TWO-PHASE ANAEROBIC DIGESTION OF WASTEWATER WITH HIGH SALINITY

1. DESCRIPTION OF THE TWO-PHASE ANAEROBIC DIGESTION SYSTEM

A two-stage anaerobic system (acidogenic + methanogenic phase) was operated in continuous mode at lab scale with 2.5L working volume in each EGSB reactor. Briefly, the acidogenic phase was fed with diluted wastewater resulting in a fermented broth which was consequently diluted and fed to the methanogenic phase (Figure 1). Both reactors were inoculated with anaerobic granular sludge harvested from a one phase anaerobic digestion system treating brewery wastewater. Certain variables were controlled or measured online such as Temperature (30◦C), pH, redox, volume of gas produced and biogas composition.

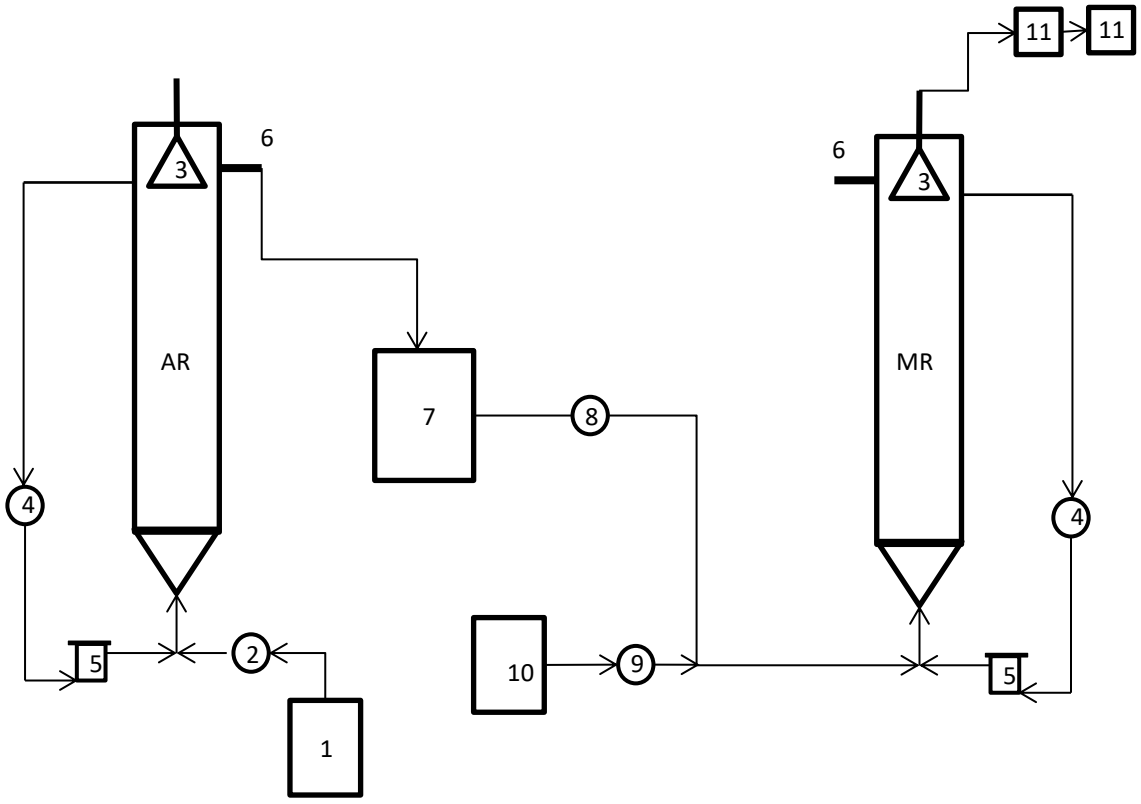
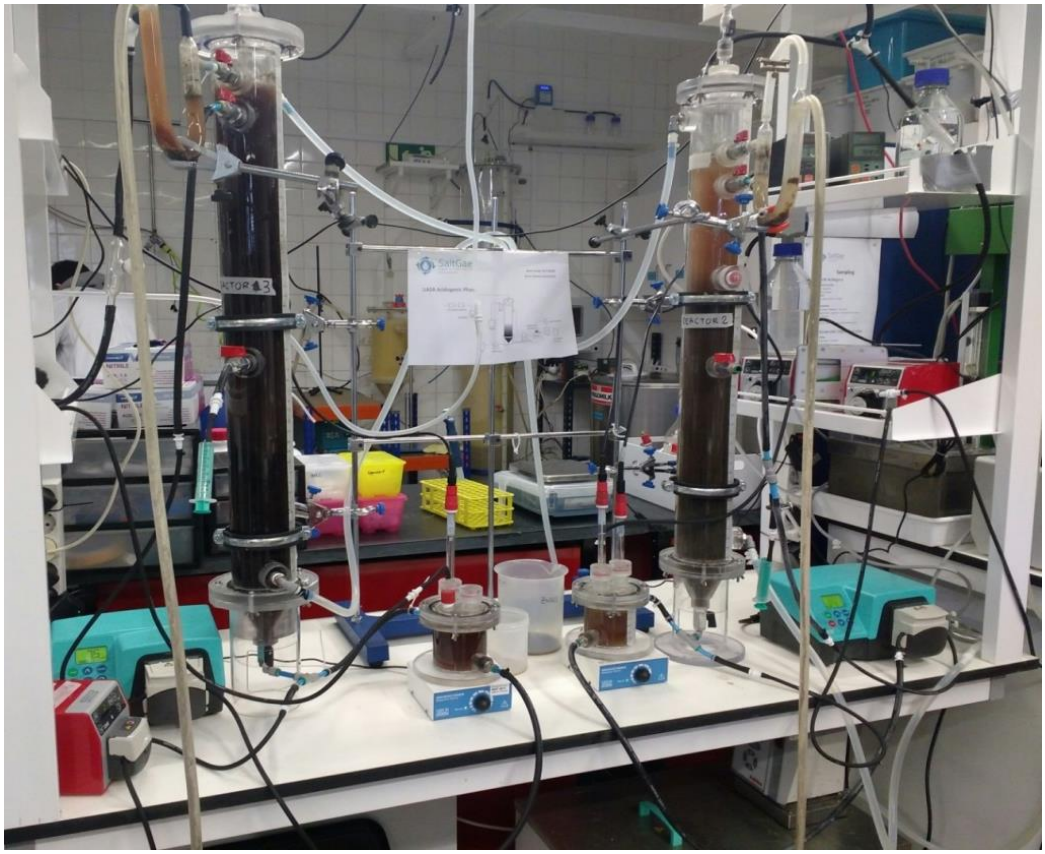


