



A comprehensive evaluation of cheese whey to produce biogas in the Canary Islands

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ARTICLE INFO

Keywords:

Dairy industry

Methane

Biochemical methane potential

Anaerobic digestion

Bioenergy

ABSTRACT

Cheese whey (CW) is a by-product of the cheese industry with pollution potential if not properly managed. This study evaluates biogas potential from CW samples from the Canary Islands. Empirical data were used to evaluate biogas potential at cheese factory, municipality, insular and regional level. 24 samples of CW were collected from 17 different farms across the Canaries, including different industries (artisan/industrial), different milk types (cow, goat, sheep, cow + goat, goat + sheep, cow + goat + sheep) and different post-treatments (cottage cheese production, filtering and skimming, inverse osmosis) to study their physical and chemical composition and biogas potential through Biochemical Methane Potential assays. Composition showed significant differences between industrial and artisan manufacturers, showing higher organic matter concentration in artisan CW. Methane potential varied from $450.6 \pm 0.2 \text{ L kg}^{-1}$ to $861.2 \pm 28.8 \text{ L kg}^{-1}$ (on basis of volatile solids). Artisan CW showed a higher methane potential ($\text{m}^3 \text{ t}^{-1}$ of fresh matter) than industrial CW, whereas no differences were observed depending on the milk type. Post-treatments, further processing at factories and degradation at environmental conditions changed CW properties and biogas potential. Results showed that CW should be fed fast into digesters to avoid acidification and the loss of biogas potential. In the Canary Islands 81.95 million litres of CW are produced annually, which could be converted into 4.5 million m^3 of biogas with the potential to contribute 108 TJ y^{-1} of renewable energy into the energy matrix. Valorisation of CW is a promising alternative for small and medium farms/industries in the Canary Islands, which could replace fossil energy with biogas.

1. Introduction

Cheese whey (CW) is an agro-industrial by-product resulting from the cheese manufacturing process. Any cheese industry, regardless of its size and manufacturing method, will inevitably generate this by-product [1,2]. CW has a high nutritional value; therefore, it is normally used to produce cottage cheese (ricotta), food supplements or pharmaceutical products after physical treatments such as ultrafiltration and reverse osmosis [3]. However, small and medium scale cheese manufacturers cannot afford the necessary investment for further processing CW [4,5], and this valuable resource then becomes a potential pollutant. If CW reaches the soil, it may disrupt its physicochemical properties, whereas if CW is poured into water, it may deplete oxygen affecting aquatic life [1]. In this case, CW should be properly treated to avoid environmental

pollution or illegal discharges into the sewage system. According to the high biodegradability of CW, biological processes are often used as stand-alone systems or in combination with other physicochemical processes [2,6].

CW composition depends on several factors, such as the milk type and its quality (composition), the manufacturing process, the amount of yeast, the acid and other additives used for coagulation, temperature, and period of coagulation, etc. Depending on the casein precipitation method two different CW types are obtained: acidic whey ($\text{pH} < 5$) and sweet whey ($\text{pH} = 6\text{--}7$) [6,7]. Besides the acidity, the main difference of both types of CWs is the mineral content and the composition of the proteins. The acidic whey is produced after fermentation when organic or mineral acids are added, whereas the sweet whey is produced by the addition of proteolytic enzymes [1,6].

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<https://doi.org/10.1016/j.biombioe.2023.107008>

Received 28 November 2022; Received in revised form 29 October 2023; Accepted 19 November 2023

Available online 26 November 2023

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Composition of CW described in literature ranges between 0.18 and 60 kg m⁻³ lactose, 0.08–11.0 kg m⁻³ fats, 1.4–100 kg m⁻³ proteins, 10–189 kg m⁻³ mineral salts and a large percentage of water (87.6–93.4 %). The CW chemical oxygen demand (COD) can be variable (0.6–102.1 kg m⁻³) reaching high values due to the presence of lactose [2,6,8,9]. CW retains about 55 % of the milk nutrients and between 80 and 95 % of the milk volume, depending on the cheese yield [1,10]. Cheese yield, at the same time, will depend on two main factors: (i) milk composition (mainly fat and protein content, which will depend on animal species, lactation stage, feeding systems, etc.) and the manufacturing process (cold storage, heating, coagulation, pressing, etc.) [9]. There have been many attempts to predict cheese yield based on the milk composition, leading to a variety of equations for different cheese manufacturing process, showing the complexity in predicting cheese yield and, therefore, CW production and composition [11]. Typical values for the three types of milk mostly used (cow, goat and sheep) are 10 kg cheese per 100 kg of cow/goat milk, and 15 kg cheese per 100 kg of sheep milk [6]. However, there are significant variations for cheese yield in literature. For instance, Pazzola et al. [12] showed a cheese yield for goat milk of 15.73 % (curd yield), whereas Lucey and Kelly [13] reported cheddar cheese yields of 10.1 % and 13.35 % depending on the cow breed.

Previous studies showed that the annual volume of CW production in the Canary Islands ranges between 70 000 and 90 000 m³, most of it at small, artisan industries [14]. The cheese industry in the Canary Islands is rich and diverse, producing a large variety of cheeses from goat, sheep, or cow milk and their mixtures, which are worldwide known and appreciated [15]. However, only a small fraction of the CW produced in the Canary Islands is properly treated through biological or physical treatments, used for feeding animals or for agricultural purposes (no official data are available regarding appropriate treatment of CW). The rest is discharged to the sewage system or into the ground, with negative effects to local water treatment system and to the environment. Moreover, these practices can lead to high fines and legal problems for cheese manufacturers.

