Anaerobic digestion of agroalimentary industry wastes at laboratory scale

Ania Escudero[1*], Arrate Lacalle[1], Fernando Blanco[1], Miriam Pinto[1], Jose Javier Leniz[2], Agustín Esparta[3]
(1) NEIKER-TECNALIA Basque Institute for Agricultural Research and Development, via Berreaga 1, 48160 Derio, Spain
(2) ONITEK S.L., Society for Energy and Environment, Bizkaia Technology Park, Building. 101 – C, 48170 Zamudio, Spain
(3) ONDOAN S. Coop., Bizkaia Technology Park, Building. 101 – C, 48170 Zamudio, Spain
*Corresponding author: aescudero@neiker.net

Abstract
The aim of this work was to evaluate anaerobic digestion as a valid treatment process for agroalimentary industries' wastes. A series of laboratory experiments were performed in 8 L tank digesters at 38ºC, fed semi-continuously with different mixtures of these wastes. The influence of HRT and temperature in the system was also studied. With a loading rate of 1.88 gVS $L^{-1}d^{-1}$ and 30 days of HRT, biogas productions of 0.8L $L^{-1}d^{-1}$ and 21L per kg of substrate added were achieved. With a higher HRT, although the biogas production decreased, due to a lower loading rate, the biogas production per amount of substrate added increased (30L kg^{-1}). At 43ºC, the productions achieved were higher (1.14L $L^{-1}d^{-1}$); however a slight accumulation of VFA was observed. Replacing a 2.5% of sheep manure by corn forage or glycerine in the mixture, the biogas productions increased mainly due to a higher volatile solid content in the corn forage and a greater degradability of glycerine.

Introduction
Waste generation is a constantly increasing problem of modern societies that has been observed already since the industrial revolution. Waste production has come to a point of being a severe worldwide issue that needs urgent and accurate measures [1]. The European Community has identified this need and has laid the basis for an environmental policy guided by three axes: reduction of waste, valorization of waste and treatment of waste. Agroalimentary industry wastes cause important environmental problems as their high nutrient and organic content, therefore, the treatment of some of these residues has emerged as a major concern.
Anaerobic digestion has become and established a proven technology as a means of managing organic wastes [2]. This technology can be a suitable treatment in the management and valorisation of agroalimentary industries' wastes, as in this process the organic matter is degraded to methane which can be used as an energy source to replace fossil fuels and thereby reduce carbon dioxide emissions [3]. Furthermore, only small amounts of sludge are produced during the process. This sludge retains most of the nutrients from the starting material and can be applied to soil as a fertilizer [1].
In addition, this technology has evolved quickly and can be competitive with aerobic systems, especially for treating industrial wastewater and organic solid waste with high organic loading. In anaerobic treatment, combined digestion is the term used to describe the combined treatment of several waste with complementary characteristics, being one of the main advantages of the anaerobic technology. Thus, the principal aim of this work was to evaluate the anaerobic digestion as a valid treatment process for some of these wastes.

Material and Methods
Inoculum and agroalimentary industries' wastes
The reactors were inoculated with methanogenically active biomass from the Iurreta wastewater treatment plant (Spain). The total solid (TS) and volatile solid (VS) contents of the inoculum were 4.2 and 1.9 % respectively; the pH was 8.0 and the chemical oxygen demand (COD) was 18.3 gO_2 L^{-1}.
For the following assays, different problematic wastes in the area were selected, such as pig slurry, cheese whey and sheep manure. The main criteria for achieving an adequate substrate mixture for co-digestion were: (1) TS content in the mixture must be sufficiently low to avoid hydraulic problems in

digesters, (2) mixture's C/N ratio should not be too low as it could affect the biogas production in the system and (3) cheese whey content in the mixture should not be excessive (around less than 40%) as it can lead to a system acidification [4]. Following these criteria, a mixture of 65% pig slurry, 35% cheese whey and 5% sheep manure was established.

