

# Evaluation of biogas production from horse manure and assessment of biogas pathways in Portugal

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June 2017

## Abstract

This work studied the potential of co-digestion of horse manure and swine slurry and the integration of biogas in the Portuguese energy sector. Different co-digestion feeding mixtures were tested with increasing shares of horse manure (HM:PS in terms of percentage of volatile solids inlet): C0 (0:100), C1 (10:90), C2 (13:87) and C3 (20:80), with a mechanical pre-treatment. C3 allowed the best synergetic effect between the microbial consortia of pig slurry and the high C/N ratio of horse manure, yielding the highest SMP of all cycles, 258.3 L.kgvs<sup>-1</sup> and the highest SCOD removal efficiency, 68.5%.

An assessment of biogas and biomethane production potentials in Portugal, from different organic residues, was also done. The expended energy and greenhouse gases (GHG) emissions were analysed for three utilisation pathways: combustion in a cogeneration unit, upgrading for partial substitution of natural gas and upgrading for utilisation as transport fuel. Analysing the energy consumption ratio of each scenario, the first one was the least dispendious, followed by the second (+13.5%) and the third, which showed the highest consumption (+21.1%). The GHG emissions followed the same tendency of energy consumption, with a range of values of 23.9 – 58.8 g<sub>CO2eq</sub>.MJ<sub>biomethane</sub><sup>-1</sup>. The first scenario had the lowest GHG emissions, followed by the second (+37.2%) and third (+39.1%) scenarios. Horse manure and swine slurry are adequate co-substrates for anaerobic co-digestion and this process is a promising waste management solution, at regional-scale, for Portugal. Biomethane is a sustainable energy alternative to natural gas, based on energy consumption and environmental impact.

**Keywords:** co-digestion, horse dung, pig manure, methane yield, energy assessment, emissions

## 1. Introduction

In Portugal, the use of natural gas has increased by 5% in the last decade [1]. The constant attempts to shift for renewable energy sources have justified the continuous study of biogas as an alternative to natural gas. The potential nation-wide production of biogas (as well as the feasibility of this type of energy source as an alternative pathway to the utilisation of natural gas) has not been extensively studied up to date. Currently, there are sixty-five installed biogas plants in the country, located predominantly at the central and northern regions, which treat mostly landfill wastes, wastewater treatment sludges and urban solid wastes [2].

Legislation which promotes biofuels for transports is being approved by the government, mainly due to legislative pressure of the EC. In 2012, a new decree-law was published for the concession, planning and remodelling of natural gas and liquified natural gas infrastructures, as cleaner alternative fuels to diesel and petrol [3]. Another law was published in 2014, which created a series of tax deductions for the utilisation of natural gas and liquified petroleum gas vehicles and economic incentives for the abatement of vehicles at the end of life period [4]. None of these laws specify incentives for biomethane implementation in Portugal, however they are a good starting point for the promotion of this fuel as a green energy and, following the tendency of biomethane share in the European renewable energy market, this seems a promising prospective for the country.

Anaerobic co-digestion has been studied for a very long time. A predetermined mixture of substrates can improve the feedstock quality and the biological process inside the digester, thereby enhancing methane production [5]. By mixing two or more substrates, toxic compounds can be diluted, the biodegradation accelerated, the balance of nutrients and carbon/nitrogen (C/N) ratio improved and a synergetic effect of microorganisms obtained, resulting in process stabilisation [6]. Pig slurry is a good base substrate for anaerobic co-digestion, due to its high water content (facilitates drier substrates pumping), high buffering capacity (avoids abrupt pH fluctuations) and high nutrient content (generates an adequate bacterial growth) [7]. Horse manure is highly fibrous and has a high C/N ratio, but with an adequate pre-treatment it is expected that its addition to pig slurry would enhance biogas yields.

Co-digestion is a more desirable exploitation of organic residues for biogas production and efficient solution to waste management problems, over mono-digestion. However, to the date there are few studies about co-digestion of horse manure and swine slurry and the management of these residues poses a considerable enough problem in Portugal to justify the interest for this study. Also, the studies made for quantification and potential utilisations of biogas and biomethane in Portugal made only a superficial assessment of the possibility of mono and co-digestion mixtures exploitation, without quantifying the energy consumption and greenhouse gases emissions derived from each scenario. This thesis aims to solve this literature gap and improve the knowledge on these topics, to help the understanding of biogas production in Portugal.

## 2. Data and methods

### 2.1. Experimental design

#### Materials:

Horse manure (HM) was obtained from an equestrian centre that houses sixty-seven horses and disposes an annual manure volume of 240 tonnes. One fresh sample of horse manure mixed with spent wheat straw bedding was collected and weighted, amounting to a quantity of 1727 g and, afterwards, the spent straw was removed. The removed spent wheat straw was also weighted and amounted to 239 g, which corresponded to 13.8% of the total sample weight. The separated horse faeces, which were used as co-substrate, had a dry matter content of 23.5% (% wet weight) and an organic matter content of 88.7% (% dry matter), values which are in accordance to the literature [8]. Pig slurries (PS) were provided by a swine livestock facility and collected from the storage tank of the slurry management system. The samples had remnants of grains and solid manure fractions, so they were sieved with a strainer with a mesh size of 2 mm, to remove the residues. After sieving, the remaining liquid fractions and horse faeces were stored at 4°C.

#### Pre-treatment:

To avoid clogging problems, a pre-treatment of the mixture of manures was delineated. The desired quantity of horse manure was weighted in a digital balance, with an accuracy of  $\pm 0.005$  g. The liquid fraction of swine slurry was added to the weighted horse manure, until 1 L of mixture was obtained, and the total weight was measured. The mixture was then grinded with a kitchen blender of 150 W, for five minutes and sieved with the strainer of mesh size 2 mm, to extract residues and straw fragments. The sieving process was repeated until no more liquid could be separated from the solid fraction of the mixture. The liquid and solid fractions were then weighted individually and 90.6% of the total weight corresponded to the liquid fraction of the fresh matter, which was used as feedstock. The remaining 9.4% corresponded to the solid fraction of the fresh matter and could not be exploited, therefore being disposed of. No significant differences in solid fraction weights obtained were registered.

#### Characterisation of feeding mixtures:

The experiment was divided in four cycles with different mixtures and five HRTs. A control cycle was conducted first, only with swine slurry as feeding stock of the system, to serve as a comparison basis. The following three cycles were fed with horse manure and swine slurry mixtures. The cycles had increasing proportions of horse manure, with the purpose of increasing TCOD and SCOD contents, having been weighted, per litre of swine slurry, 20 g for C1, 40 g for C2 and 60 g for C3. To verify this increase, every mixture was characterised before the beginning of each respective HRT and it was observed that the addition of horse manure increases TS, VS, TCOD and SCOD contents compared to sole swine slurry and this resulted in HM:PS ratios of 0:100 (C0), 10:90 (C1), 13:87 (C2) and 20:80 (C3), in terms of inlet %VS. The results obtained are presented in Table 1.