Figure 1 – Top: Schematic representation of the two-phase anaerobic digestion system. 1 – Influent tank; 2, 8,9 - feeding pumps; 3 – Gas solid liquid separator; 4 – recirculation pumps; 5 – pH and redox sensors holder; 6 – Outlet; 7 – storage tank; 10 – Water for dilution; 11- CH_4 and CO_2 sensors: AR – acidogenic reactor; MR – methanogenic reactor. **Bottom:** Picture of the lab scale AD set up.



In addition, samples were taken regularly to assess process performance. For this, COD, sugars, proteins, VFA´s+ethanol+lactate, NH_4^++PO_4^{2-}, TSS and VSS (as an indication of biomass), Ca^+, Na^+, K^+, Cl^-, SO_4^{2-} were analysed. Samples for microbiological analysis were also taken and stored.

Furthermore, batch tests were performed to evaluate the effect of different parameters on the acidification degree and on the biomethane production potential.

2. WASTEWATER CHARACTERIZATION

The wastewater used in the present work corresponds to the wastewater originated from raw hide storage throughout a period. After reception, each wastewater sample was characterized as seen in table 1. The characteristics varied between each lot of wastewater received, particularly regarding COD, protein and sodium contents. Dilutions must be made taking into account not only the inhibition of sodium, but also the COD and protein concentrations as the biomass treating this wastewater must have sufficient substrate to thrive.

