UNIVERSITAT DE VIC
UNIVERSITAT CENTRAL DE CATALUNYA
Escola de Doctorat

Techno-Economic Assessment of Anaerobic co-digestions of livestock manure with agro-industrial by-products

PhD thesis by

Seyed Mostafa Imeni

PhD program of Experimental science and Technology

Faculty of Bioscience and Technology

Department of Bioscience- BETA Tech Center (TECNIO Network), U Science Tech,

University of Vic-Central University of Catalonia,

Vic, Barcelona, Spain

June 2019

Thesis supervised by:

Dr. Joan Colón Jorda
&
Dr. Sergio Ponsá Salas

This study was carried out within the framework of the "INNOLACT" project (EFA005/15 INNOLACT) under the program INTERREG POCTEFA and co-financed by the European Regional Development Fund.

“No donation of people is better than spreading science” - Prophet Mohammad

“I have many more things to say to you, but you cannot bear them now. “But when He, the Spirit of truth, comes, He will guide you into all the truth; for He will not speak on His own initiative, but whatever He hears, He will speak; and He will disclose to you what is to come”
- The Bible, Gospel of John, Chapter 16, verse 12-14

“Love God and He will enable you to love others even when they disappoint you.”
– Francine Rivers

“God gave you a gift of 86,400 seconds today. Have you used one to say ‘thank you?”
– William Arthur Ward

“Live your life like you are alive forever and prepare for the death like you will die tomorrow”
- Imam Hassan (624-670 AD)

“…since then, during the past 33 years, I looked in the mirror every morning and asked myself, if today were the last day of my life, would I want to do what I am about to do today? And whenever the answer has been no for too many days in a row, I know I need to change something”.
- Steve Jobs

Acknowledgement:

Presenting this thesis was never possible without helps and supports of different people who all were my family during the time I was far from home. People who I learned from, laughed and enjoyed of being with them and faced difficulties and problems on their side. Being that much far away from home for the first time and in a different culture was a challenge for me. All difficult moments I had are now a sweet memory which not only I don't regret but also I miss many of them and this could not happen without my amazing friends, colleagues, professors and in one word, my BETA family.

Working in a young and international research group was not just working and improving in science but also every moment of it was a lesson for my life. Apart from beliefs, cultures, races and etc., how human being is close to each other and why people around the world do not try to focus on so many common things we have instead of differences!

I truly appreciate all of you and I truly love all of you and I wish the best for you in every moment of your life.

I appreciate supports of all my friends, families and colleagues during this time and also I want to give special thanks to people who had the most influence on me to achieve this level:

To my parents. None of my achievements during my whole life was possible without your great support. You always did your best for me without any expectation.

To my Sister Nastaran who I always say, we owe her the happiness of our family, thank you

پدر و مادر عزیز تر از جانم، بابت همه زحمات و حمایت های بی دریغ شما، بابت همه از خود گذشتگی هایتان و بابت بی نهایت مهر و محبتی که در تمام طول عمرم به من داشتید، از شما سپاسگزارم هرچند هرگز نمی توانم ذره ای از بزرگواریتان را جبران کنم اما از خداوند متعال برای شما طول عمر با عزت همراه با سلامتی و برکت و روزی زیاد خواستارم و همیشه محتاج دعای خیرتان هستم.

To Dr. Joan Colón. You are a hardworking, kind and amazing supervisor. A real scientist who can handle all difficulties in the moments that most people lose hope. There is no word to describe how important you are for me. Without your supports none of these were possible. You taught me more important things in life than just science and projects. I wish you the best in your life and I always am proud to be your student.

To Dr. Sergio Ponsá. The best director I have ever had. You are the reason I started this journey. Without your supports and your kindness, I could never continue my career specially in the hard moments and difficult situations. As I always said to my family and some friends, you are the bomb of energy. Every time I had a meeting with you, my motivation and energy was increased to continue this way. Thank you for your supports, thank you for your trust on me when I needed and thank you for everything.