In this context, anaerobic digestion (AD) appears as one of the options for the management of CW produced in small and medium scale cheese manufacturers cheese industries in the Canary Islands. During this process, the COD decreases, biogas is produced, and the CW is converted to a nutrient rich, stable by-product, the digestate, which can be used as fertiliser. Biogas could replace the diesel or gas fuel generally used in water boilers to pasteurise milk before coagulation, reducing energy bills and greenhouse gases emissions. If no pasteurisation of milk is done prior to coagulation, biogas may be used for heating water for other industrial processes, e.g. cleaning, and/or for electricity generation. On the other hand, digestate keeps the nutrients contained in the original CW but with the organic matter in stable form after degradation. In this way, it can be used directly as fertiliser in agriculture, albeit further considerations should be taken in those cases, such as its macro- and micronutrient content, soil features, crop demands and limits to its application due to sanitary or environmental legislation.

Biogas production will depend on the CW characteristics and composition, which will depend, as explained before, on the cheese manufacturing process and milk type. Several authors have studied the biogas production from CW [16–19], showing high methane yields ranging between 166 and 369 L kg⁻¹ on COD basis, and sharp decreases (>98 %) in total COD. CW has an acid profile with pH values lower than 5 for acidic whey and between 6 and 7 for sweet whey [6], low alkalinity and low buffer capacity [20], leading to quick acidification of digesters [19]. pH is a critical parameter for anaerobic digestion, the degradation process performs optimally at neutral pH values (6.8–7.4). Lower pH values can inhibit methane-producing activity, which would stop digestion and biogas production [21].

CW has also been studied as co-substrate for the co-digestion of different animal manures, such as cow manure or hen droppings [22, 23]. However, previous studies have paid little attention to the influence of milk origin and the manufacturing process on biogas production.

This study provides a thorough evaluation of CWs produced in the Canary Islands as substrates for biogas production, firstly, based on physical and chemical composition, and Biochemical Methane Potential (BMP) of CW samples taken at 17 cheese industries of different types (artisan and industrial), from different milk types and mixtures, including post-treated and secondary CW. Secondly, governmental statistics from milk production and processing are used to estimate the CW production in the Canary Islands and the biogas production potential for each cheese industry, municipality, and island, providing a comprehensive view of the energy potential by AD from CW in the Canarian Archipelago.

2. Material and methods

2.1. Cheese whey and inoculum

The CW samples were collected from 17 farms and cheese industries on five islands of the Canaries (Tenerife, Gran Canaria, Fuerteventura, Lanzarote, and El Hierro). On each farm/industry, fresh samples (produced in the same day) were collected and kept refrigerated. After the first physical and chemical analyses, samples were frozen until they were used in the Biochemical Methane Potential (BMP) assays to determine biogas and methane yields. A total of 24 samples were obtained from the different farms/industries. More than one sample was collected in the same industry if different manufacturing process or CW post-treatment were applied.

The inoculum used was originally obtained from a full-scale digester located in Gran Canaria, that treats sewage sludge from municipal wastewater.

The CW samples were grouped into different categories according to the milk used for making the cheese: cow (CCW), goat (GCW), sheep (SCW), cow + goat (CGCW), goat + sheep (GSCW), cow + goat + sheep (CGSCW), but also depending on the manufacturing process: industrial (ICW) or artisan (ACW). Regardless of the cheese production capacity, the latter refers here to the lack of milk pasteurisation before coagulation. In contrast, in this study, industrial cheese production involves the pasteurisation of milk. Based on this, 17 CW samples were from industrial cheese manufacturers and 7 from artisan cheese manufacturers. Regarding milk type, 6 samples came from cow milk, 5 from goat milk, 2 from sheep milk, 6 from a mixture of cow and goat milks, 3 from a mixture of goat and sheep milks, and 2 from a mixture of cow, goat and sheep milks. Of all these samples, three were post-treated in two of the cheese factories which participated in the study. The first sample was obtained after the production of cottage cheese in ‘*Quesería de Benijos*’ (Tenerife, Canary Islands). Cottage cheese is only produced from GCW in this factory, obtaining a secondary CW which lost part of its organic matter. The second sample was filtered and skimmed with industrial equipment as part of the post-treatment process to manage CW in ‘*Quesería Maxorata*’ (Fuerteventura, Canary Islands). The last sample was subjected to a reverse osmosis post-treatment, after filtering and skimming, in ‘*Quesería Maxorata*’.

Lastly, one sample was stored outdoors in a one cubic meter tank at environmental conditions before being fed into a pilot scale plant (results are not part of this study and will be reported in due course). This sample was monitored for two weeks to study its changes in composition and biogas and methane yield.

Samples which suffered any post-treatment and degradation at environmental conditions were not included in the calculations of the average and standard error values for the composition, biogas and methane yield of each category.

2.2. Biochemical Methane Potential assays

Biogas potential was analysed through BMP assays performed using a commercial Biogas Batch Fermentation System (Dr.-Ing. RITTER Apparatebau GmbH & Co. KG, Germany) and following the German Standard

VDI 4630 (Verein Deutscher Ingenieure) [24] for the fermentation of organic material. In summary, each substrate was mixed with inoculum in each reactor (1 L total capacity) preserving the following volatile solids (VS) ratio: $VS_{\text{substrate}}/VS_{\text{inoculum}} < 0.5$. Substrate to inoculum ratio was kept under 0.5 to prevent inhibition, ensuring that the substrate was not overlarge in proportion to the inoculum [24].

Then, they were left in anaerobic conditions after purging headspace with N_2 , at controlled temperature (37°C) and with constant agitation for 30–45 days (depending on the biogas production rate). Each BMP assay was finished when the daily biogas production was less than 1 % of the accumulated biogas production after 3 or more days. Biogas produced in each reactor was collected in 1 L biogas bags. When the bag was full, its composition was analysed with a commercial biogas analyser (Multitec 545, Sewerin, Germany) for measuring CH_4 , CO_2 , H_2S and O_2 content. In the case of the blank reactors, biogas composition was analysed at the end of the assay if biogas production from each reactor was less than 1 L.