Table 1 – Characteristics of the wastewater received

WW reception date	16/01/2017	02/03/2017	21/03/2017	06/09/2017
pH	7.78	n.d.	7.58	6.70
Conductivity (mS)	149.80	n.d.	132.10	79.20
COD total (g/L)	11.35	1.00	8.70	n.d.
COD soluble (g/L)	7.95	0.67	6.32	5.52
Proteins (g/L)	4.55	n.d.	3.38	1.04
Sugar (g/L)	0.03	n.d.	0.06	n.d.
Total VFA (gCOD/L)	2.02	n.d.	1.21	1.98
Cl- (g/L)	132.11	n.d.	103.20	45.87
Ca+ (mg/L)	944.60	n.d.	123.00	0.11
Na+ (g/L)	88.84	n.d.	51.90	42.70
K+ (g/L)	n.d.	n.d.	0.72	0.37
SO_4^{2-} (g/L)	5.54	n.d.	n.d.	n.d.
P-PO_4 (mg/L)	70.53	n.d.	68.40	63.20
N-NH_3 (mg/L)	189.69	n.d.	147.60	322.50
TSS (g/L)	30.80	n.d.	24.40	13.60
VSS (g/L)	2.38	n.d.	1.6	1.15

n.d. not determined or under detection limit

3. PERFORMANCE OF THE ACIDOGENIC PHASE

3.1 Effect of salinity and pH on Acidogenesis – batch tests

Batch tests were performed to assess the acidogenic biodegradability of the wastewater at different pH (5.5, 7.0 and 8.0) and by using different dilutions to achieve different salinities (0.97-57.42 g Na+/L) at pH 7.0.

a. Methodology

500mL bottles were used, inoculated with 20% of non-adapted anaerobic granular biomass which was incubated at 30˚C prior to the experiments in order to consume all endogenous substrate. All the different conditions (table 2) were tested in triplicate. F, I and L were negative control groups, i.e., only water and buffer were added to the granules. G was a positive control, i.e., no wastewater was added and casein was added as substrate. All batch tests were performed at 30ºC and had duration of approximately 30 days.

Table 1 – pH, COD and sodium concentrations applied to each acidogenic batch test**.**

	pH	COD (g/L)	[Na+] (g/L)
A	7.0	6.89	57.42±2.48
B		5.66	48.26±1.66
C		4.35	36.05±1.06
D		2.18	19.88±2.13
E		0.87	9.79±1.79
F		0.00	0.97±0.06
G		6.75	1.00
H	5.5	6.89	54.32±0.30
I		0.00	0.23±0.02
J	8.0	6.89	58.03±2.90
K		0.00	0.22±0.02

Samples were taken daily to analyse the production of fermentation products, monitoring the lag, exponential and stationary phase of each treatment. In addition, VSS/TSS, nutrients (NH_4^+ and PO_4^{3-}), COD and protein were measured at the start and end of each treatment.

Based on the analysis performed, several parameters were calculated, such as acidification degree (DA) (Equation 1) and the specific acidification rate (SAR) (Equation 2).

The DA (%) was determined using the following equation:

$$\boldsymbol{DA = \frac{[FP]}{[COD_{total}]} \times 100} \qquad \text{Equation 1}$$

where, $[FP]$ corresponds to the sum of the concentration of VFAs, lactate and ethanol at the end of each treatment and $[COD_{total}]$ corresponds the total COD at the start of treatment.

