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Ammonia Concentration and pH Control in Pilot Scale Two-Phase Anaerobic Digestion of Food Waste for Hydrogen Production: Focus on Start-up

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This paper deals with the start-up strategy of a two-phases thermophilic anaerobic digestion process treating food waste, optimized for the production of hydrogen and methane. In order to keep the pH of the dark fermentation reactor in the optimal H_2 production range (5-6), recirculation of anaerobic digested sludge was used. A drawback of such approach is the accumulation of ammonia into the system with the risk of hydrogenogenic and methanogenic processes inhibition. Therefore this study was focused on the investigation of the recirculation ratio that allows to carry out the start-up phase control approach at pilot scale. Two pilot scale stirred reactors were used; the experiment was set-up considering two recirculation ratio of 0.4 and 1, maintaining the organic loading rate in the first and second phase of 18-20 $kg_{total\ volatile\ solids}/m^3d$ and 4.5 $kg_{total\ volatile\ solids}/m^3d$ respectively. The hydraulic retention time applied was of 3.3 days in the first and of 12.7 days in the second phase. A promising start-up strategy was obtained applying a recirculation ratio of 1; the partial alkalinity content in the second reactor of about 2,800 $mgCaCO_3/L$ allowed to reach a pH value in the first reactor of 5.5 after 10 days.

1. Introduction

Several studies showed the advantages of using hydrogen in combustion engines and found that the addition of small amounts (5–10%) of H_2 to enrich CH_4 biogas, improves the quality of gas combustion. The most interesting aspect arising from the implementation of such mixtures is that hydrogen extends the lean burn natural gas limit. Under these operating conditions, it is possible to achieve lower emission of nitrogen oxides and unburned hydrocarbons. For this reason, many researchers have been focused to optimize the two phases anaerobic digestion process (dark fermentation, DF and anaerobic digestion, AD) to produce H_2 and CH_4.

It was widely demonstrated that pH condition and temperature condition affect the activity of hydrogenase enzyme in the H_2 production process. The optimal condition reported for best enzyme activity was observed to be between pH 5 and 6 with an optimum value at 5.5, and at 55 °C of working temperature (Valdez-Vazquez et al. 2009, Hallenbeck et al. 2009). During fermentative metabolism the organic acids accumulate, decreasing both pH value and H_2 production as a consequence. The study of pH control in dark fermentation was carried out by a number of researchers during the past 10 years, developing several strategies: literature reported lots of thermal or chemical pretreatments used in order to selects the spore forming bacteria and inhibiting the hydrogenotrofic methanogens (Shin et al. 2005, Gòmez et al. 2006, Lee et al. 2010); in a two phase approach the selection occurs inside the fermentative reactor thanks to low pH and low hydraulic retention time (HRT) applied allowing methanogenic microorganism wash out or even their inhibition.

There are several studies that confirm how the hydrogenogenic fermentative pathways could be optimized at pH values above 5. This could be explained considering that when lowering the pH, the consequent increasing of deprotonated species of volatile fatty acids (especially acetic acid) allowed an inhibitory action; so when the

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pH is less than 4 a metabolic shift could happen from hydrogenogenic to solvatogenic pathways, reducing the inhybitory effect of fatty acids. Basically, when the hydrogenase enzyme is inhibited, the reduced ferredoxin is oxidized by nicotinamide adenine dinucleotide (NAD+), and the NADH generated reduces the acetyl-CoA and butyryl-CoA to ethanol and butanol (the so called solvatogenic pathway), respectively. For these reasons when lactic acid, ethanol and butanol are produced, they are not related to hydrogen production; furthermore, the formation of propionate and for-mate indicates the consumption of hydrogen.

From a microbiological point of view even Baronofsky et al. (1984) demonstrated the uncoulping effect caused by acetic acid to *Clostridium thermoaceticum* when pH decrease.

In order to produce hydrogen it is possible to use different organic substrate, but in this experimentation was considered the organic fraction of municipal solid waste (OFMSW), due to its continuous production ad high environmental impact if wrongly disposed. The possibility of using these substrates in dark fermentation for hydrogen production was studied by Cavinato et al. (2011, 2012), Gottardo et al. (2013), Chinellato et al. (2013), but it was not discussed yet the strat-up strategy of the two-phase process for hydrogen production. In this experimental trials two recirculation ratio of 0.4 and 1 were tested taking into account ammonia and pH values of the digegestate effluent recirculated.