2.3. Physical and chemical analysis

Substrate, inoculum and reactor content (once substrate and inoculum were mixed at appropriate ratio) were analysed to determine the physical and chemical composition. In addition, the reactor content was analysed again after the BMP assay finished. For each mixture the analyses were repeated 3 times. If one of the replicates deviated greatly from the other two, it was discarded for the statistical analysis. The physical and chemical parameters determined for each sample were: total solids (TS), volatile solids (VS), total and soluble chemical oxygen demand (COD_t, COD_s), pH, electrical conductivity (EC), and partial and total alkalinity (PA, TA). TS and VS were determined according to APHA [25]. Volatile solids (VS) are equivalent to organic dry matter, volatile dry matter, or loss on ignition (550°C), being the fraction from which biogas is produced under anaerobic conditions. COD_t and COD_s were measured following the method 410.4 of the U.S. Environmental Protection Agency. EC and pH were measured by direct immersion of the EC or the pH probe into the stirred CW, inoculum or mixtures samples. Finally, PA and TA were measured according to Ripley et al. [26].

2.4. Cheese whey production and biogas potential in the Canary Islands

CW production in the Canary Islands was calculated based on the regional statistics of milk production, commercialization, and transformation, called INFOLAC (unified information system for the dairy sector), kindly provided by the General Directorate of Livestock of the Canary Islands Government.

This system includes information for each farmer that processes its own milk (and milk which is bought to a third farmer) and each industry that buys milk from one or several farmers and does a transformation. Information includes quantity and type of milk which is processed and the geolocation of the farm/industry. With this information, CW production and biogas potential from CW was calculated based on the coefficients shown in Table 1.

Biogas and methane yields were calculated based on the mean experimental values obtained in this study for each CW type (cow, goat and milk). Since cheese yield (i.e., amount of cheese produced from 100 kg of milk) depends on several factors, it is very difficult to provide a single value valid for all the producers on the Canary Islands. For instance, Pazzola et al. [12] obtained a 15.73 % of cheese yield working with goat milk at laboratory conditions. Aldalur et al. [9] reported cheese yields of 2–3% for sheep cheeses in rural areas of the northern Spanish region, whereas Hayaloglu et al. [27] stated that the average yield of fresh Turkish white cheese from sheep milk was 26–28 kg/100 kg while that from goats or cow's milk was 15–16 kg/100 kg. In this study figures like those reported by Refs. [12,27] were considered, based on knowledge of regional experts and artisan farmers (see Table 1).

Table 1

Data used for the calculation of cheese whey (CW) production and biogas potential from CW in the Canary Islands. STP = standard temperature and pressure conditions.

Parameter	Cow	Goat	Sheep
Cheese Yield (kg/100 kg milk)	12.5	16.7	22.2
CW yield (kg/100 kg milk)	87.5	83.3	77.8
Biogas yield ($L\ kg^{-1}$) ^a	836.02	882.62	861.64
Methane yield ($L\ kg^{-1}$) ^a	577.84	573.68	577.52
Biogas production ($m^3\ t^{-1}$) ^b	46.79	63.49	65.65
Methane production ($m^3\ t^{-1}$) ^b	32.34	41.27	44.00
Lower Heating Value CH_4 ($MJ\ kg^{-3}$)	50		
Density of methane at STP ($kg\ m^{-3}$)	0.7175		
Electrical efficiency (%)	33		
Thermal efficiency (%)	90		

^a Biogas and methane yields are expressed on a volatile solid basis.

^b Biogas and methane production are expressed on a basis of tonnes of CW.

2.5. Statistical analysis

ANOVA statistical analyses were performed to determine significant differences of biogas yield, methane yield ($L\ kg^{-1}$ on VS basis and $m^3\ t^{-1}$ on fresh matter basis) and CW composition. The Tukey post hoc analysis was used to establish which groups were significantly different ($p < 0.05$). With those data sets that did not fulfil the normal distribution requirement, a Kruskal-Wallis analyses was performed. If the homogeneity of variances did not exist, the Welch statistic was used ($p < 0.05$) followed by a Games Howell post hoc analysis ($p < 0.05$). All statistical analyses were performed using the SPSS v.26.0.0 software (IBM Corporation, USA).

3. Results and discussion

3.1. Cheese whey characterization

The CW composition depending on the manufacturing process and the milk type is shown in Table 2. The average ($\pm$ standard error) pH of the different samples was 5.72 ± 0.22 , varying between 3.63 and 6.89. EC was high for all samples ($9.82 \pm 1.49\ mS\ cm^{-1}$). The high variation in EC can be attributed to differences in the manufacturing process

Table 2

Composition of cheese whey (CW) samples depending on manufacturing process and milk type.

CW type	pH	EC ($mS\ cm^{-1}$)	TS (%)	VS (%)	COD _t (g L^{-1})	COD _s (g L^{-1})
ACW (n = 7)	6.0 ^a (0.3)	8.7 ^a (2.1)	7.6 ^a (0.4)	6.9 ^a (0.3)	102.7 ^a (5.7)	78.8 ^a (3.7)
ICW (n = 14)	5.6 ^a (0.3)	10.4 ^a (2.0)	6.9 ^b (0.6)	6.1 ^b (0.5)	88.3 ^b (6.0)	71.1 ^a (6.3)
CCW (n = 6)	5.1 (0.5)	11.6 (3.1)	6.5 (0.4)	5.6 (0.4)	83.2 (4.2)	68.7 (2.6)
GCW (n = 4)	6.3 (0.1)	7.1 (0.3)	7.8 (0.8)	7.2 (0.8)	95.3 (8.6)	74.2 (1.6)
SCW (n = 2)	5.9 (0.4)	13.7 (7.3)	8.7 (0.7)	7.6 (0.2)	112.1 (6.1)	91.1 (7.2)
CGCW (n = 4)	6.1 (0.5)	6.3 (0.2)	7.1 (0.4)	6.6 (0.4)	97.0 (10.3)	71.7 (1.4)
GSCW (n = 3)	6.0 (0.1)	6.6 (0.2)	7.4 (0.2)	6.8 (0.2)	95.7 (5.9)	78.5 (0.6)
CGSCW (n = 2)	5.1 (1.3)	17.9 (10.8)	6.3 (1.4)	5.0 (0.6)	87.5 (10.8)	67.0 (2.0)