The SAR (gFP/(gCOD.gVSS.day)) was determined using the following equation:

$$\boldsymbol{SAR = \frac{FP_{final} - FP_{initial}}{[COD_{total}].[VSS].\Delta t}} \qquad \text{Equation 2}$$

where FP_{final} and $FP_{initial}$ is the FP concentration during stationary and lag phase, respectively, $[COD_{total}]$ corresponds the total COD concentration at the start of each treatment, $[VSS]$ is the concentration of VSS and Δt is the time duration of the exponential phase.

b. Results

Sodium had a visible effect on the performance of the acidogenic community (Figure 2). However, when diluting the wastewater the COD was simultaneously decreased and as such, also the COD concentrations played an important role in the performance. Interestingly, at lower sodium concentrations (< 30 g/L) both SAR and DA were the lowest which could be due to the lower COD concentrations (< 3g/L), i.e., less bioavailable substrate for the conversions. The best SAR (0.0038±.0006 gFP/(gCOD.gVSS.day)) and DA (78.45±8.02%) were obtained at 36 gNa^+/L and initial COD of 4.35 g/L. Nevertheless, high DA was obtained even at sodium concentrations close to 60 g/L (70.75±1.00%). Higher sodium concentrations seem to impact mainly the rate, i.e., longer residence times are needed when working at high sodium concentrations.

Comparing to the SAR obtained for the positive control, group G, (0.0228±0.0083 gFP/(gCOD.gVSS.day)) the group with highest sodium (~60 gNa^+/L) tested presented 66% inhibition. These values are better than those obtained by Lefebre et al., (2007), where 85% inhibition of acidogenesis was obtained at NaCl concentrations above 60 g/L, i.e., 23.6 gNa^+/L, using ethanol as substrate.

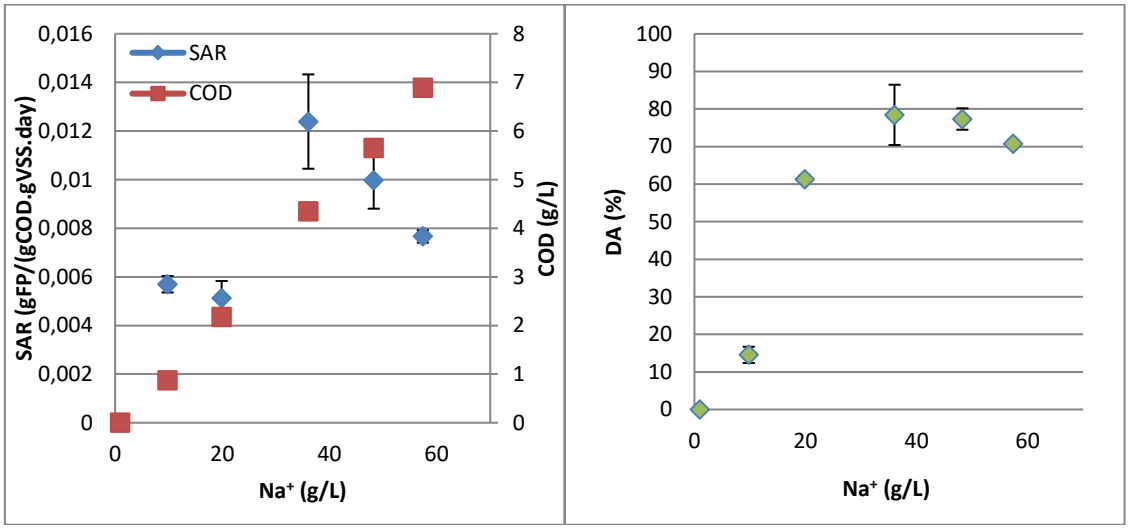


Figure 2 – Effect of sodium and COD concentrations on the specific acidification rate (SAR) and acidification degrees (DA).

The increase of salinity (and increase of COD) seems to have clear impact on the profile of the FP (Figure 3). Higher salinities led to higher concentrations of acetate and butyrate. Isovalerate remained stable when sodium concentrations were above 30 g/L but increased at concentrations below 20 g/L. The enrichment in acetate at higher salinities (and higher COD) is very favourable for the methanogenesis, as methanogenic microorganisms utilize acetate as main substrate.

