5-4</sub>). In order to decide on the most appropriate approach for our final objectives (i.e., precision as high as possible while maintenance as low as possible), we performed a careful comparison between the different calculations:

a) The Kapp method with TA and V<sub>A5-4</sub> (Kapp, 1992),
b) The Anderson method with pH 5.1 and pH 3.5 (Anderson and Yang, 1992),
c) Calculation from measurements of TA and PA at pH 5.75,
d) The Moosburger method using added volumes of acid between pH 6.7 and 5.9 and between pH 5.7 and 4.3.

It was experimentally noted that the Kapp method has the lowest residual standard deviation while being the most robust facing clogging of the pHmeter. It was thus decided to use the Kapp method but to modify it in order to determine also the bicarbonate concentration.

**MATERIALS AND METHODS**

**Wastewater and bioreactor**

The effluents are raw industrial wine wastewaters obtained from local wineries in the area of Narbonne, France. Neither sterile nor homogeneous, this wastewater has changing characteristics with COD ranging from 15 to 45 g/l and total VFAs from 1 to 8 g/l. The process is an up-flow anaerobic fixed bed reactor made of a circular column of 3.5 m height, 0.6 m diameter and a useful volume of 0.948 m³.

**Sampling and on-line titration**

In order to reduce cost, a self-made titrimetric sensor was developed (see Figure 1). This sensor is made of a pH electrode (Heito, France) in a titration vessel (internal diameter of 2 cm and height of 12 cm). Cleaning of the cell, introducing of the sample and adding of acid is realised by two 10-ml syringes, twelve valves and two step-by-step bipolar motor (48 steps/tour) connected to an electronic device made of two 8255 components and managed by a 66 MHz PC486 computer. A pump is also managed to ensure bulling with air in the cell and good mixing of the sample and the acid. The overall operation of the titrimetric sensor is managed by self-made software.

During the titration, 2 ml of sample is introduced by gravitation in the vessel and pH is recorded during the titration of the sample adding HCl acid (0.1N) from the syringe (1 rotation of the motor introduces 5 µl of acid) from initial pH to 5.75 and then 3 (in fact, it would have been enough to realise titration only until 4 since calculations only require this value but 3 is a good compromise to avoid influence of noise from the pHmeter).

Duration between introduction of the sample and ending of the calculation after titration is less than 3 minutes. In addition, the computer allows the titrimetric sensor to be fully autonomous since it manages the sample taking, the titration operation and the calculation of total and partial alkalinity together with VFAs and bicarbonate concentrations. Automatic calibration of the pHmeter is also performed using buffering solutions of pH 4 and 7. Last but not least, calibration of the overall titrimetric sensor is automatically performed using soda 0.1N (100 meq/l) instead sample from the anaerobic digestion process.

Typical titration curves are shown in Figure 2. Buffer effect of bicarbonate induces a plateau between pH 7 and 6 while the presence of VFAs modifies the slope of the curve after pH 5. These curves are recorded as pH with respect to rotations of the motor used for acid addition but they can be easily translated as pH = f(volume of acid added).

In order to check first the linearity of the titrimetric sensor, measurements were performed using a sample from the reactor (69.9 meq/l) diluted several times with tap water (8 meq/l). All measurements were performed 3 times each. As can be seen in Figure 3, linearity is very good for both partial and total alkalinity ($r^2 > 0.999$). Repeatability and reproducibility of the measurements were also carefully checked and very similar results were obtained.
RESULTS

In 1997, it was then decided to implement this sensor on the process to perform measurements in the reactor every 30 minutes. This sampling time could have been lowered to 3 minutes but it was judged enough to provide dynamical behaviour of the process while not inducing high consumption of the reactants.

As an illustration of the results obtained, Figure 4 shows a two month period of operation in 1999 for VFAs measurements without any human intervention on the titrimer (between day 28 and 29, an electrical problem made the process stop and data were lost). It can be noted that on-line VFAs measurements from the titrimer and manual analysis from gas chromatography are very closed despite a broad range of operating conditions. In addition, the increase of noise signal of the titrimer after day 36 (due to pipes and pHmeter clogging) did not modify the accuracy of the titrimer. At day 56, the titrimer was cleaned and the pHmeter manually recalibrated. Noise in the measuring signal was then similar to the one observed between day 0 and 36.

This sensor has been shown to provide very useful information for process monitoring and control. For example, regulation of the ratio TA/PA was possible and VFAs accumulation in the reactor was avoided despite large disturbances in the influent (Bernard et al., 2001). In another application, direct regulation of VFAs has been very efficiently performed for different setpoints using a fuzzy logic based control strategy (Puñal et al., 2002).

Figure 1. Schematic view of the titrimetric sensor

Figure 2. Typical titration curves obtained for different VFA and bicarbonate concentrations

Figure 3. Checking linearity of the PA and TA measurements from the titrimetric sensor using tap water (8 meq/l) and a diluted sample (69.9 meq/l without dilution)

Figure 4. Comparison over 2 months without any human interaction of the results provided by the on-line titrimer and VFAs manually obtained from gas chromatography.
CONCLUSIONS

A self-made titrimetric sensor for measurements of total and partial alkalinity and estimation of volatile fatty acids and bicarbonate concentrations has been developed and tested over a five year period of daily use with one measurement every 30 minutes. This sensor has been shown to be very reliable providing very useful information for process monitoring and control in real time (one measurement last less than 3 minutes). Last but not least, this sensor is very cheap (less than 3000 US dollars) and requires manual maintenance that is fully compatible with industrial applications.

REFERENCES