**Table 1** - Feeding mixtures characterisations (results are given as averages and ranges of duplicate analytical measurements)

Characteristics	C0	C1	C2	C3 (1 <sup>st</sup> HRT)	C3 (2 <sup>nd</sup> HRT)
pH	7.1 $\pm$ 0.02	7.6 $\pm$ 0.17	7.6 $\pm$ 0.14	7.8 $\pm$ 0.11	7.5 $\pm$ 0.10
EC [mS.cm <sup>-1</sup> ]	10.8 $\pm$ 0.99	8.3 $\pm$ 0.20	8.5 $\pm$ 0.08	9.7 $\pm$ 1.3	7.6 $\pm$ 1.02
TS [g.L <sup>-1</sup> ]	12.6 $\pm$ 1.98	14.8 $\pm$ 2.04	16.0 $\pm$ 0.20	14.7 $\pm$ 2.59	9.4 $\pm$ 1.17
VS [g.L <sup>-1</sup> ]	8.9 $\pm$ 1.8	10.2 $\pm$ 1.27	10.8 $\pm$ 0.18	9.7 $\pm$ 1.98	5.6 $\pm$ 0.16
VS/TS [%]	70.7	68.9	67.6	66.4	66.1
TCOD [g.L <sup>-1</sup> ]	19.34 $\pm$ 3.98	16.51 $\pm$ 2.42	17.95 $\pm$ 1.58	15.64 $\pm$ 3.89	9.28 $\pm$ 0.81
SCOD [g.L <sup>-1</sup> ]	9.09 $\pm$ 1.86	4.07 $\pm$ 0.72	3.69 $\pm$ 0.14	3.75 $\pm$ 0.29	4.0 $\pm$ 0.18
SCOD/TCOD [%]	47.0	24.6	20.5	24.0	43.1
TKN [g.L <sup>-1</sup> ]	1.72 $\pm$ 0.37	1.13 $\pm$ 0.02	1.12 $\pm$ 0.01	1.10 $\pm$ 0.02	0.57 $\pm$ 0.01
N-NH <sub>4</sub> <sup>+</sup> [g.L <sup>-1</sup> ]	1.20 $\pm$ 0.25	0.71 $\pm$ 0.01	0.70 $\pm$ 0.01	0.76 $\pm$ 0.08	0.40 $\pm$ 0.01
TC [g.L <sup>-1</sup> ]	5.16 $\pm$ 1.04	5.92 $\pm$ 0.74	6.27 $\pm$ 0.11	5.65 $\pm$ 1.16	3.25 $\pm$ 0.16
C/N	3	5	6	5	6

The lower SCOD/TCOD ratios have significant variations due to changing environmental conditions at the swine livestock facility, such as different feeding diets of the animals and different waste collection practices. The swine slurry used in the first HRT of C3 had the lowest TCOD and SCOD contents, so this cycle was repeated for a second HRT, with the same operational parameters, to better evaluate the digestion process stability and performance.

Experimental configuration:

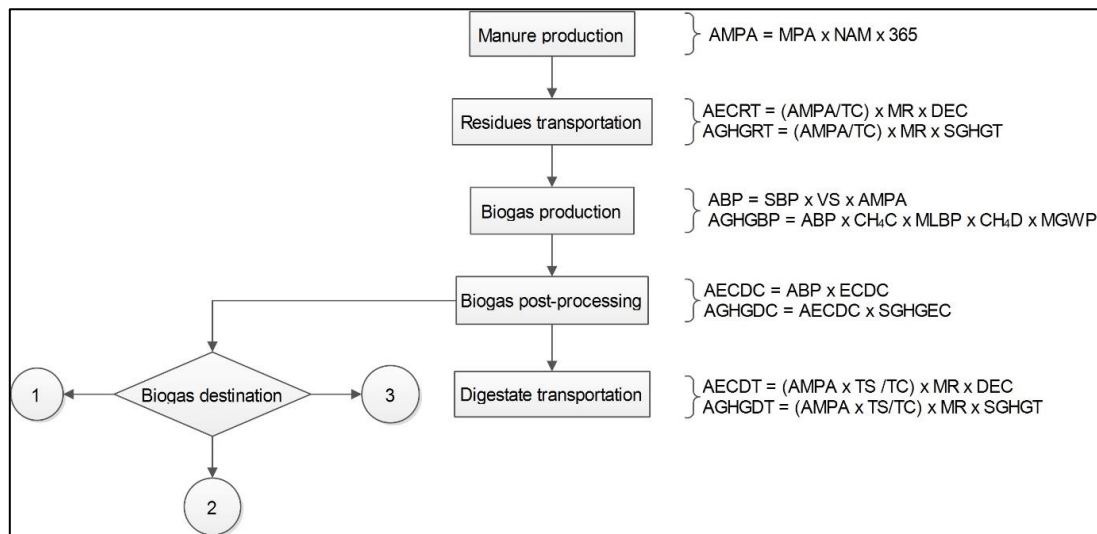
The experimental installation is controlled by a programmable logic controller (PLC) system and consists of a CSTR with total volume of 6.86 L and working volume of 4.8 L. The reactor includes a heating system controlled by a thermostat with an accuracy of  $\pm 0.5$  °C, a mechanical stirrer (50 rpm), a feeding pump (120 rpm) and a gas flowmeter with an accuracy of  $\pm 3\%$ . The reactor was fed with 1500 mL of substrate equally divided along the week, which results in  $214 \text{ mL}\cdot\text{day}^{-1}$  of digested volume and the stirrer is activated 2 min before the feeding period and deactivated 2 min after the feeding, to promote a better homogenisation of the organic matter inside the digester and to facilitate the release of gas bubbles. The set-up configuration of the experiments is shown in Table 2.

**Table 2** – Set-up configuration of the experimental assays

Cycle	HRT [days]	T [°C]	HM:PS [%VS inlet]	HM:PS [%TCOD inlet]	OLR [ $\text{kgvs}\cdot\text{m}^{-3}\cdot\text{day}^{-1}$ ]
C0 – Control cycle	23	$36 \pm 0.5$	0:100	0:100	$0.556 \pm 0.11$
C1 - First cycle	23	$37 \pm 0.7$	10:90	11:89	$0.638 \pm 0.08$
C2 - Second cycle	23	$37 \pm 0.9$	13:87	14:86	$0.675 \pm 0.01$
C3 - Third cycle (1 <sup>st</sup> HRT)	23	$37 \pm 0.8$	20:80	22:78	$0.608 \pm 0.25$
C3 - Third cycle (2 <sup>nd</sup> HRT)	23	$37 \pm 0.8$	20:80	22:78	$0.345 \pm 0.06$

**2.2. Quantification of biogas production potential in Portugal**

An assessment of the energy consumption and greenhouse gases (GHG) emissions associated to the biogas production pathway was also done with a flow scheme of calculations as shown in Figure 1.