In last assay, in order to study the significance of C/N ratio and TS content in the feeding substrate, two different mixtures were prepared for feeding two different digesters, replacing a 2.5% of sheep manure by a 2.5% of glycerine in first mixture and by a 2.5% of corn forage in second one. The characteristics of different mixtures for co-digestion are shown in Table 1.

The substrate was pasteurized for 2 h at 70ºC in a thermostatic bath before being fed into the reactors for anaerobic digestion.

Table 1: C/N ratio and TS and VS content in the different mixtures used for co-digestion.

	% Waste mixture	C (%)	N (%)	C/N	C/N mixture	%ST	g ST	% ST mixture	%SV	g SV	% SV mixture
Pig slurry	65	1.4	0.3	5.1	**9.8**	1.7	1.1	**7.5**	1	1	**5.7**
Cheese whey	30	3.1	0.2	18.5		5.7	1.7		5	2	
Sheep manure	5	41.8	2.2	19.2		94	5		70	4	
Pig slurry	65	1.4	0.3	5.1	**10.9**	1.7	1.1	**7.8**	1	1	**6.2**
Cheese whey	30	3.1	0.2	18.5		5.7	1.7		5	2	
Sheep manure	2.5	41.8	2.2	19.2		94	2		70	2	
Corn forrage	2.5	47.8	0.8	61.3		97	2		92	2	
Pig slurry	65	1.4	0.3	5.1	**9.7**	1.7	1.1	**5.5**	1	1	**4**
Cheese whey	30	3.1	0.2	18.5		5.7	1.7		5	2	
Sheep manure	2.5	41.8	2.2	19.2		94	2		70	2	
Glycerine	2.5	1.4	0.1	14.0		12	0		4.7	0	

Digesters

The digestion experiments were performed in three glass tank reactors of volume 8 L, which were equipped with a mechanical shaker (IKA Eurostar power P4 model, operating at 13 rpm), a thermostatic bath with recirculation (Hubber, CC-250 B model, set at 35ºC), a pHmeter (KNICK 911 model, with Polilite Lab electrode for a range of 0-14 pH), a gas flowmeter (Ritter MilliGas counter MGC-1) and gas sampling bags (RITTER 5, 10, 40 and 60L).

The feeding was carried out by an in-feed located at the top of the digesters. A two-way peristaltic pump (Masterflex L / S Model 7554-85) was used to extract the digestate and introduce the substrate in the digesters simultaneously to avoid pressure changes inside them.

Experimental procedure

The digesters were initially charged with 8L of inoculum and thereafter fed once a day with a mixture of 65% pig slurry, 35% cheese whey and 5% of sheep manure, except at weekends. Firstly a gradual acclimatation of the inoculum was necessary to enable the stability of the system to be assessed [5] increasing the loading rate from 0.41 to 1.88 gVS L^{-1} d^{-1} and the Hydraulic Retention Time (HRT) from 90 to 30 days as the system reached stability. The stability was verified by periodic determination of the following control parameters: alkalinity, biogas production, pH, redox potential and biogas composition.

Afterwards, the influence of two control parameters in anaerobic digestion process was studied (temperature and HRT) increasing the temperature of one of the digesters to 43ºC and the HRT to 45 days in other. Finally, in last assay, in order to study the significance of C/N ratio and TS content in the feeding substrate, two different mixtures were prepared for feeding two different digesters, replacing a 2.5% of sheep manure by a 2.5% of glycerine in first mixture and by a 2.5% of corn forage in second one.

Results and discussion

The gradual increase in the loading rate led to an increase in the relative production of biogas, which reached approximately 0.8 L L^{-1} d^{-1}, which means that with a HRT of 30 days and a loading rate of 1.88 gVS L^{-1} d^{-1} around 21L biogas per kg of substrate added were achieved, with a 59-61% methane concentration. With these operating conditions, the system maintained the stability, based on a constant pH and alkalinity evolution along the assay. Thus, it seems reasonable to believe that a mixture of pig slurry, cheese whey and sheep manure in a 65:30:5 ratio, with a TS content of 7.5% and a C/N ratio of 9.8, appears to be an appropriate input substrate for the anaerobic digestion process.