ACW=Artisan CW; ICW=Industrial CW; CCW=Cow CW; GCW = Goat CW; SCW=Sheep CW; CGCW=Cow + Goat CW; GSCW = Goat + Sheep CW; CGSCW=Cow + Goat + Sheep CW; Values: average (standard error); n = number of samples; EC = electrical conductivity; TS = total solids; VS = volatile solids; COD_t = total chemical oxygen demand; COD_s = soluble chemical oxygen demand. Significant differences between groups are shown with different letters ($p < 0.05$).

because some industries use table salt (NaCl) in the coagulation vessel, while others do not. In addition, when milk is pasteurised, calcium chloride (CaCl_2) is also used to improve milk coagulation, further increasing the EC. The highest value was 28.7 mS cm^{-1} for a CW obtained from an industrial manufacturer that uses NaCl and CaCl_2 in the coagulation vessel.

TS content was high, with an average value of $7.16 \pm 0.27 \%$, being the highest 10.16% and the lowest 4.94% . VS content (in terms of %TS) was also very high, with most samples around 90% , indicating that CW contains a large fraction of organic matter. TS and VS in CW are a result of the cheese coagulation efficiency in the coagulation vessel, which is dependent on the cheese yield. Higher cheese yields will lead to lower TS and VS content in the resulting CW. Regarding total and soluble COD, values were in the range indicated in the literature [2]. The COD_t varied between 69.15 and 125.79 g L^{-1} with an average value of $93.06 \pm 3.34 \text{ g L}^{-1}$, where a large part was soluble ($80.3 \pm 2.1 \%$), indicating a high and fast biodegradability. Like solid content, COD in the CW depends on the organic matter, which is not retained in the cheese, but left after coagulation in the CW. Therefore, higher coagulation efficiencies led to lower COD (both total and soluble) and consequently, lower polluting potential of CW. Average PA was very low ($290.8 \pm 38.6 \text{ mg L}^{-1} \text{ CaCO}_3$) showing the low pH value and buffer capacity of CW, regardless of its origin. For calculating these average values, data from samples that had a post-treatment were not included.

The results of the statistical analyses to determine if the manufacturing process and/or the milk type have influence on the CW composition were also included. Thus, the industrial process is associated with lower TS, VS and COD_t concentrations compared to the artisan process, probably because of a better use of the milk to produce cheese (i.e., a higher coagulation efficiency). This can be consequence of the use of CaCl_2 to increase the rate of coagulation. No significant differences were observed in the CW composition depending on milk type ($p < 0.05$).

Fig. 1 shows the variation of the CW composition when (a) degradation at environmental conditions occurred for two weeks, (b) when post-treatment was applied and (c) when cottage cheese was made from CW. Degradation at environmental conditions occurs very quickly due to the high content of lactose, which is used by microorganisms as main substrate thus, changing the properties of CW [28]. TS and VS decreased 10.6 and 15.5% after two weeks, respectively. The greatest change took place in pH, with a high decrease (from 5.76 to 3.95). These rapid changes in CW properties highlight the importance of immediate transfer to the anaerobic digester, by avoiding long periods of storage at environmental conditions. In this way, CW will keep original methane potential, since organic matter, in the form of VS, will not degrade outside the digester. Moreover, pH will not decrease, avoiding a faster acidification of the digester after feeding [4]. Post-treatment of CW also caused high variations of the composition. Filtration and skimming decreased OM content and EC by retaining part of the organic matter in the form of cheese fines and decreasing fat content contained in the CW. Inverse osmosis caused a high increase in TS, VS and EC in the concentrate fraction, which normally retained most of the proteins [3]. Furthermore, the use of CW to make cottage cheese led to a reduction in TS and VS without a clear effect in pH nor EC. These changes were expected since cottage cheese whey (CCCW) (also called secondary cheese whey) has been shown to include 50% of the original solids content of CW [29].

3.2. Biogas production from cheese whey

All 24 CW samples processed in 8 series of BMP assays showed high biogas production with high methane content ($>65 \%$). An industrial CGSCW had the highest biogas and methane yield production (1202.0 ± 41.6 and $861.2 \pm 28.8 \text{ L kg}^{-1}$ on VS basis, respectively). The lowest biogas and methane yield (654.2 ± 1.0 and $450.6 \pm 0.2 \text{ L kg}^{-1}$ on VS basis) was observed in an artisan GSCW.

Fig. 2 shows the biogas and methane yields for each CW type.