- AMPA = annual manure production per animal category [ $\text{ton}\cdot\text{m}^{-1}$ ]
- NAM = number of animals per municipality
- MPA = manure production per animal category [ $\text{ton}\cdot\text{m}\cdot\text{day}^{-1}$ ]
- AECRT = annual energy consumption for residues transportation [MJ]
- TC = truck capacity [ton]
- MR = municipality radius [km]
- DEC = diesel energy consumption [ $\text{MJ}\cdot\text{km}^{-1}$ ]
- AGHGRT = annual GHG emissions from residues transportation [ $\text{tonCO}_2\text{eq}$ ]
- SGHGT = specific GHG emissions from transportation [ $\text{tonCO}_2\text{eq}\cdot\text{km}^{-1}$ ]
- ABP = annual biogas production per animal category and type of digester [ $\text{m}^3$ ]
- SBP = specific biogas production per animal category and type of digester [ $\text{m}^3\cdot\text{tonVS}^{-1}$ ]
- VS = volatile solids content in manure [%]
- AGHGBP = annual GHG emissions from biogas production [ $\text{tonCO}_2\text{eq}$ ]
- CH<sub>4</sub>C = methane content in biogas [%]
- MLBP = methane losses from biogas production [ $\text{ton}\cdot\text{tonCH}_4^{-1}$ ]
- CH<sub>4</sub>D = methane density [ $\text{ton}\cdot\text{m}^{-3}$ ]
- MGWP = methane global warming potential [ $\text{tonCO}_2\text{eq}$ ]
- AECDC = annual energy consumption for dehumidification and compression [MJ]
- ECDC = energy consumption for dehumidification and compression [ $\text{MJ}\cdot\text{MJ}_{\text{biogas}}^{-1}$ ]
- AGHGDC = annual GHG emissions from dehumidification and compression [ $\text{tonCO}_2\text{eq}$ ]
- SGHGEC = specific GHG emissions from electricity consumption [ $\text{tonCO}_2\text{eq}\cdot\text{MJe}^{-1}$ ]
- AECDT = annual energy consumption for digestate transportation [MJ]
- TS = total solids content in manure [%]
- AGHGDT = annual GHG emissions from digestate transportation [ $\text{tonCO}_2\text{eq}$ ]

**Figure 1** - Flow scheme of calculations for assessment of biogas production

A life-cycle inventory approach was undertaken [9], to quantify the expended energy and associated GHG emissions in each step of the biogas production pathway that was considered. The functional unit considered was 1 MJ of biogas, ready to be used in its destination. The boundaries of the modelled system for biogas production considered a centralised biogas production at a municipal scale, with manure collection from farms and posterior transportation to a large-scale biogas plant, where the digestion process occurs. The analysis was divided into steps of the process, which were: residues production, residues transportation to centralised plant, biogas production from residues, biogas post-processing, biogas destination and digestate transportation back to the collection site.

Three possible scenarios of biogas utilisation were considered: combustion in a Combined Heat and Power (CHP) unit (1), upgrading to biomethane for natural gas grid injection (2) and upgrading to biomethane for utilisation as fuel in road vehicles (3). The upgrading technology considered was the Vacuum Pressure Swing Adsorption (VPSA), since this is the only type of upgrading equipment commercialised in Portugal [2]. For all steps, electric and thermal (when applied) energy consumption was considered, as well as GHG emissions considering the three most impacting gases in terms of global warming potential (GWP): CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O. The potential biogas production from each substrate could be obtained from the respective specific biogas productions (SBP), as shown in Table 3.

**Table 3** - Specific biogas productions considered, by substrate and type of digester

Substrate	Total solids content [%FM]	Volatile solids content [%FM]	Specific biogas production [m <sup>3</sup> .ton <sub>TS</sub> <sup>-1</sup> ]	Specific biogas production [m <sup>3</sup> .ton <sub>VS</sub> <sup>-1</sup> ]	Digester	Methane content [%]	References
OFMSW	32.0	-	274.0	-	Dry	57.5	[10], [11]
	-	30.0	-	571.0	CSTR	60.0	[12], [13]
Wastewater sludge	-	39.6	-	418.4	CSTR	70.0	[14]–[16]
Equine manure	38.0	32.5	-	355.3	Dry	54.0	[8], [17]
Swine slurry	5.4	4.5	-	582.0	PFR	70.0	[18]–[20]
	5.4	4.5	-	289.0	CSTR	66.0	[18], [20], [21]
Bovine manure	8.1	6.0	-	373.0	PFR	59.0	[22]–[25]
	8.1	6.0	-	342.8	CSTR	58.5	[21], [23], [24], [26]
Poultry manure	10.2	8.0	-	361.5	CSTR	59.0	[27], [28]

### 3. Results and discussion

#### 3.1. Biogas production from co-digestion of horse manure and pig slurry

The addition of horse manure originated a decrease of the nitrogen compounds of the mixtures, more specifically, a 16% decrease of TKN and a 26% decrease of N-NH<sub>4</sub><sup>+</sup>, from C0 to C1. Horse manure has high C/N ratios [29], and the its addition to the mixture improved C/N ratio to double the initial value by the third cycle, C2.

By the fourth cycle, C3, N-NH<sub>4</sub><sup>+</sup> content decreased 36.7%, compared with the control cycle, due to the addition of horse manure. Although ammonium is an essential nutrient for bacterial growth, it may have an inhibitory effect on the methanogenesis phase of anaerobic digestion when showing high concentrations with the maximum concentration of N-NH<sub>4</sub><sup>+</sup>, before co-digestion instability, occurring at 1.7 g.L<sup>-1</sup> [30]. The values of N-NH<sub>4</sub><sup>+</sup> concentrations obtained for each feeding mixture were well below the threshold limit established for all the HRTs, which eliminates the possibility of ammonia inhibition of the bacterial activity and, hence, the risk of methane production decrease.

Overall, the evolution of the digestate characteristics followed a tendency in accordance with the one of the feeding mixtures, as was expected. The ideal pH range for anaerobic digestion is very narrow: 6.8–7.2; below 6.8 the growth rate of methanogens is greatly reduced, while an excessively alkaline pH can lead to disintegration of microbial granules and subsequent failure of the process [31]. pH values of the digestate were slightly alkaline for all HRTs, however, due to the good buffering capacity of pig slurry, there was no instability of the bacterial activity inside the reactor. These values also indicate a good possibility of the digestate being used as a biofertiliser in the future, after being submitted to an organic amendment process to prevent nitrification of the soils, [32].

The results obtained for each HRT are presented in Table 4. For evaluation of anaerobic digestion process stability, SELR and TA values were monitored. The methanogenic bacteria growth capacity is exceeded if SELR values are higher than 0.4 kg<sub>TCOD</sub>.day<sup>-1</sup>.kg<sub>VSS</sub><sup>-1</sup>, which may result in methanogenesis inhibition and even process failure [33]. SELR values were always lower than the threshold of instability, which indicated that the reactor was always stable throughout the experiments. By the fourth cycle, C3,

SELR was half of the advisable maximum value, which indicates that the manure quantity can still be increased without risk of digester instability or failure.