2. Materials and methods

2.1 Experimental set-up

In this experimentation two stirred reactors (CSTR) with 230 L of working volume each were used for the experimentation tests. The reactors were heated by hot water recirculation system and maintained at 55 °C using electrical heater controlled by a PT100-based thermostatic probe. The feeding system was semi – continuous, arranged once per day. The biowaste was reduced in size using a grinder and mixed with tap water in order to reduce the solid content. During the experiment (about 30 d), the Organic Loading Rate (OLR) and Hydraulic Retention Time (HRT) were maintained at about 18 kg of total volatile solids (TVS) per m^3d and 4.5 $kgTVS/m^3d$ for first and second phase respectively. The only parameter changed was the recirculation ratio that was set at 0.4 in the first run tested and 1 in the second run. The first phase reactor was filled up with about 30 L of organic waste and 170 L of tap water in order to obtain a TS content of about 8%. The second phase was inoculated with anaerobic sludge of previous experimentation. The tests started after reaching the working temperature.

2.2 Analytical methods

The monitoring program was based on 2/3 times per week analysis in terms of total and volatile solids content, chemical oxygen demand, Total Kjidehal Nitrogen (TKN) and Total Phosphorus (TP). The process stability parameters, namely pH, volatile fatty acid content and speciation, total and partial alkalinity and ammonia, were checked daily. All the analyses were carried out in accordance with the Standard Methods (APHA–AWWA–WEF 2012). Gas productions were monitored continuously by a gas flow meter (Ritter Company, drum- type wet-test volumetric gas meters), while the hydrogen content was measured by a gas-chromatograph (GC Agilent Technology 6890 N) equipped with the column HP-PLOT MOLESIEVE, 30 x 0.53 mm ID x 25 um film, using a thermal conductivity detector and argon as gas carrier.

2.3 Substrate characterisation

The organic waste used in this experimental test was collected in Treviso area and it showed the composition reported in Table 1: fruit and vegetable waste were typically half of the waste material, while pasta/bread and meat/seafood represented another 25% of the wasted food. Some 10% of the material was un-classified (melt material) (Micolucci et al. 2015).

Table 1: organic waste composition (Micolucci et al. 2015)

Composition	Wet Weight %	Dry Weight %
Fruits & vegetables	46-58	38-42
Other kitchen waste *	16-25	15-22
Paper & cardboard	9-14	7-12
Not classifiable	8-14	6-12

Biowaste compositional analysis (of five samples) showed that food waste was more than 82% of the total (on wet weight) while the remaining parts were paper (11%) and inert materials (7%) like glass and metals or textiles

3. Results and discussion

It is firstly important to take into account that this is a two phase process with a recirculation of sludge from methanogenic reactor to the dark fermentation reactor. That means that an equilibrium occurs between the two reactors, influencing each other in terms of buffer capacity, pH and ammonia content.

Usually in a two phases system treating biowaste, the first reactor dedicated to the fermentation step is characterised by low pH due to the formation of organic acids, with pH value ranges from about 3,5 to 5 (Bolozonella et al, 2003). The application of sludge recirculation in a two phase process aimed to bio hydrogen production, has a double outcome: first one is to supply alkalinity in the form of HCO_3^- in order to keep the pH in the right range for hydrogenase enzyme, the other is the increasing of ammnia until inhibitory concentrations.

It is important to highlight that the ion HCO_3^- (that control the pH in the first reactor) is in equilibrium with CO_2 dissolved and correlated with the pH (Figure 1); at pH below 5 the molar fraction of HCO_3^- is low, while increasing the pH above 5, the molar fraction rapidly increase with pH. A correct start-up strategy must cause a rapid pH increasing in the fermentative reactor allowing a buffer accumulation, but at the same time the accumulation of ammonia up to inhibitory values must be avoided.

In Figure 1 are indicated the distribution based on pH of those species involved in the buffer system.