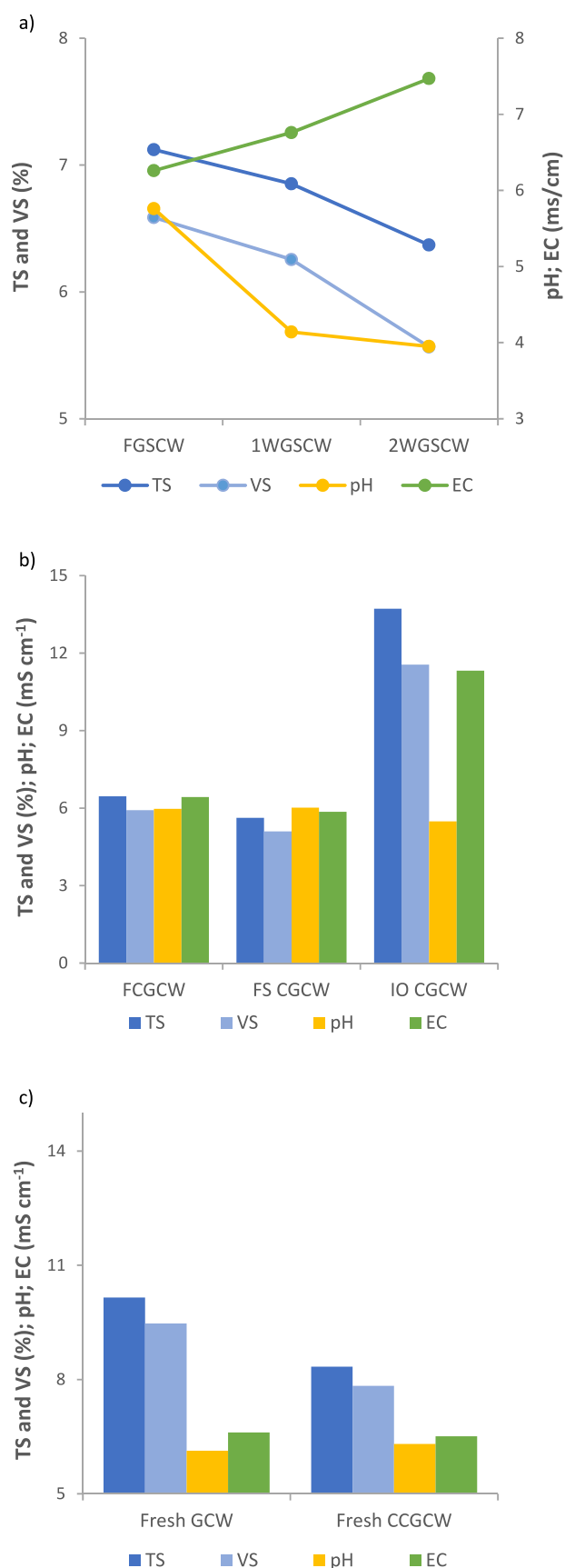
Expressing these in L kg^{-1} on VS basis, no significant differences were found, neither according to the manufacturing process (ICW vs. ACW) (Fig. 2a), nor according to the milk type used (Fig. 2b) (significant differences are shown in Fig. 2 with different letters: lowercase are used for biogas yield and capital letters for methane yield in Fig. 2a and b, whereas lowercase letters are used for methane yield in terms of fresh matter in Fig. 2c and d). However, methane yield based on CW were significantly different between ACW ($55.7 \pm 3.0 \text{ m}^3 \text{ t}^{-1}$) and ICW ($35.2 \pm 3.1 \text{ m}^3 \text{ t}^{-1}$) (Fig. 2c). This is a consequence of the lowest transformation rate in the artisan cheese production process, which led to CW with higher organic matter content than in ICW. Regarding milk type, all CW showed a high biogas and methane yields, being around $40 \text{ m}^3 \text{ t}^{-1}$ (Fig. 2d). The SCW had the highest methane yield ($44.0 \pm 0.8 \text{ m}^3 \text{ t}^{-1}$), which is reasonable because of its highest fat, lactose and protein content in milk compared to other species [30]. Values obtained in this study are similar to those observed by other authors. Escalante et al. [4] showed methane yields between 510 and 600 L kg^{-1} on VS basis, for CWs obtained in small dairy companies. Labatut et al. [31] showed a methane yield slightly lower of 423.6 L kg^{-1} on VS basis, whereas Fernández et al. [32] obtained a smaller value of 314.5 L kg^{-1} on COD basis (397 L kg^{-1} on VS basis). Unfortunately, previous studies did not analyse in a great extent the milk origin and type of manufacturing process used to make cheese.

Biogas and methane yields depend on sample composition, which may change according to milk type and manufacturing process (mainly due to the coagulation efficiency). In general, sheep milk is significantly higher in solids than goat and cow milk, containing more fats and proteins [33], which should lead to a higher biogas production if these differences remain in CW.

Hydrogen sulfide (H_2S) content in biogas varied for each sample analysed, being between 5 and $582 \text{ cm}^3 \text{ m}^{-3}$. In terms of differences between cheese production process, ICW showed an average H_2S content of $262 \pm 25 \text{ cm}^3 \text{ m}^{-3}$, whereas ACW H_2S content was $155 \pm 49 \text{ cm}^3 \text{ m}^{-3}$. Regarding the origin of the milk, GCW showed the highest H_2S content ($314 \pm 38 \text{ cm}^3 \text{ m}^{-3}$), whereas CGSCW showed the lowest H_2S content ($170 \pm 39 \text{ cm}^3 \text{ m}^{-3}$). Given the low values of H_2S content in biogas, no relevant differences were observed between groups. Moreover, no significant differences were observed with an ANOVA analysis ($p > 0.05$) for H_2S between production process (ICW vs. ACW) and milk origin.

The use of CW for further nutritional uses (such as cottage cheese production) should be a priority for those cheese industries that can afford such investments according to the circular economy principles. However, if there are no chances to use the CW for further nutritional uses, it can be converted to biogas with high efficiency conversion. In this study, Cottage Cheese Goat Cheese Whey (CCGCW) showed high biogas and methane yields, although being lower (746.3 ± 31.2 and $520.6 \pm 15.0 \text{ L kg}^{-1}$ on VS basis, respectively) than the original GCW (870.0 ± 37.0 and $598.2 \pm 30.8 \text{ L kg}^{-1}$ on VS basis, respectively). This decrease in biogas production is a consequence of the loss of most of the proteins remaining in the GCW [34], and leaving in the CCGCW only carbohydrates, mainly lactose [35]. As it is well known, sugars generally produce less biogas than proteins per unit of organic matter [36], leading to the decrease in biogas yield. In fact, methane potential also decreased from 56.65 in GCW to $40.82 \text{ m}^3 \text{ t}^{-1}$ in CCGCW. Despite this lower biogas and methane yields, the use of GCW for cottage cheese production followed by biogas production from CCGCW is a better route for the complete valorisation of CW with high energy yields.