To Anna Busquets, you trained me and many other people in BETA in the lab; your knowledge and experience in experimental work was always the key and solution for our problems. Thank you so much.

To Carlos Corchado, my best friend, brother, colleague and family member here. Since the time I met you many things changed for me, words are too weak to describe how happy I am to have you. I always wish you the best Doctor sin appendicitis!!

To. Dr. Jonatan Ovejero for being a kind and nice friend and colleague. Thank you for your helps.

To Dr. Albert Palou, The nice and kind friend from the first day. It was a pleasure meeting and hosting you in Iran and I hope to meet you there again.

To Dr Laia Llenas, Thank you for your supports. I always have the best wishes for you

To Dr. Lara Pelaz, your kindness and supports in our cooperation surely influenced positively my career. Thank you so much

To Ester & Mabel, the fantastic young researchers that at least for me, you changed the atmosphere of BETA to a completely happy and energetic group. With you is impossible to finish a day without smiling. Thanks a lot

To Daniel, Carmen, Lidia, Nagore, Jordi and Imane. My dear friends and colleagues that all of you inspired me in a different way for the life. Thank you for everything guys. I have learned from all of you and I am so proud to have you as my friends.

To Hossein Eivazzadeh, my dear brother and friend. During all these time you have ignored the distance between us and never let me feel alone. Despite of long distance between us, whenever I needed you, you were around. Thank you so much

To my cousin Hassan for giving me energy and motivation and for your supports. You were handling many things alone all these time while I left our cooperation for another experience in my life. Thank you for your kindness and your supports my brother.

ABSTRACT:

Deposition of excess amount of livestock waste when they are not properly treated has a notable environmental impacts specially on soil and undergrounds water. Livestock waste as a biodegradable waste can be treated and recycle to finally obtain compost or biogas which means green energy and fertilizer/soil-amendment products. In general biodegradable waste receives especial attention in the European Legislation (Revised Framework Directive 2008/98/CE) and therefore, is necessary to develop suitable facilities to treat these types of waste and assure the correct and efficient operation of such treatment and management facilities.

Anaerobic digestion of dairy cattle manure is a common practice; however, the low biogas yield of manure can hamper the profitability of anaerobic digestion systems in small to medium dairy cattle farms. To make this technology more attractive to farmers, an increase in biogas yield per cubic meter of reactor could be achieved by co-digesting animal manure with an abundant and easy accessible co-substrate such as agricultural by-products like wheat straw (in its raw form or pre-treated) and dairy industry by-products like cheese whey.

In addition of increase in biogas production which can be translated to production of more energy, economic feasibility of implementation of anaerobic digestion plants in the farms is a must. However, there is scarce information provided in scientific literature about economic feasibility of implementation of such plants in small to medium cattle farms.

Thus, in this thesis a techno-economic assessment of anaerobic co-digestion of animal manure and wheat straw (in the raw form and pretreated) or cheese whey was carried out.

The technological assessment was carried out at lab scale using batch and semi-continuous reactors. With the data obtained, an economic model was developed in order to investigate the

profitability of anaerobic co-digestion plants in small to medium dairy cattle farms, sensitivity analyses were carried out to investigate important parameters (e.g. electricity price) on the overall economic performance of the system.

The results obtained from the techno-economic assessment showed that for a farm of 250 adult cattle heads the revenues generated in an anaerobic mono-digestion process are not able to offset the initial required investment. However, the co-digestion of manure with raw or briquetted straw showed positive economic performance and positive returns (Net Present values > 0, Internal Rate of Return > 9 % and a Return of the investment in 11 years) as well as the co-digestion of manure with 30% of cheese whey which showed positive returns (Net Present values > 0, Internal Rate of Return > 11% and a Return of the investment in 9 years). For farmers willing to implement anaerobic digestion, Electricity selling price, and the price of the straw are the key parameters to determine the profitability of the system.