When the HRT was increased to 45 days, the related biogas production decreased slightly to 0.75 L L^{-1} d^{-1}, and the average production of biogas per kg of substrate added was 30 L, higher than the 21 L produced with a HRT of 30 days. Comparing biogas productions obtained by operating the digester with a HRT of 45 and 30 days, we can observe that though the relative production was less when the HRT was higher, due mainly to a lower loading rate, biogas production per amount of substrate added was higher. Therefore, it seems reasonable to conclude that with 30 days of TRH the substrate was not degraded as much as when the TRH was 45 days.

Operating the digester at 43ºC with a HRT of 30 days and a loading rate of 1.88 gVS L^{-1} d^{-1}, the average relative production was 1.14 L L^{-1} d^{-1} and the biogas production per kg of substrate added reached values close to 29L, higher than the ones obtained at 38ºC (0.8 L L^{-1} d^{-1} and 21L kg^{-1} respectively). However, while the biogas production increases with higher temperature, this parameter also plays an important role in the toxic effect of specific inhibitory compounds (ammonium, sulphide, volatile fatty acids, etc.) because of the higher growing rate of the microorganisms at higher temperatures [6]. After 30 days of digestion, an accumulation of volatile fatty acids (VFA) was observed causing a decrease in the pH of the medium. Nevertheless, the system was able to get over this instability, recovering initial pH and alkalinity values.

Replacing a part of sheep manure by corn forage, the productions increase, achieving a biogas production per kg of substrate added close to 31L and an average relative production of 1.04 L L^{-1} d^{-1}. According to prior degradability tests carried out, the corn forage has a degradability ratio of around 5% and the sheep manure close to 17%, so the higher biogas production with corn forage was not due to its higher degradability rate. Therefore, it seems reasonable to conclude that this higher production was a result of corn forage's higher VS content and consequently a higher loading rate in the digester (2.06 gVS L^{-1} d^{-1}).

Replacing a part of sheep manure by glycerine, the biogas productions increased, achieving a biogas production per kg of substrate added close to 33L and an average relative production of 1.23 L L^{-1} d^{-1}, even with a lower VS content of the glycerine and consequently a lower feeding loading rate (1.37 gVS L^{-1} d^{-1}). According to previous degradability tests carried out, the glycerine has a degradation rate of about 60%, so this increased production in this assay seems to be due to a higher degradation of glycerine compared to sheep manure.

The biogas composition in reactors remained constant throughout the assays (at about 59-61 % of CH_4).

Slight accumulation of ammonium was observed in all assays, up to a concentration of 4 g L^{-1}. The threshold considered as inhibitory varies widely, between 1.7 and 14 g L^{-1} [7, 8], and therefore, as an accumulation of large amounts of ammonical nitrogen, in conjunction with changes in pH, can produce inhibitory concentrations of ammonia, it must be kept under control.

Conclusion and perspectives

Based on the results, it appears reasonable to conclude that anaerobic digestion, with a gradual acclimatation of the inoculum, seems to be a suitable treatment process for different agroalimentary industries' wastes tested, achieving biogas relative productions up to 0.8 L L^{-1} d^{-1} and 21 L per kg of substrate added with a loading rate and HRT of 1.88 gVS L^{-1} d^{-1} and 30 days respectively.

A mixture of pig manure, cheese whey and sheep manure in a 65:30:5 ratio seemed to be a suitable substrate for an anaerobic digestion process, since no inhibition was observed in the system.

With a higher HRT, although the biogas production decreased due to a lower loading rate, the biogas production per amount of substrate added increased, because as the substrate was maintained longer in the digester, its degradation was greater.
Although biogas production increased with the temperature increase caused by a greater growing rate of microorganisms, the temperature also plays an important role in the toxic/inhibitory effect of different compounds (ammonium sulphide, volatile fatty acids, etc.), leading to a slight accumulation of VFA.
Replacing a 2.5% of sheep manure by corn forage in the mixture, the biogas productions increased mainly due to a higher VS content in the corn forage. Likewise, replacing sheep manure by glycerine, the productions of biogas obtained were higher caused by a greater degradability of this last substrate.

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