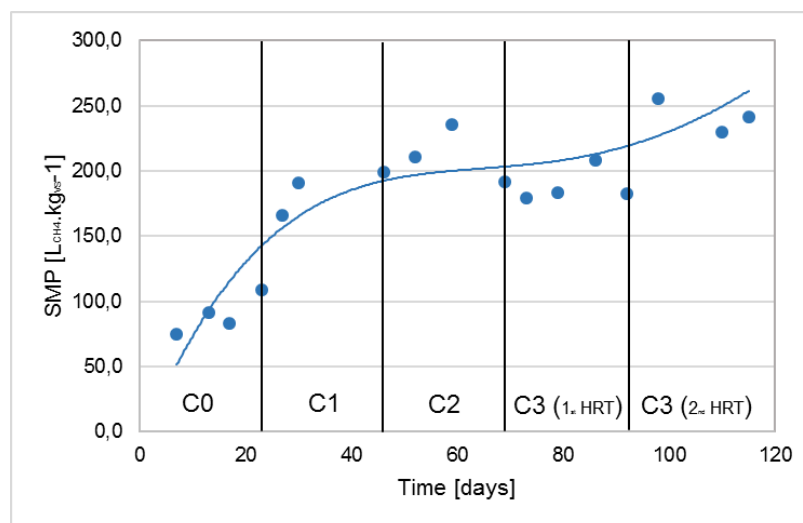
**Table 4** - Operational and stability parameters of each hydraulic retention time (HRT)

Parameters	C0	C1	C2	C3 (1 <sup>st</sup> HRT)	C3 (2 <sup>nd</sup> HRT)
GPR [ $\text{m}^3 \cdot \text{m}^{-3} \cdot \text{day}^{-1}$ ]	$0.071 \pm 0.02$	$0.105 \pm 0.04$	$0.123 \pm 0.03$	$0.120 \pm 0.03$	$0.072 \pm 0.03$
Biogas quality [%CH <sub>4</sub> ]	57.3	69.0	69.7	68.0	68.0
SGP [ $\text{L} \cdot \text{kg}^{-1}_{\text{VS}}$ ]	$151.7 \pm 27.8$	$258.6 \pm 29.4$	$288.8 \pm 45.1$	$318.5 \pm 32.3$	$380.0 \pm 36.0$
SMP [ $\text{L} \cdot \text{kg}^{-1}_{\text{VS}}$ ]	$86.9 \pm 15.9$	$178.4 \pm 20.3$	$201.3 \pm 31.4$	$215.6 \pm 21.9$	$258.3 \pm 24.2$
TCOD reduction [%]	52.0	47.4	47.7	48.5	48.4
SCOD reduction [%]	49.9	57.7	57.9	58.4	54.0
SELR [ $\text{kg}_{\text{TCOD}} \cdot \text{day}^{-1} \cdot \text{kg}_{\text{VSS}}^{-1}$ ]	0.296	0.196	0.260	0.223	68.5
Total Alkalinity [ $\text{g}_{\text{CaCO}_3} \cdot \text{L}^{-1}$ ]	$3.76 \pm 0.18$	$4.40 \pm 0.20$	$3.00 \pm 0.20$	$3.50 \pm 0.10$	0.252

Alkalinity is the capacity of the digester medium to neutralise the volatile fatty acids (VFA) generated during the process and, therefore, to mitigate pH changes [34]. The TA values were above the lower limit advisable for assuring stable process conditions,  $1.5 \text{ g}_{\text{CaCO}_3} \cdot \text{L}^{-1}$  and below the maximum  $9.1 \text{ g}_{\text{CaCO}_3} \cdot \text{L}^{-1}$  previously reported in pig slurry co-digestion studies, which assured the stability of the digester [34], [35].

It is known that changes in OLR affect the methane production, due to resulting changes in VFA production, which may inhibit the methanogenic bacteria activity [36]. Analysing the reactor performance, it was observed that gas production rate (GPR) shows an evolution proportional to that of OLR. The initial GPR increase was slower than the increase of OLR due to the lag phase of microbial response to the higher quantity of organic compounds available, which is in accordance with the observations of Ferguson *et al.* (2017). As the microbial community adapts to the feedstock, the lag phase reduces and GPR changes at a faster pace with OLR. Similar behaviour has been reported in pig slurry co-digestion studies [35]. The second HRT of C3 had the lowest averaged OLR of all cycles,  $0.345 \text{ kg}_{\text{VS}} \cdot \text{m}^{-3} \cdot \text{day}^{-1}$ , due to the very diluted pig slurry used, which explains the decrease of the GPR. The addition of horse manure to the feeding mixtures increased the percentage of methane in the biogas, with C2 registering the highest methane content of all HRTs, 69.7%. This value was higher than the ones reported by Smith & Almquist (2013) – 65% from co-digestion of horse manure with food waste – and by Mönch-Tegeger *et al.* (2014) – 54% from co-digestion with other manures and food wastes, which indicated that the co-digestion of horse manure with pig slurry in a liquid state digestion system is a promising technique, provided that an adequate pre-treatment is applied.

Methane yield on a VS basis allows a better comprehension of the adequacy of the substrates for biogas production. Analysing the SGP yields throughout the experiment, it was clear that C1 had a 1.7-fold increase when compared to C0, while C2 and C3 had 1.9-fold and 2.1-fold increases, respectively. SMP yields (on a  $\text{L} \cdot \text{kg}_{\text{VS}}^{-1}$  basis) showed similar tendencies, with a 2-fold increase for C1, 2.3-fold increase for C2 and C3 showing the best SMP increase, 2.5-fold, which corresponded to a maximum SMP of  $215.6 \text{ L} \cdot \text{kg}_{\text{VS}}^{-1}$ . The consistent increase of SMP obtained until C3 and the relatively low SELR at the fourth cycle indicated a good possibility of continued SMP increase in further studies. The SMP (in terms of  $\text{L} \cdot \text{kg}_{\text{VS}}^{-1}$ ) evolution along the course of experiments can be seen in Figure 2.



**Figure 2** - Specific methane production, SMP (in  $\text{L} \cdot \text{kg}_{\text{VS}}^{-1}$ ), evolution throughout the duration of the experiment

Although the OLR decreased in the second HRT of C3, the feeding mixture used had the highest VDS content, 3.8 g.L<sup>-1</sup>, and the highest SCOD/TCOD ratio, 43.1%, which implies that the organic matter content is more readily available for biodegradation, thus improving the digestion process. This is confirmed by the increase of SCOD removal efficiency, which reaches the maximum value, 68.5%, in the second HRT of C3. As such, since the VDS content and SCOD/TCOD ratio were the highest for this period, the digestion process was optimised, and the highest SMP obtained, in the fifth HRT, even though OLR decreased by half by that period.