The degradation process of a sample of artisan GSCW also influenced the biogas and methane yields. Biodegradation at environmental conditions, which happens if the CW is not fed directly into the digester, led to a higher biogas yield and a slightly increase in methane yield (in terms of L kg^{-1} on VS basis) (Fig. 3a), although no significant differences were observed with a Kruskal-Wallis analyses with the original GSCW (p values were higher than 0.05). This increase is probably due to a higher availability of lactose, proteins and fats, which are converted into



(caption on next column)

Fig. 1. Composition variation according to the biological degradation/post-treatment of different Cheese Whey Samples (CW): a) natural degradation process of a fresh sample of Goat + Sheep CW (FGSCW) after one (1WGSCW) and two weeks (2WGSCW); b) Fresh Cow + Goat CW (FCGCW) after filtration and skimming (FS CGCW) and after inverse osmosis (IO CGCW); c) Goat CW (GCW) after cottage cheese production from fresh GCW (CCGCW). TS = Total Solids; VS = Volatile Solids; EC = electrical conductivity.

volatile fatty acids during the degradation at environmental conditions of CW [20] and readily converted to biogas by anaerobic bacteria. However, Powell et al. [20] did not observe a decrease nor increase in the CW conversion efficiency into biogas in a continuous digester in co-digestion with sewage sludge after 8 months of CW storage. In this study, methane production (in terms of $\text{m}^3 \text{t}^{-1}$) showed a gradual decrease (Fig. 3b) (without statistically significant differences), because of the loss of organic matter in the samples converted into CO_2 during the degradation process (see Fig. 1a). Additionally, a higher H_2S content was observed in CW partially degraded at environmental conditions before AD, increasing from 244 ± 45 in the fresh sample to 300 ± 2 and $582 \pm 605 \text{ cm}^3 \text{m}^{-3}$ for the one week and two weeks degraded samples. H_2S is a result of the competition between sulfate reducing bacteria (SRB) and methanogens in the digester. As already said, CW partially degraded at environmental conditions probably had higher concentrations of volatile fatty acids than the fresh sample, leading to a faster AD process with a short destabilization process which favoured SRB bacteria at the expense of methanogens. In fact, H_2S content was high at the beginning of the assay (close to $500 \text{ cm}^3 \text{m}^{-3}$ in the first measurements), decreasing during the experiment to less than $16 \text{ cm}^3 \text{m}^{-3}$.

3.3. Cheese whey production and biogas potential in the Canary Islands

CW production and biogas potential from CW was calculated at farm, municipal and regional level, using data shown in Table 1. Fig. 4 shows a summary of the main data obtained from the analysis of the INFOLAC database. At a regional level, 81.95 million L of CW are produced annually, which could be converted into 4.5 million m^3 of biogas (3.0 million m^3 of CH_4). So, annual primary energy production from biogas from CW could add up to 30 072 MWh (108 TJ) per year to the energy system of the archipelago. The Canary Islands dependence on fossil fuels is still very high: renewable energy (6756 TJ y^{-1}) accounts only up to 4.1 % of the primary energy ($163 956 \text{ TJ y}^{-1}$) consumed in the archipelago. This percentage increases up to 5.7 % when referring to the final energy consumption ($117 918 \text{ TJ y}^{-1}$) [37]. In this context, the potential primary energy production from biogas from CW is not negligible, accounting up to 1.6 % of the renewable energy produced. In addition, they would contribute to the decarbonisation of sectors that are difficult to electrify, since the biogas would be mostly used to produce thermal energy on farm/industry level.

On an island basis, Gran Canaria is the island with a higher CW production (43.9 million L per year) followed by Fuerteventura (17.9 million L per year) and Tenerife (11.2 million L per year). Daily, up to 4105 m^3 , 2008 m^3 and 1158 m^3 of methane could be produced from CW in each of these four islands, respectively.

There are 42 industries which buy milk from several farmers, five of them also producing their own milk. Moreover, there are 196 farmers which produce and transform their own milk into cheese, making a total of 238 farms/industries producing cheese. Fig. 5 shows the size distribution of farmers and industries in the Canary Islands which transforms milk into cheese in terms of (a) CW produced per day and (b) potential electrical energy and (c) potential thermal energy production from biogas from CW. As can be seen, most of them are very small-scale farmers/industries. Production of less than 200 L per day of CW represents more than 63 % of the total number of farms. Consequently, most farmers and industries would not be able to produce biogas to run a generator higher than 3 kW of electrical power (82.4 %) or a boiler higher than 10 kW of thermal power (65.5 %). However, there is still a