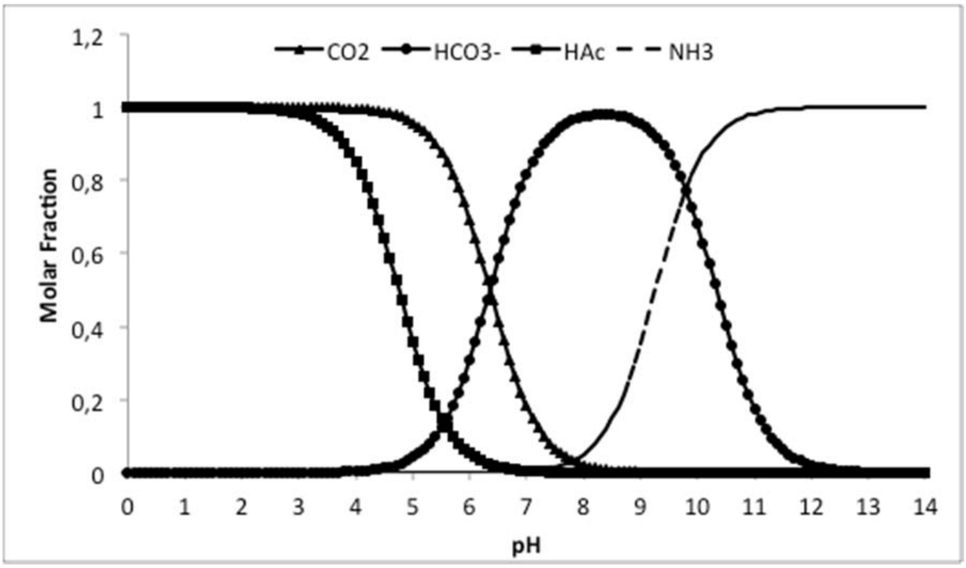

Figure 1: species equilibrium at different pH.

But in a two phase system the characteristics of anaerobic sludge is strictly correlated to the first phase fermented sludge and this means that if the anaerobic sludge has a good amount of partial alkalinity it is possible to send back to fermentation the right amount of HCO_3^- able to increase the pH above 5.5. As consequence the alkalinity of the second phase increase too, creating a continuous feed-back.

Considering previous study results, two recirculation ratios were tested, low (0.4 Qr) and high (1 Qr).

The first run tested with the recirculation ratio of 0.4 was carried out for about 20 days. At the beginning the ammonia concentration in the first phase was less than 500 mg/L with a pH of 4.7 (Figure 2); after 6 days the pH reached 4.85 with slight increase in SHP, but then pH decreased to 4.65 and the specific hydrogen production observed, descreased to about 45 LH_2/kgTVS. During this period the digested sludge was characterised by a decreased partial alkalinity from 2,600 to 2,250 $mgCaCO_3$/L and an average pH of 7.78 (Figure 3). This low concentration of partial alkalinity in the second reactor reflects the low concentration of HCO_3^- in the first reactor; this was mainly caused by the low pH of the system that drove the equilibrium of HCO_3^- and CO_2 in favour of carbon dioxide.

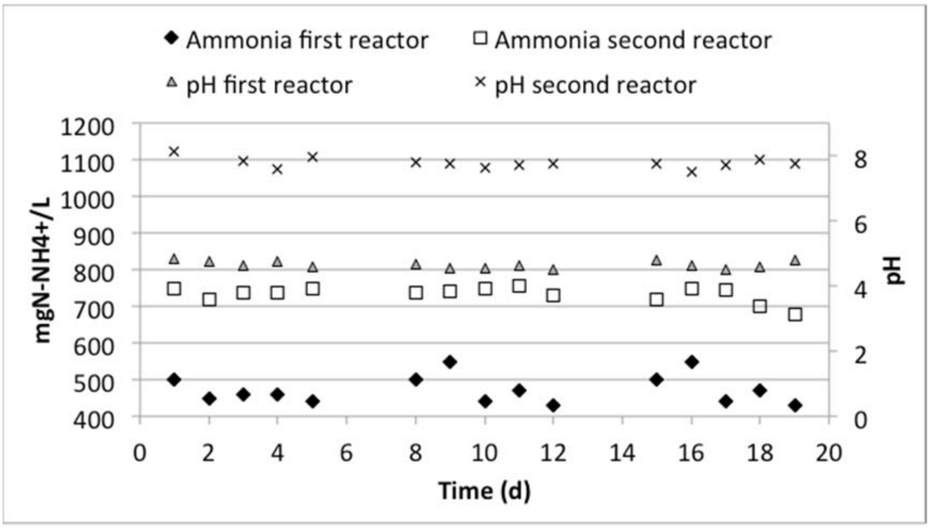

Figure 2: Ammonia and pH of first and second reactor during start-up with Qr 0.4.