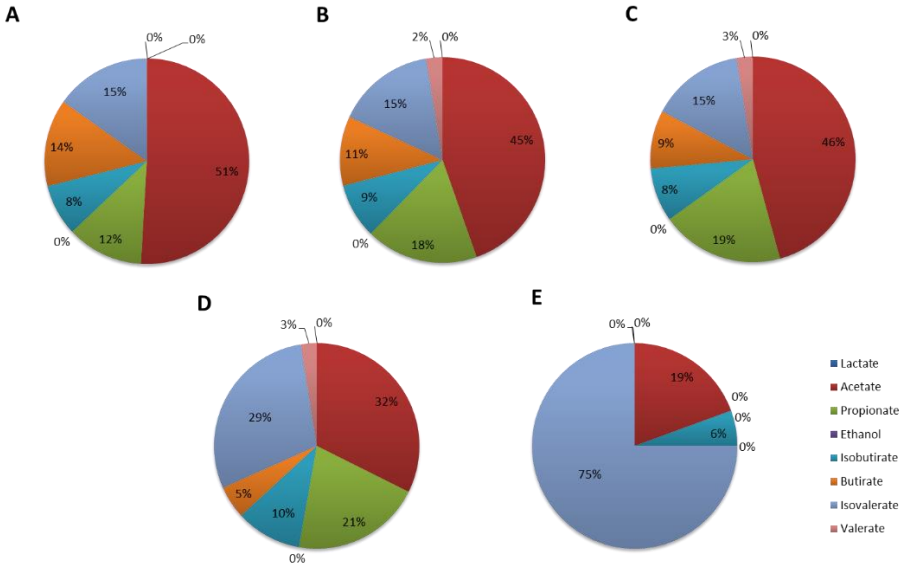


Figure 3 – Effect of sodium on the profile of the fermentation products (A – 57.42±2.48 gNa^+/L; B - 48.26±1.66 gNa^+/L; C - 36.05±1.06 gNa^+/L; D - 19.88±2.13 gNa^+/L; E - 9.79±1.79 gNa^+/L).

pH also had a visible effect on the acidogenesis performance (Figure 4). However, the results obtained are not straightforward. While SAR increased with the increase of pH, reaching its maximum (0.022±0.001) at pH 8.0, the DA was higher (70.75±1.00%) at pH 7.0. On one hand, higher pH seems to speed up the acidification process by a factor of 2.8 (higher SAR). On the other hand, the higher DA at pH 7.0 might be an indication that, given enough time, more substrate can be converted to fermentation products. In addition, the wastewater had a good buffering capacity at neutral pH. Thus, and keeping in mind the costs involved for pH control, pH 7.0 is suggested for the acidogenic phase.

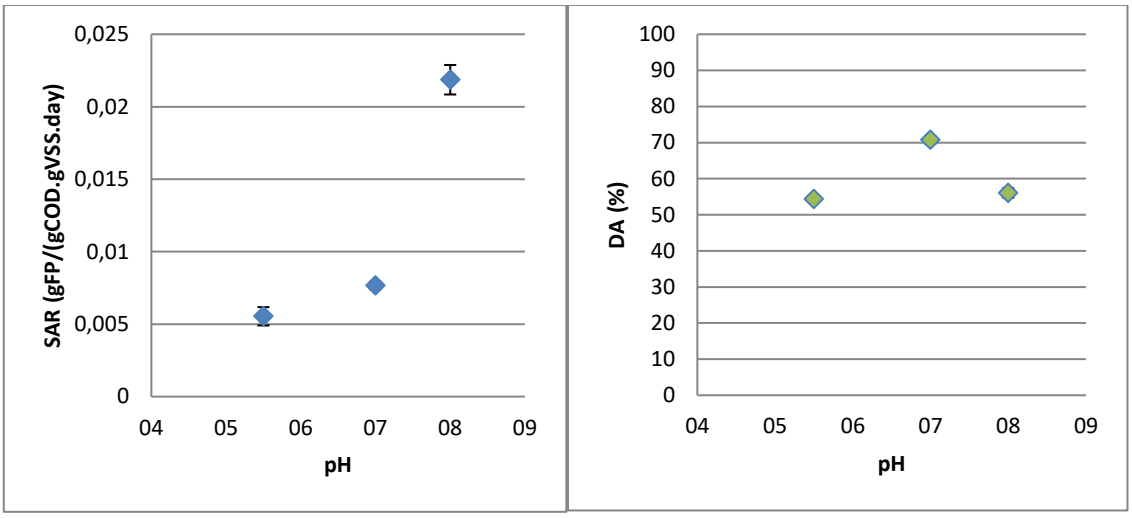


Figure 4 - Effect of pH on the specific acidification rate and acidification degrees.