Biogas quality, regarding the methane percentage, improved, as the content increased 12% from C0 to C1, indicating a good synergetic effect between the manures, while the addition of more horse manure did not further improve the CH<sub>4</sub> content. Hydrogen sulphide measurements are strongly influenced by the typical high content of sulphur of pig slurry. Hence, an eventual reduction of H<sub>2</sub>S content of the biogas was not detected by the gas analyser, due to the maximum limit of detection being 1500 ppm. The experiments conducted allowed a good comprehension of the performance of co-digestion of horse manure and swine slurry and demonstrated that the mixture may be successfully implemented at large-scale, however some aspects must be addressed for better results. Due to the small-scale of the reactor, more repetitions of each cycle are recommended to guarantee the quality of the results. Also, although only circa 10% of the mixture was disposed of, this solid fraction was largely composed by horse manure, which did not completely solve the problem of waste management. Experiments on large-scale reactors, that can pump higher solid fractions without clogging problems, would also be interesting to test the complete inclusion of horse manure and, thus, close the mass balance.

### 3.1. Biogas potential from different substrates in Portugal

The national biogas and biomethane production potentials obtained are of 592.5 Mm<sup>3</sup> and 310.0 Mm<sup>3</sup>, respectively. If the totality of biogas were to be converted into electric energy it would cover circa 4.7% of 50469 GWh of total electricity consumed and imported in Portugal in 2016 [37].

Analysing the animal manures as substrates for mono-digestion, bovine manure had the highest biogas potential result of all the manures. When considering biogas production in a CSTR, the result obtained from bovine manure corresponded to 38% of the total potential. Biogas production from poultry manure in CSTR corresponded to a much smaller fraction, 8% of the total potential production and from swine slurry in the same type of digester, 3% of total potential production (see Table 5).

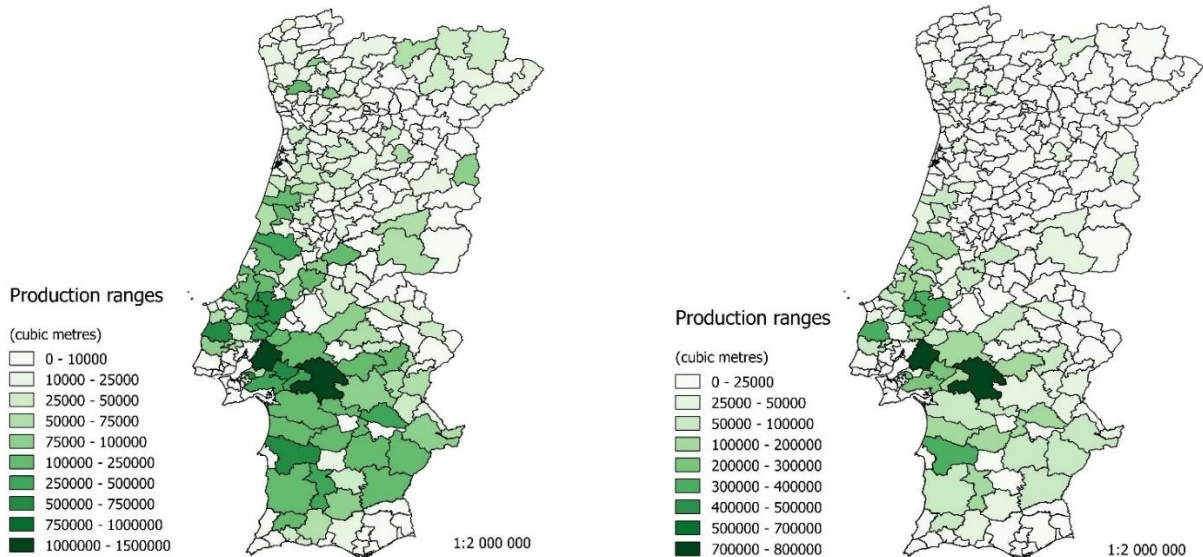
When considering the possibility of co-digestion of horse manure and swine slurry, the calculated potential of biogas and biomethane reaches 17.9 Mm<sup>3</sup> and 10.5 Mm<sup>3</sup>, respectively. At first analysis, the results seem to indicate that the co-digestion of horse manure and swine slurry is not an efficient biogas production pathway at a national level, since the results obtained for sole equine manure and sole swine slurry were higher than the one obtained for the mixture. However, this is because a co-digestion scenario is highly dependent on the availability of animals at the study site, and these have different dispersions per municipality. For this reason, a more detailed study, at a municipal level, must be conducted, for a better evaluation of the co-digestion mixture potential utilisation at large-scale facilities.

**Table 5** - Potential biogas and biomethane production in Portugal, per substrate and type of digester (CSTR – continuously stirred tank reactor, PFR – plug-flow reactor, Dry – dry anaerobic digestion)

Substrate	Annual biogas production [Mm <sup>3</sup> ]			Annual biomethane production from VPSA [Mm <sup>3</sup> ]		
	CSTR	PFR	Dry	CSTR	PFR	Dry
OFMSW	247.9	-	126.9	130.0	-	62.8
Sewage sludge	54.7	-	-	32.9	-	-
Bovine manure	225.7	245.4	-	113.5	124.5	-
Poultry manure	46.2	-	-	23.4	-	-
Equine manure	-	-	25.8	-	-	12.0
Swine slurry	18.0	36.1	-	10.2	21.7	-
<b>Total</b>	<b>592.5</b>	<b>281.5</b>	<b>152.7</b>	<b>310.0</b>	<b>146.2</b>	<b>74.8</b>

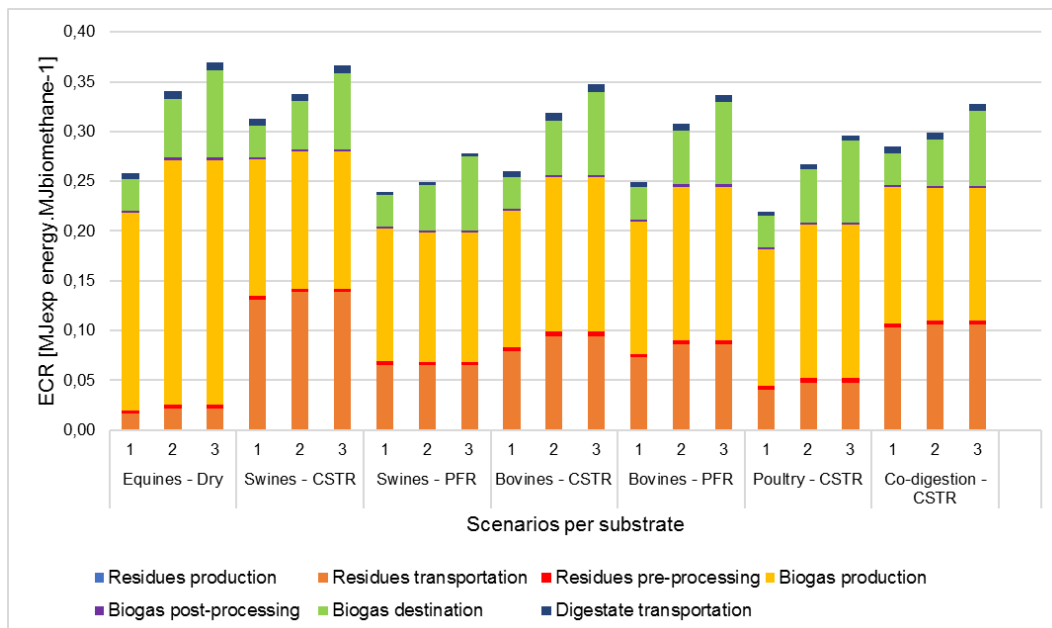
No studies of poultry manure utilisation in PFR digesters were found in the literature review, but analysing the results of swine and bovine manures in Table 5, it can be concluded that these digesters have better performance than CSTRs.