Moreover, pre-treatments to increase the straw biogas production have been assessed and evaluated from a technic and economic perspective. Alkali and microwave-alkali straw pre-treatments showed the best results with an increase in biogas production of 156 % and 92 % compared to raw straw.

Resum:

L’aplicació al sol d’una quantitat excessiva de dejeccions ramaderes, pot tenir un impacte ambiental notable sobretot en sòls i aigües subterrànies. Les dejeccions ramaderes com a residus biodegradables es poden tractar i reciclar per obtenir recursos (compost o biogàs) i per tant la producció d’energia renovable i productes fertilitzants. En general, els residus biodegradables reben una especial atenció a la legislació europea (Revised Framework Directive 2008/98 / CE) i, per tant, és necessari desenvolupar instal·lacions adequades per tractar i reciclar aquest tipus de residus i assegurar el funcionament correcte i eficaç d'aquestes instal·lacions de tractament i gestió.

La digestió anaeròbia dels fems i purins és una pràctica habitual; no obstant, el baix potencial de producció de biogàs pot dificultar la rendibilitat dels sistemes de digestió anaeròbia en explotacions ramaderes de petita i mitjana producció. Així doncs, perquè aquesta tecnologia sigui més atractiva per als agricultors, es podria aconseguir un increment de la producció de biogàs co-digerint els fems animals amb un co-substrat abundant i accessible, com ara subproductes agrícoles com la palla de blat (en forma crua o pre-tractats) i derivats de la indústria làctia com el sèrum de formatge.

A més de l'augment de la producció de biogàs i conseqüentment de la producció energètica, afavoreix la viabilitat econòmica de les tecnologies i plantes de digestió anaeròbia a explotacions ramaderes petites i mitjanes. No obstant això, hi ha poca informació disponible en la literatura científica sobre la viabilitat tecno-econòmica de l'aplicació d'aquestes plantes en explotacions ramaderes petites i mitjanes.

Per tant, en aquesta tesi es va dur a terme una avaluació tecnoeconòmica de la co-digestió anaeròbia de fems de bestiar i palla de blat (en forma crua i pretratada) i amb sèrum de llet.

L'avaluació tecnològica es va realitzar a escala de laboratori mitjançant reactors discontinus i semicontinguts. Amb les dades obtingudes, es va desenvolupar un model econòmic per investigar la rendibilitat de les plantes de co-digestió anaeròbia en explotacions ramaderes petites i mitjanes; també es va realitzar un anàlisis de sensibilitat per investigar l’efecte de paràmetres importants (per exemple, el preu de l'electricitat) sobre el rendiment econòmic global del sistema.

Els resultats obtinguts a partir de l’avaluació tecnoeconòmica van mostrar que per a una granja de 250 caps de bestiar adult, els ingressos generats en un procés de digestió anaeròbia no són capaços de compensar la inversió inicial necessària. No obstant això, la co-digestió de fems amb palla crua o briquetada ha mostrat uns rendiments econòmics positius (valors actuals nets> 0, taxa interna de retorn> 9% i retorn de la inversió en 11 anys), així com la co-digestió de fems amb un 30% de sèrum de llet amb resultats econòmics també positius (valors actuals nets> 0, taxa interna de retorn> 11% i retorn de la inversió en 9 anys). Pels agricultors disposats a aplicar la digestió anaeròbia, el preu de venda de l'electricitat i el preu de la palla són els paràmetres clau per determinar la rendibilitat del sistema.

A més a més, s'han provat i avaluat els tractaments previs per augmentar la producció de biogàs de palla des d'una perspectiva tècnica i econòmica. Els pre-tractaments alcalins i de microones-alcalins amb palla van mostrar els millors resultats amb un augment de la producció de biogàs del 156% i del 92% respectivament en comparació amb la palla crua.