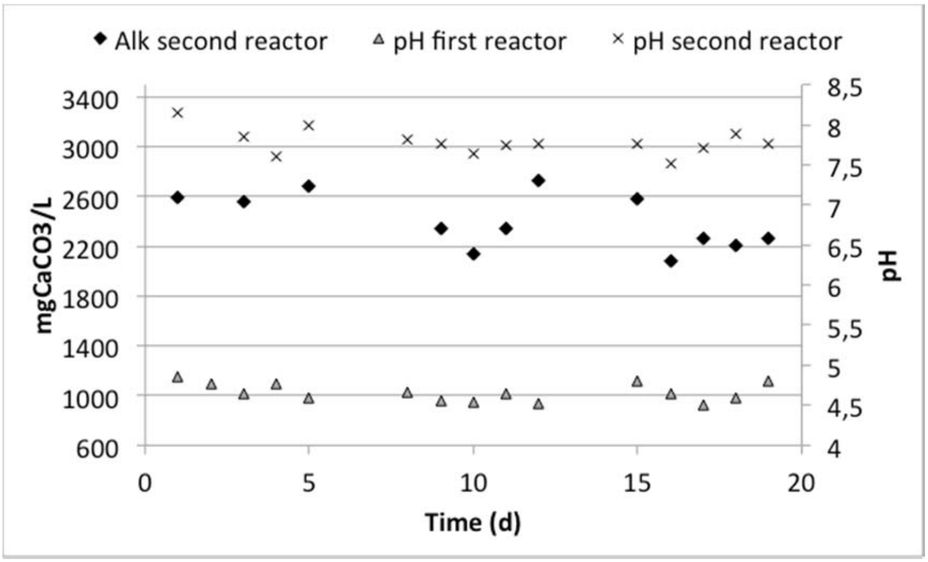

Figure 3: Alkalinity and pH of first and second reactor during start-up with Qr 0.4.

In order to perform a new start-up the reactors were emptied and filled up again: this justified the different initial chemical-physical characteristics. A higher recirculation ratio (Qr of 1) was applied for 10 consecutives days, in order to allow a buffer accumulation in the first reactor: in ten days the ammonia increased from 800 to 1,200 mg/L, similar to the second reactor, and the pH increased from 4.7 to 5.5 (Figure 4).

Considering the characteristics of anaerobic sludge recirculated it was possible to observe that the partial alkalinity content was stable at 2,740 mg$CaCO_3$/L and even the pH was stable at 8. With that alkalinity it was possible to observe an increasing even in the first reactor, in fact the amount of alkalinity as HCO_3^- rose up from about 350 to 1,200 mg$CaCO_3$/L with a consequent increasing in pH at 5.5, the right pH value for dark fermentation hydrogen production (Figure 5). Despite of the pH value, the high ammonia concentration resulted in a inhibition of hydrogen production (40 LH_2/kgTVS) after 9 days.