The maps obtained for the co-digestion mixture were a blend of the maps of the biogas and biomethane potentials from equine manure and swine slurry, as is presented in Figure 3. It is interesting to notice that the maps are more similar to the ones of pig slurry, since this manure has the highest proportion in the mixture (80% VS).



**Figure 3** - Maps of biogas (left) and biomethane (right) potential (in  $m^3$ ) from co-digestion mixture in CSTR per Portuguese municipality

The ECR of each process step, for the three utilisation pathways and systems considered, are represented in Figure 4. The first scenario had the lowest total ECR ratio, followed by the second (+13.5%) and third (+21.1%) scenarios, in ascending order. The natural gas consumed in Portugal is imported via two main pathways: by land (which implies a consumption of  $0.21 \text{ MJ.MJ}_{\text{CNG}}^{-1}$ ) and by ocean (which implies a consumption of  $0.33 \text{ MJ.MJ}_{\text{CNG}}^{-1}$ ) [38]. Comparing the results with the ones obtained for biomethane, the values of this study are slightly higher, but in the range of the ones obtained for natural gas, which indicates that biomethane is a sustainable and interesting alternative to natural gas as a green energy source.



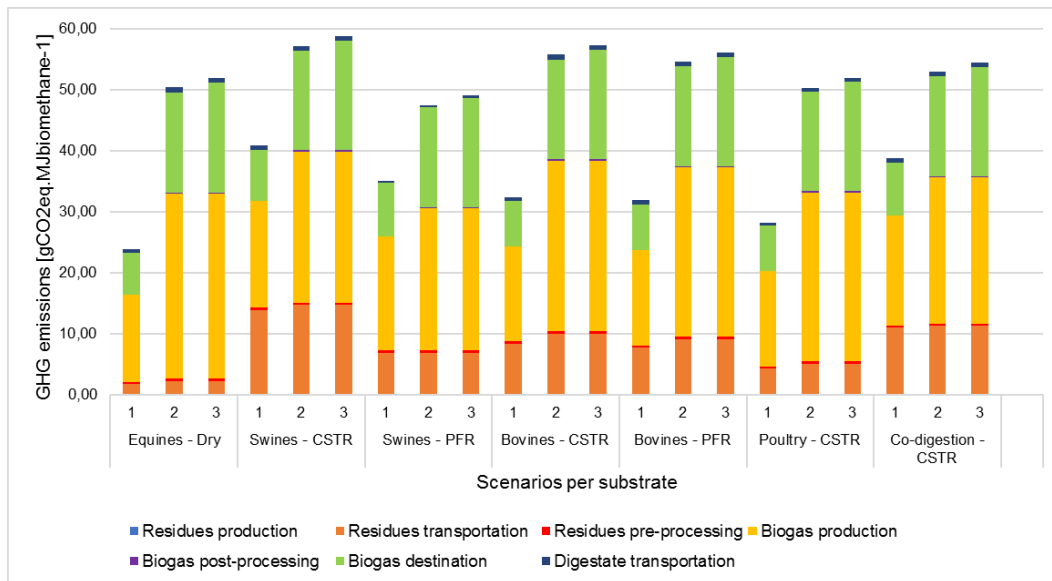
**Figure 4** - Energy consumption ratio (expressed as  $\text{MJ}_{\text{exp energy}}.\text{MJ}_{\text{biomethane}}^{-1}$ ) of each process step, per substrate, type of digester and scenario considered

The step with highest ECR is the biogas production, with a range of  $0.12 - 0.24 \text{ MJ}_{\text{exp energy}}.\text{MJ}_{\text{biomethane}}^{-1}$ , which represents circa 70% of total energy consumption for dry digesters, 46% for CSTR digesters and 48.5% for PFR digesters. The variations of energy input for plant operation are due to heating requirements (higher for dry systems) and auxiliary mechanical equipment (more significant in CSTRs). Studies on energy assessment of biogas systems in Sweden and Germany had also identified this step as the highest energy consumer of the process [39], [40]. These studies also affirmed that, for transportation distances of manure over a certain distance, the ECR turned negative, due to the output of energy not compensating the energy expended in transportation.

The second most demanding step is the biogas destination, which is 12.4% of total energy consumption for scenario 1, 17.1% for scenario 2 and 24.4% for scenario 3. Scenario 2 and 3 do not reflect the uneven distribution of the gas pipeline, which is located predominantly on the west coast, nor the location of refuelling GNL stations, which may affect significantly the ECR ratio. This is a consideration that must be contemplated in future investigations.

The residues transportation implied an energy consumption that ranged from 6.1% (horse manure) to 40.1% (swine slurry), depending on the substrate considered and the different animal populations in Portugal. In a decentralised scenario, these consumptions are not included and the overall energy consumption of biogas production is lower, due to the lower amount of organic matter fed, and ECR ratio is, consequently, lower than reported.

The total GHG emissions for each process step, type of substrate and scenario considered can be observed in Figure 5.



**Figure 5** - GHG emissions ratio (expressed as  $\text{gCO}_2\text{eq.MJ}_{\text{biomethane}}^{-1}$ ) of each process step, per substrate, type of digester and scenario considered

The results follow the same tendency as the ECR, as expected, with a range of values of 23.9 – 58.8  $\text{gCO}_2\text{eq.MJ}_{\text{biomethane}}^{-1}$ , with scenario 1 having the lowest GHG emissions, followed by scenarios 2 (+37.2%) and 3 (+39.1%). The higher difference obtained between the first scenario and the other two derives from the auto-consumption of energy in scenario 1, which allowed to avoid 36.7% of GHG emissions from electricity and heating provided by the national grid. This step was also denoted as having the highest emissions, with a range of values of 14.4 – 30.2  $\text{gCO}_2\text{eq.MJ}_{\text{biomethane}}^{-1}$ . One other study also identified biogas production as the highest energy consumer step of the entire process, with a value of 33  $\text{gCO}_2\text{eq.MJ}_{\text{biomethane}}^{-1}$  [41].