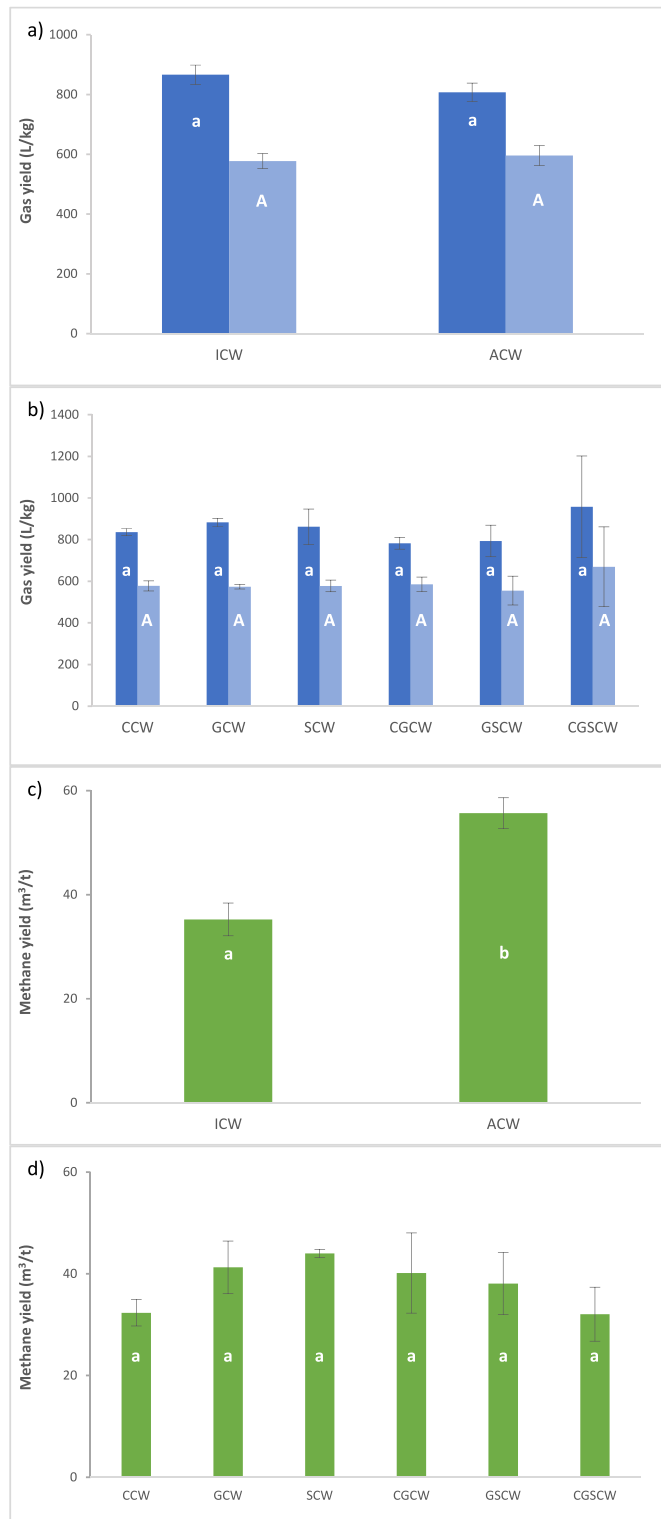


Fig. 2. Biogas (dark blue bars) and methane (light blue bars) yields on VS basis for cheese whey (CW) samples: a) industrial (ICW) and artisan (ACW) CWs; b) cow (CCW), goat (GCW), sheep (SCW), cow + goat (CGCW), goat + sheep (GSCW), cow + goat + sheep (CGSCW) CWs. Methane yields expressed in $\text{m}^3 \text{t}^{-1}$ of fresh matter for CWs obtained from different making process (c); and milk type (d). Error bars indicate standard errors. Significant differences ($p < 0.05$) between groups are shown with different letters (lowercase for biogas yield and capital letters for methane yield in a and b; lowercase for methane yield in c and d). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

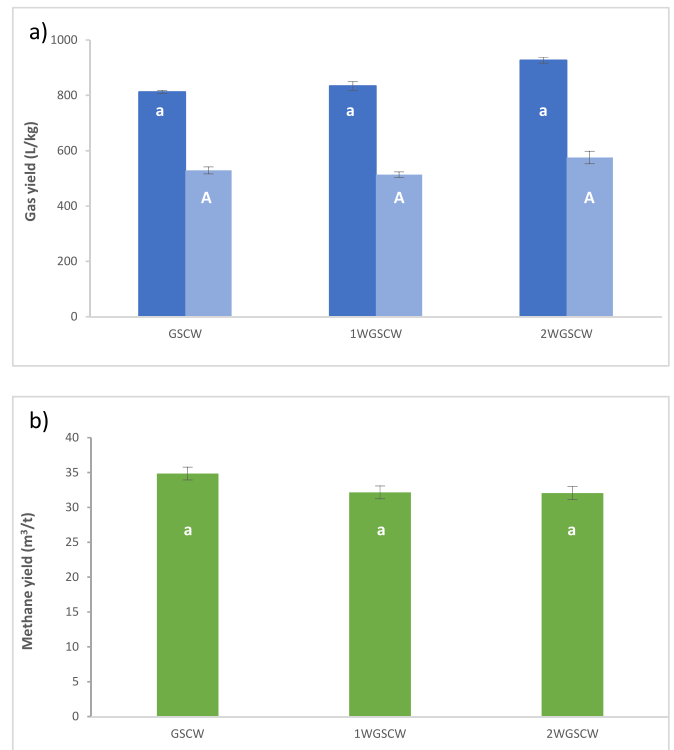


Fig. 3. Biogas (dark blue bars) and methane (light blue bars) yields for goat + sheep cheese whey (GSCW) samples with one (1WGSCW) and two weeks (2WGSCW) of natural degradation. Biogas and methane yields expressed in L kg^{-1} on VS basis (a); Methane yield in $\text{m}^3 \text{t}^{-1}$ of fresh matter (b). Error bars indicate standard errors. Same letters denote that not significant differences ($p < 0.05$) exist between groups (lower case for biogas yield and capital letters for methane yield). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

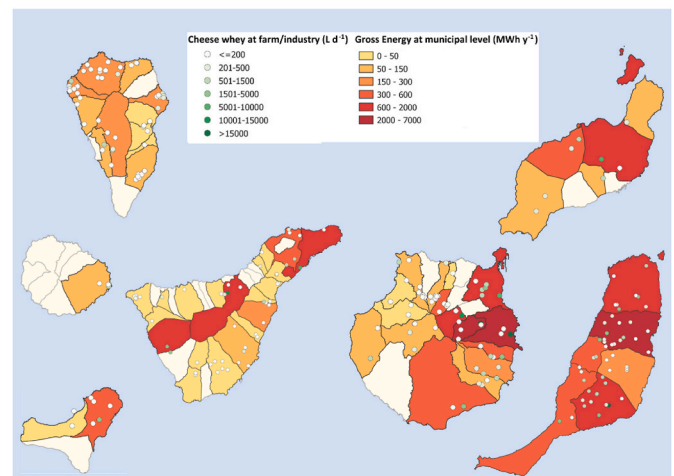


Fig. 4. Gross energy potential from biogas from the anaerobic digestion of cheese whey at municipal level and cheese whey production at farm/industry level (○).

great potential to produce biogas in small-scale industries/farmers at domestic level since most of them use propane to heat up milk before coagulation. Successful experiences have been carried out at psychrophilic range, showing that small scale anaerobic digestion of CW is viable with low investment costs for small industries and farms [38], constituting a model which can be replicated in warm and temperate regions such as the Canary Islands. Furthermore, these transformation