Although to a lesser extent than sodium concentrations pH also had an effect in the FP profile (Figure 5). More acidic pH resulted in higher percentage of butyrate and lower percentage of isovalerate. No obvious difference in the FP profile can be seen between pH 7.0 and 8.0.

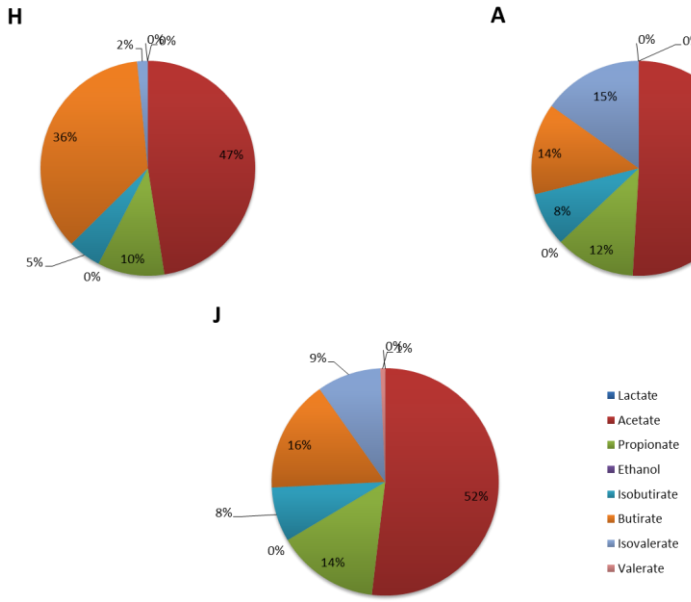


Figure 5 - Effect of pH on the profile of the fermentation products (A – pH 7.0; H – pH 5.5; J – pH 8.0)

4. CONCLUSIONS

The development of anaerobic digestion technologies for SALTGAE project to treat waste/wastewater containing high salinity has implied the following steps:

- Optimization of acidogenic reactor at lab-scale
- Optimization of methanogenic reactor at lab-scale
- Optimization of solid phase anaerobic digestion at lab-scale
- Optimization of CO_2 recovery

As a conclusion of the work done on the optimization of the acidogenic phase, tests showed that the anaerobic microorganisms in the granules used were capable of converting the organic matter present in the pickling wastewater to fermented product even at sodium concentrations as high as 57 gNa^+/L. At pH 6.5, an acidification degree up to 80.66±19.21% was reached at an OLR of 1.24 gCOD/L.d. To our knowledge, such a high salinity was never reported in anaerobic granular bioreactors. The system proved to be robust and can operate efficiently under dynamic feeding with no apparent destruction of granules.

Regarding the optimization of the methanogenic phase, the methanogenic community needed longer time to adjust to the high salinity conditions. Adapting the microbial culture to increasing amounts of sodium proved to be successful (low inhibition) and the methanogenic community was capable of coping with feedstock with sodium concentration of 14 gNa^+/L, producing 0.49 LCH_4/d.

The limit values for sodium in two phase anaerobic granular filters were set based on laboratory experiment to avoid inhibition in mesophilic anaerobic treatment:

- Acidogenic reactor: a sodium concentration of maximally 50 g Na+/L
- Methanogenic reactor: a sodium concentration of maximally 20 g Na+/L

The test in continuous operation has been demonstrated at larger, pilot scale, with successful gradually adaptation of microbial culture in the granules to high salinity. The sodium concentration in the Acidogenic reactor has been up to 38.7 g Na+/L and in the Methanogenic reactor up to 25.1 g Na+/L.

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