Scenario 3 was the one with highest total GHG emissions (approximately 54.2  $\text{gCO}_2\text{eq.MJ}_{\text{biomethane}}^{-1}$ ), as expected from energy analysis. For natural gas, GHG emissions ratio is 16.1  $\text{gCO}_2\text{eq.MJ}_{\text{CNG}}^{-1}$  for land transportation and 17.8  $\text{gCO}_2\text{eq.MJ}_{\text{CNG}}^{-1}$  for ocean transportation [38]. Biomethane seems a worse alternative to natural gas in terms of environmental impact but if a credit of avoided emissions from manure collection is applied [42], the ratio of each scenario may be considerably lower and biomethane may be a greener and more sustainable alternative to natural gas.

After the analysis of ECR, the four most adequate municipalities for the application of a centralised biogas plant, based on each substrate, were determined. By assessing the higher density in terms of animals per  $\text{km}^2$  and considering the municipalities with higher energy efficiency in the production of biogas, it was possible to identify the most adequate ones per substrate.

For the co-digestion analysis, a slightly different approach was necessary, since to the substrate is a mixture of residues. Based on the used quantities of horse manure and swine slurry, the total number of each animal type per  $\text{km}^2$  to achieve the maximum utilisation of residues was calculated. The most adequate municipalities for co-digestion mixture were then obtained, as follows: Benavente, Rio Maior, Cartaxo and Sobral de Monte Agraço. The municipalities were different from the ones obtained for sole horse manure and for sole swine slurry, which indicates that the mixture has higher potential of biogas production in these (and others) specific regions, although the global potential seems to indicate otherwise.



## 4. Conclusions and further work

The objectives of this thesis were to study the co-digestion of horse manure and swine slurry, as a waste management for these residues, to quantify the potential production of biogas and biomethane from the most promising organic residues in Portugal and assess the energy consumptions and greenhouse gases (GHG) emissions for the three pathways considered (utilisation of biogas in CHP, purification to biomethane for natural gas substitution in national grid and purification and compression for utilisation as bio-CNG in vehicles).

Although OLR decreased by half in the fifth HRT, C3, with HM:PS ratio of 20:80 (%VS inlet), showed the best synergetic effect between the microbial consortia of pig slurry and the high C/N ratio of horse manure, due to the high VDS and SCOD/TCOD ratio, yielding the highest SMP, 258.3 L.kg<sub>VS</sub><sup>-1</sup>, and the highest SCOD removal efficiency, 68.5%, of all the periods. Compared to the control period, which consisted of mono-digestion of pig slurry, this corresponded to a 3.0-fold increase of SMP, which proved the better performance of co-digestion relative to single feedstocks digestion.

In the assessment of biogas and biomethane potentials in Portugal, the productions estimated were of 592.5 Mm<sup>3</sup> and 310.0 Mm<sup>3</sup>, respectively. If the totality of biogas is converted to electric energy, it can cover circa 4.7% of 50469 GWh of total electricity consumed and imported in Portugal in 2016. Bovine manure digestion in CSTR has the largest potential for this technology, corresponding to 38% of the total biogas production. National biogas and biomethane potentials of co-digestion mixture were 17.9 Mm<sup>3</sup> and 10.5 Mm<sup>3</sup>, respectively, which seems a worse solution than mono-digestion of these substrates. However, co-digestion studies must be made at a municipal scale, due to different dispersions of organic residues.

Analysing ECR of each scenario, 1, which considered biogas utilisation in CHP for heat and electricity production, had the lowest value, followed by 2 (+13.5%) and by 3 (+21.1%). ECR varied accordingly with the amount of each type of residue, with the biogas production step representing the largest portion of energy consumption, with a range of values from 0.12 to 0.24 MJ<sub>exp energy</sub>.MJ<sub>biomethane</sub><sup>-1</sup>. Comparing technologies, the ECR of the biogas production step represented circa 70% of total ECR for dry digesters, 46% for CSTR digesters and 48.5% for PFR digesters. The highest value obtained for dry digesters was justified by the higher heating requirements. The step with second highest ECR obtained was the biogas destination, which amounted to 12.4% of total ECR for the first scenario, 17.1% for the second and 24.4% for the third.

GHG emissions follow the same tendency of ECR, with a range of values of 23.9 – 58.8 gCO<sub>2eq</sub>.MJ<sub>biomethane</sub><sup>-1</sup>. Scenario 1 has always the lowest GHG emissions, followed by scenarios 2 (+37.2%) and 3 (+39.1%). The difference between the first and the other two was more accentuated than when ECR was analysed due to the last two having GHG emissions associated with the supply of electricity from the national grid, which contributed to worse environmental impact.

It was possible to conclude that horse manure and swine slurry are adequate co-substrates for anaerobic co-digestion and that this process is a promising waste management solution, at a regional-scale, for Portugal. It could also be concluded that biomethane is sustainable, green energy alternative to natural gas, in terms of energy consumption and GHG emissions.

## 5. References

- [1] Eurostat, "Eurostat Data Navigation Tree," 2016.
- [2] I. Cabrita, L. Silva, I. P. Marques, S. Di Bernardino, and F. Gírio, "Avaliação do Potencial e Impacto do Biometano em Portugal," 2016.
- [3] DR, *Decreto-Lei nº 231/2012*. Governo de Portugal, 2012.
- [4] DR, *Lei nº 82-D/2014*. Assembleia da República, 2014, pp. 1–37.
- [5] J. Mata-Alvarez, S. Macé, and P. Llabrés, "Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives," *Bioresour. Technol.*, vol. 74, no. 1, pp. 3–16, 2000.
- [6] A. Khalid, M. Arshad, M. Anjum, T. Mahmood, and L. Dawson, "The anaerobic digestion of solid organic waste," *Waste Manag.*, vol. 31, no. 8, pp. 1737–1744, 2011.
- [7] L. J. Ferreira, "Reciclagem descentralizada de resíduos orgânicos industriais através do processo de codigestão anaeróbia com chorumes de suinicultura," Instituto Superior de Agronomia, 2014.
- [8] S. Kusch, H. Oechsner, and T. Jungbluth, "Biogas production with horse dung in solid-phase digestion systems," *Bioresour. Technol.*, vol. 99, no. 5, pp. 1280–1292, 2008.
- [9] P. C. Ferrão, *Introdução à Gestão Ambiental: a avaliação do ciclo de vida dos produtos*, 1ª edição. IST Press, 1998.
- [10] W. Six and L. De Baere, "Dry anaerobic conversion of municipal solid waste by means of the DRANCO process," *Water Sci. Technol.*, vol. 25, no. 7, pp. 295–300, 1992.
- [11] P. Weiland, "Anaerobic waste digestion in Germany – Status and recent developments," *Biodegradation*, vol. 11, pp. 415–421, 2001.
- [12] A. Davidsson, C. Gruvberger, T. H. Christensen, T. L. Hansen, and J. la C. Jansen, "Methane yield in source-sorted organic fraction of municipal solid waste," *Waste Manag.*, vol. 27, pp. 406–414, 2007.