Table of Contents

List of Tables

List of Figures

Abbreviations and Symbols

AD	Anaerobic digestion	
BD	Bulk density	$Kg.L^{-1}$
BMP	Biological Methane potential in n days	$NL_{CH4}.Kg^{-1}OM$
BS	Briquetted straw	
C	Carbon	
$CaCO_3$	Calcium Carbonate	
CAPEX	Capital Costs	€
C/N	Carbon to Nitrogen ratio	
CH_4	Methane	
CI	Cash inflow	€
C_I	Inert fraction	%
CO	Cash out flow	€
CO_2	Carbon dioxide	
COD	Chemical oxygen demand	$mg.L^{-1}$
C_R	Rapidly biodegradable fraction	%
C_S	Slowly biodegradable fraction	%
C_W	Remaining Carbon in the sample	%
CW	Cheese whey	
DM	Dry matter	%
EU	European union	
GBn	Biogas potential in n days	$NL_{biogas}.Kg^{-1}{}_{VS}$ or $NL_{biogas}.Kg^{-1}{}_{COD}$

GC	Gas chromatography	
GHG	Greenhouse gases	
HCL	Hydrochloric acid	
HRT	Hydraulic retention time	days
i_0	Discount rate	%
IRR	Internal rate of return	%
IPP	Investment payback period	years
K_R	Rapid rate constant	$days^{-1}$
K_S	Slow rate constant	$days^{-1}$
M	Cumulative biogas	$NL_{biogas}.Kg^{-1}_{VS}$ or $NL_{biogas}.Kg^{-1}_{COD}$
MC	Moisture content	%
MSW	Municipal solid waste	
M_M	Monthly amount of manure enters in reactor	Kg COD
M_{CW}	Monthly amount of cheese whey enters in reactor	Kg COD
n	Life span of project	years
na	Not analyzed	
NaOH	Sodium hydroxide	
N_2	Nitrogen gas	
NH_3	Ammonia	
N_2O	Nitrogen Oxide	
NPV	Net present value	€
NG	Negative	
O_2	Oxygen gas	

OFMSW	Organic fraction of municipal solid waste	
OM	Organic matter	
OLR	Organic loading rate	$KgVS.m^{-3}.d^{-1}$ or $KgCOD.m^{-3}.d^{-1}$
OPEX	Operative costs	€
P	Maximum biogas potential	$NL_{biogas}.Kg^{-1}_{VS}$ or $NL_{biogas}.Kg^{-1}_{COD}$
RS	Raw straw	
RM	Raw manure	
t	Time	hours or days
T	Temperature	K or °C
TCD	Thermal conductivity detector	
TNK	Total Nitrogen Kjeldal	
TOC	Total organic Carbon	% dry matter
TS	Total solids	%
V	Volume	L or mL
VFA	Volatile fatty acids	
VS	Volatile solids	% dry matter
$V_{37°C,n}$	V of biogas (or methane) produced during n days	L
$Vnet_{37°C}$	Net V of biogas (or methane) produced during n days	L
V_m	Volume of manure biogas production	$m^3.Kg^{-1}COD$
V_{CW}	Volume of cheese whey biogas production	$m^3.Kg^{-1}COD$

Chapter 1:

Introduction

1.1. *Waste management and legislation in European Union*

Growth in industrialized countries, together with the new potential economies in development such as China, India and South America, are strongly accompanied by increasing amounts of waste, causing unnecessary losses of materials and energy, environmental damage and negative effects on health and quality of life. This has already become a worldwide problem and absorbed concerns about the consequences of non-controlled industrial and urban design and social growth.