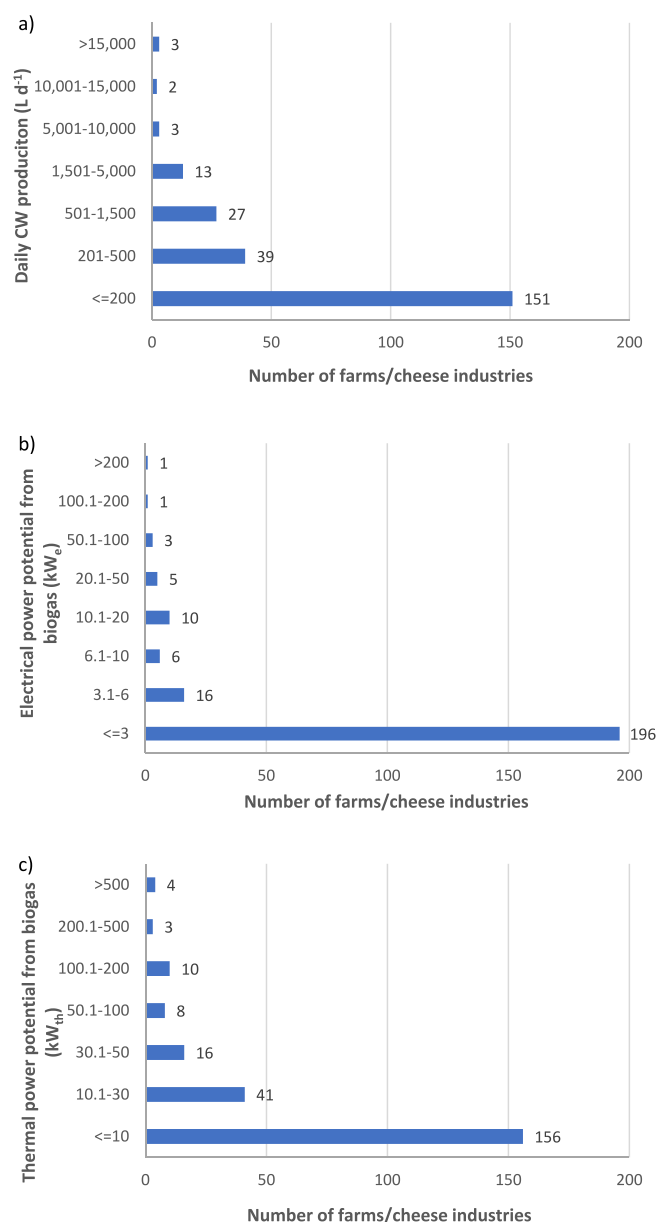


Fig. 5. Size distribution of farmers and industries transforming milk into cheese in the Canary Islands. (a) Cheese whey production per farm/industry (b) power of an electrical generator with 33 % efficiency working during 24 h per day, which could be run based on biogas production potential from cheese whey (c) power of a boiler with 90 % efficiency, which could be run during 8 h per day based on biogas production potential from cheese whey.

into biogas would lead to a sharp decrease in COD levels in the digester effluent.

On the other hand, it should be noted that there are some industries with high potential for transforming CW into biogas to use it as energy source. For instance, 25 farms/industries have potential to produce enough biogas to run a boiler with a thermal power >50 kW during 8 h per day. Most industries pasteurise milk and use diesel for fuelling these boilers which work in a discontinuous way. The use of biogas in these cases would be almost straightforward, since with the substitution of the burner the boilers would be able to use biogas instead of diesel.

The small scale of the livestock industry has already been identified as one of the limitations for the deployment of biogas in the Canary Islands, whereas the cooperation between farmers is scarce in the Canary Islands [39]. Moreover, when promoting centralized AD plants,

there are some factors that should be considered.

- Canary Islands lack a natural gas network, which would make large biogas plants profitable by the conversion of biogas to biomethane and its injection into the national gas grid. The high levelized cost of energy of centralized biogas plants in Europe (64–180 € MWh⁻¹) makes difficult to recover the investment by selling electricity competing with solar and wind energy [40].
- Most of the territory in the Canary Islands has some kind of protection, with the rest of the territory suffering from a strong pressure on residential and tourist uses. Therefore, it is very difficult to locate centralized biogas plants, treating large quantities of wastes, without raising social concerns and criticism [38].

Therefore, the development of small-scale/domestic technologies for individual farmers and industries seems crucial to take advantage of the potential biogas production from CW in the Canary Islands.

4. Conclusions

Cheese whey (CW) showed high methane potentials, varying between 25.2 and 66.4 m³ t⁻¹ on fresh matter basis. Artisan CW (ACW) showed significantly higher methane yields than industrial CW (ICW) due to a lower coagulation efficiency during the cheese manufacturing process. In this sense, ICW also showed lower TS, VS and COD_t content than ACW. The further use of goat milk CW for cottage cheese production led to a secondary CW that could also be used for energy purposes with a methane yield of 40.82 m³ t⁻¹. Moreover, degradation at environmental conditions of CW led to a fast acidification of CW, which could be problematic for the anaerobic digestion process, and to a decrease in methane yields due to the loss of organic matter, highlighting the importance of a fast feeding into digesters. CW production in the Canary Islands was estimated in 81.95 million L per year. Based on experimental results, this CW could be converted to 4.5 million m³ of biogas, contributing up to 108 TJ y⁻¹ to replace fossil fuels. Based on these results, biogas production from CW is a promising alternative for small and medium farms and cheese industries, which could satisfy their energy needs from biogas at farm and industry level, converting a potential pollutant to a source of renewable energy and biofertilizers.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by Programa de Cooperación Interreg MAC 2014–2020, AD4MAC Project (*Fomento de la economía circular y las energías renovables mediante la digestión anaeróbica de residuos y sub-productos orgánicos en la Macaronesia*) (MAC2/1.1b/350).

A shorter version of this study was previously a contribution to the 30th European Biomass Conference and Exhibition under the title 'A comprehensive evaluation of cheese whey for biogas production'.

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