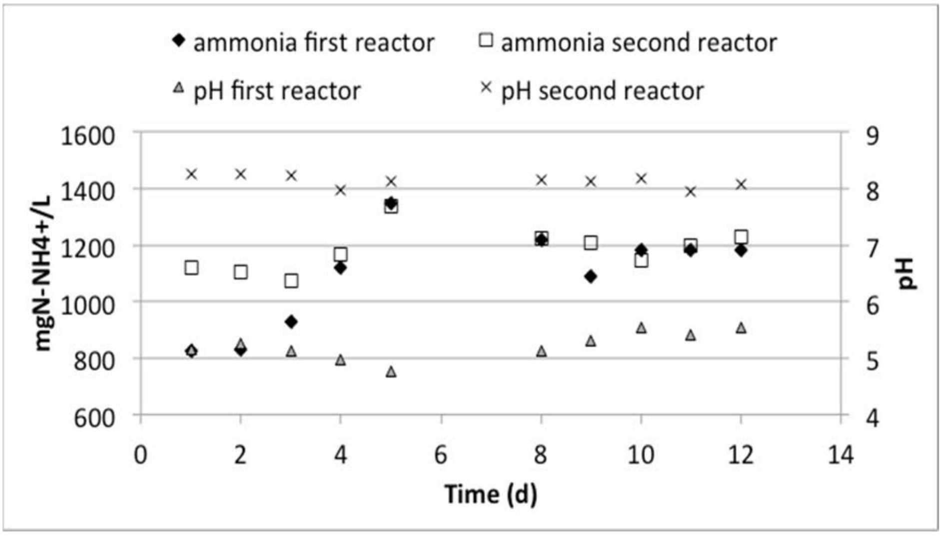

Figure 4: Ammonia and pH of first and second reactor during start-up with Qr 1.

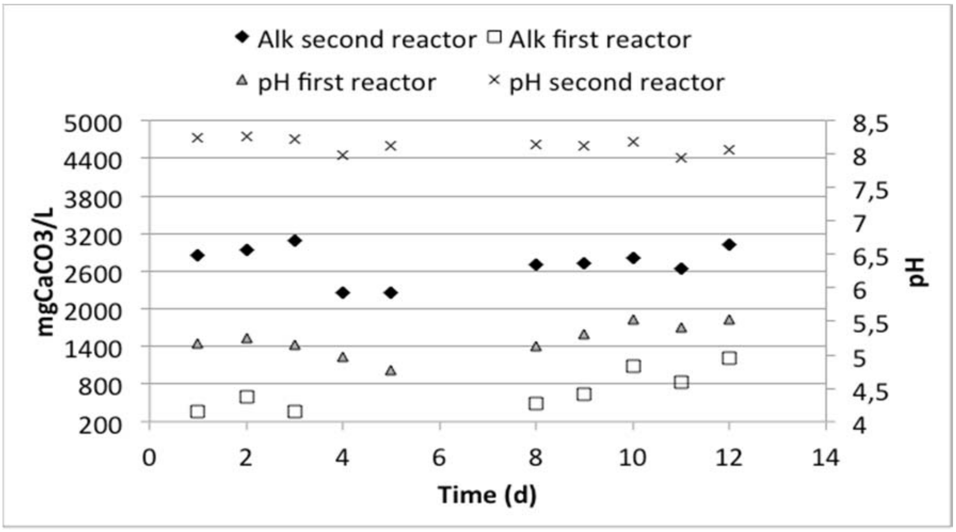

Figure 5: Alkalinity and pH of first and second reactor during start-up with Qr 1.

This means that it is possible to reach the ideal condition for hydrogen production only when the recirculation flow rate was at least 1 and with an alkalinity between 2,500-3,000 $mgCaCO_3/L$. The recirculation caused an increasing of ammonia content that could cause inhibition of hydrogen production, so when reached the ph 5.5 it is necessary to reduce the recirculation flow rate at least of half. These results will be further investigated at pilot scale adopting an automatic system for controlling the Qr.

4. Conclusions

The start-up strategy preliminary results of a pilot scale two-phases thermophilic anaerobic digestion process treating OFMSW was optimized for the production of hydrogen and methane. In order to keep the pH of the dark fermentation reactor in the optimal H_2 production range (5-6), recirculation of anaerobic digested sludge was used. Different recirculation ratio were investigated in order to verify the start-up phase control approach at pilot scale. Two pilot scale stirred reactors were used; the experiment was set-up considering two recirculation ratios of 0.4 and 1, maintaining the organic loading rate in the first and second phase of 18-20 $kgTVS/m^3d$ and 4.5 $kgTVS/m^3d$ respectively. The hydraulic retention time applied was of 3.3 days in the first and of 12.7 days in the second phase. A promising start-up strategy was obtained applying a recirculation ratio of 1; the partial alkalinity content in the second reactor of about 2,800 $mgCaCO_3/L$ allowed to reach a pH value in the first reactor of 5.5 after 10 days. Then it is necessary to reduce the recirculation ratio to half in order to reduce the ammonia concentration that doubled from 600 to 1,300 mgN-NH_4/l.

Acknowledgments

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