Waste generation and management is one of the most serious problems in modern societies, and consequently strong policies on waste issues has been set in developed countries. Waste uncontrolled disposal and inappropriate management lead to severe impacts in the environment, causing water, soil and air pollution, contributing to climate change and affecting negatively to the ecosystems and human health. However, when waste is appropriately managed it becomes a resource that contributes to raw materials saving, natural resources and climate conservation and sustainable development. For a long time, waste and waste management in EU have been at the center of EU environment policy and substantial progress has been made. For example heavily polluting landfills and incinerators are being cleaned up and new techniques have been developed for the treatment of hazardous waste (European CommissionCOM(2005) 666, 2005).

In general, over the past decades the European Union has put in place a broad range of environmental legislation. As a result, air, water and soil pollution has significantly been reduced. Chemicals legislation has been modernized and the use of many toxic or hazardous substances has been restricted. Today, EU citizens enjoy some of the best water quality in the world and over 18% of EU's territory has been designated as protected areas for nature (European comission, 2014a) However, despite these successes, waste remains a problem. Waste volumes continue to grow and legislation is, in some cases, poorly implemented and there are significant differences between national approaches. The potential for waste prevention and recycling is not yet fully tapped.

More than 2.5 billion tons of waste generates in the EU every year (European Parliament, 2016). However, waste management practices vary a lot between EU countries and quite a few countries are still landfilling large amounts of municipal waste.

In addition, EU parliament is still going with ambitious goals. Recently EU released the "The circular economy package: new EU targets for recycling" (European Parliament, 2017) and set new targets for waste management. The package includes a common EU target for recycling at least 55% of municipal waste by 2025; this target would rise to 60% by 2030 and 65% by 2035. Also envisaged is a common EU target for recycling 65% of packaging waste by 2025, and 70% by 2030. There would be separate targets for specific materials:

On the other hand, turning waste into a resource is one key to a circular economy. The objectives and targets set in European legislation have been key drivers to improve waste management, stimulate innovation in recycling, limit the use of landfilling, and create incentives to change consumer behavior. If waste be re-manufactured, reused and recycled, and if one industry's waste becomes another's raw material, the societies can move to a more circular economy where waste is eliminated and resources are used in an efficient and sustainable way. Improved waste management also helps to reduce health and environmental problems, reduce greenhouse gas emissions (directly by cutting emissions from landfills and indirectly by recycling materials which would otherwise be extracted and processed), and avoid negative impacts at local level such as landscape deterioration due to landfilling, local water and air pollution, as well as littering.

The European Union's approach to waste management is based on the "waste hierarchy" which sets the following priority order when shaping waste policy and managing waste at the operational level: prevention, (preparing for) reuse, recycling, recovery and, as the least preferred option, disposal (which includes landfilling and incineration without energy recovery).

In line with this the "7th Environment Action Program" (European Parliament, 2013) sets the following priority objectives for waste policy in the EU:

- To reduce the amount of waste generated;
- To maximize recycling and re-use;
- To limit incineration to non-recyclable materials;
- To phase out landfilling to non-recyclable and non-recoverable waste;
- To ensure full implementation of the waste policy targets in all Member States.

This program will be guiding European environment policy until 2020. In order to give more long-term direction, it sets out a vision beyond that, of where it wants the Union to be by 2050:

"In 2050, we live well, within the planet's ecological limits. Our prosperity and healthy environment stem from an innovative, circular economy where nothing is wasted and where natural resources are managed sustainably, and biodiversity is protected, valued and restored in ways that enhance our society's resilience. Our low-carbon growth has long been decoupled from resource use, setting the pace for a safe and sustainable global society."

With time, waste is increasingly seen as valuable resource for industry and approaches such as re-use, recycling and energy recovery are starting to be applied to regulate wastes. It is estimated that full implementation of EU waste legislation would save €72 billion a year, increase the annual turnover of the EU waste management and recycling sector by €42 billion and create over 400,000 jobs by 2020 (European Commission - Press release Database, 2012).