- [13] J. F. Rodríguez, M. Pérez, and L. I. Romero, "Mesophilic anaerobic digestion of the organic fraction of municipal solid waste: Optimisation of the semicontinuous process," *Chem. Eng. J.*, pp. 10–15, 2012.
- [14] S. Babel, J. Sae-Tang, and a. Pecharaply, "Anaerobic co-digestion of sewage and brewery sludge for biogas production and land application," *Int. J. Environ. Sci. Technol.*, vol. 6, no. 1, pp. 131–140, 2008.
- [15] S. M. F. Leonardo, "Caracterização do Digestor Anaeróbio de Lamas Biológicas da ETAR do Choupal, em Coimbra," Instituto Superior de Engenharia de Coimbra, 2012.
- [16] N. Pinto, A. Carvalho, J. Pacheco, and E. Duarte, "Study of different ratios of primary and waste activated sludges to enhance the methane yield," *Water Environ. J.*, pp. 1–8, 2016.
- [17] M. Mönch-Tegeeder, A. Lemmer, H. Oechsner, and T. Jungbluth, "Investigation of the methane potential of horse manure," *Agric. Eng. Int. CIGR J.*, vol. 15, no. 2, pp. 161–172, 2013.
- [18] K. H. Hansen, I. Angelidaki, and B. K. Ahring, "Anaerobic digestion of swine manure: Inhibition by ammonia," *Water Res.*, vol. 32, no. 1, pp. 5–12, 1998.
- [19] P. Weiland, "Biogas production: current state and perspectives," *Appl. Microbiol. Biotechnol.*, no. 85, pp. 849–860, 2010.
- [20] D. I. Massé *et al.*, "Low-temperature anaerobic digestion of swine manure in a plug-flow reactor," *Environ. Technol.*, vol. 3330, no. November, 2013.
- [21] K. Ahlberg-eliasson, E. Nadeau, L. Levén, and A. Schnürer, "Production efficiency of Swedish farm-scale biogas plants," *Biomass Bioenergy*, vol. 97, pp. 27–37, 2017.
- [22] J. H. Martin, P. E. Wright, S. F. Inglis, and K. F. Roos, "Evaluation of the performance of a 550 cow plug-flow anaerobic digester under steady-state conditions," in *Ninth International Animal, Agricultural and Food Processing Wastes*, 2003, pp. 350–359.
- [23] I. Angelidaki and L. Ellegaard, "Codigestion of manure and organic wastes in centralized biogas plants - Status and future trends," *Appl. Biochem. Biotechnol.*, vol. 109, pp. 95–105, 2003.
- [24] K. Boe and I. Angelidaki, "Serial CSTR digester configuration for improving biogas production from manure," *Water Res.*, vol. 43, no. 1, pp. 166–172, 2009.
- [25] M. Mezzadri and V. Francescato, "Biogas from slurry in a farm with 100 dairy cows - Cogeneration from an innovative small capacity biogas plant," 2014.
- [26] Z. Mladenovska, S. Dabrowski, and B. K. Ahring, "Anaerobic digestion of manure and mixture of manure with lipids: biogas reactor performance and microbial community analysis," *Water Sci. Technol.*, vol. 48, no. 6, pp. 271–278, 1999.
- [27] L. M. Safley, R. L. Vetter, and L. D. Smith, "Management and operation of a full-scale poultry waste digester," *Poult. Sci.*, vol. 66, no. 10609, 1987.
- [28] E. Salminen and J. Rintala, "Anaerobic digestion of organic solid poultry slaughterhouse waste – a review," *Bioresour. Technol.*, vol. 83, pp. 13–26, 2002.
- [29] J. Böske, B. Wirth, F. Garlipp, J. Mumme, and H. Van den Weghe, "Anaerobic digestion of horse dung mixed with different bedding materials in an upflow solid-state (UASS) reactor at mesophilic conditions," *Bioresour. Technol.*, vol. 158, pp. 111–118, 2014.
- [30] O. Yenigün and B. Demirel, "Ammonia inhibition in anaerobic digestion : A review," *Process Biochem.*, vol. 48, no. 5–6, pp. 901–911, 2013.
- [31] A. J. Ward, P. J. Hobbs, P. J. Holliman, and D. L. Jones, "Optimisation of the anaerobic digestion of agricultural resources," *Bioresour. Technol.*, vol. 99, pp. 7928–7940, 2008.
- [32] K. Sawada and K. Toyota, "Effects of the application of digestates from wet and dry anaerobic fermentation to Japanese paddy and upland soils on short-term nitrification.," *Microbes Environ.*, vol. 30, no. 1, pp. 37–43, 2015.
- [33] P. J. Evans, D. A. Nelsen, J. C. Amador, C. Mcpherson, D. L. Parry, and H. D. Stensel, "Energy Recovery from Food Waste via Anaerobic Digestion," in *World Congress on Water, Climate and Energy*, 2012, pp. 1–4.
- [34] X. Fonoll, S. Astals, J. Dosta, and J. Mata-alvarez, "Anaerobic co-digestion of sewage sludge and fruit wastes : Evaluation of the transitory states when the co-substrate is changed," *Chem. Eng. J.*, vol. 262, pp. 1268–1274, 2015.
- [35] S. Astals, V. Nolla-ardévol, and J. Mata-alvarez, "Anaerobic co-digestion of pig manure and crude glycerol at mesophilic conditions : Biogas and digestate," *Bioresour. Technol.*, vol. 110, pp. 63–70, 2012.
- [36] R. M. W. Ferguson, F. Coulon, and R. Villa, "Organic loading rate: A promising microbial management tool in anaerobic digestion," *Water Res.*, vol. 100, pp. 348–356, 2016.
- [37] ERSE, "Caracterização da procura de energia eléctrica em 2016," 2015.
- [38] R. Edwards, J.-F. Larivé, D. Rickeard, and W. Weindorf, "Well-to-wheels analysis of future automotive fuels and powertrains in the European context," Luxembourg, 2014.
- [39] M. Berglund and P. Börjesson, "Assessment of energy performance in the life-cycle of biogas production," *Biomass Bioenergy*, vol. 30, pp. 254–266, 2006.
- [40] M. Pöschl, S. Ward, and P. Owende, "Evaluation of energy efficiency of various biogas production and utilization pathways," *Appl. Energy*, vol. 87, pp. 3305–3321, 2010.
- [41] C. Buratti, M. Barbanera, and F. Fantozzi, "Assessment of GHG emissions of biomethane from energy cereal crops in Umbria, Italy," *Appl. Energy*, vol. 108, pp. 128–136, 2013.
- [42] A. Kovacs, "Green Gas Grids," 2013.