1.2. Livestock waste:

Among different types of waste, livestock waste has a notable environmental impact on water, soil and air quality. Livestock farming is growing as the result of human dietary, nowadays worldwide the number of livestock animals are about 22.8 billion chicken, 967 million pig, 1 billion goats, 1.2 billion sheep, 1.5 billion cattle and 201 million buffaloes (FAOSTAT, 2017). Thus, the livestock sector is an important user of natural resources and has significant influence on air quality, global climate, soil quality, biodiversity and water quality by altering the biogeochemical cycles of nitrogen, phosphorus and carbon, giving rise to environmental concerns (Leip et al., 2015; Tullo et al., 2019). It is also estimated that livestock sector contribute up to 50% of the global agricultural gross domestic product (Herrero et al., 2016) and supports the livelihoods and food security of almost 1.3 billion people in developing countries (FAO, 2017).

Application of manure in agricultural land from livestock is a general practice to enrich soil with nutrients and/or for sustainable nutrient recycling (Kusari et al., 2009) but this practice causes the contamination of different environmental compartments through the entry of hazardous material contained in the manure. Unfortunately, disposal of large amount of animal manure in relatively small areas with high density of animals, results in deposition of large amount of excretory nitrogen, phosphorus, organic matter and fecal microbes which cause the contamination of water system such as surface water eutrophication and ground water nitrate enrichment (Li et al., 2016; Mallin et al., 2015). Livestock effluents have in general high content of organic matter, suspended solids, nutrients, metals and pharmaceutical compounds. Unbalanced land application of livestock manure, nutrients and antibiotics may seep from soil into ground and surface waters and negatively affect the quality of water which can lead to growth of algae, accelerating eutrophication and promoting the spread of antibiotic resistant bacteria (Almeida et al., 2017; Girard et al., 2014; Hooda et al., 2000; Martinez, 2009).

Livestock farming impacts even on air through the emissions of ammonia (NH_3) and Green House Gases (GHG) represented by methane (CH_4), nitrous oxide (N_2O) and Carbon dioxide (CO_2), arising simultaneously from animal housing, yards, manure storage and treatment and land spreading (Baldini et al., 2018; Hou et al., 2016). In the EU-28 the contribution of agriculture is more than the 94% of the total anthropogenic NH_3 emission and it is noteworthy that 75% of NH_3 emissions are originated by management of livestock manure (European Environmental Agency (EEA), 2017; Eurostat, 2017; Webb et al., 2005).

To tackle all these issues both setting strong legislation to mitigate manure environmental impacts and also developing technologies to optimize manure treatment instead of landfilling is necessary. In case of legislation, European community took notable steps and introduced the Nitrates Directive in 1991 (Directive 91/676/EEC) (EC, 1991) with the aim of reducing water pollution caused or induced by nitrates from agricultural sources setting strict limits both in surface and ground water for the concentration of nitrates (50 mg. L^{-1}) (Martinez et al., 2009). This Directive is the most important European Regulation for diminishing environmental impacts of fertilizer and manure, increasing at the same time the nitrogen use efficiency (Grinsven et al., 2012). The Nitrates Directive defines “Nitrate Vulnerable Zones” setting spatial and temporal limits to the application and imposing the threshold of 170 kg ha^{-1} per year as the maximum amount of organic N that can be supplied to fields. Similar regulations also raised in EU to maintain the amount of phosphorus contamination in soil (Amery, 2014). In case of manure treatment, different processes are being practiced nowadays such as: anaerobic digestion and aerobic biological processes (composting and nitrification-denitrification). On the other hand, livestock manure can be converted to high value products such as biogas which can produce energy. In this regard EU has set legislations and plans to develop renewable sources of energy. For example, the 2020 package is a set of binding legislation to ensure the EU meets its climate and energy targets for the year 2020. This package sets three key targets:

20% cut in greenhouse gas emissions (from 1990 levels), 20% of EU energy from renewables and 20% improvement in energy efficiency (European comission, 2010). Renewables will continue to play a key role in helping the EU meet its energy needs. EU countries agreed in 2014 on a new renewable energy target of at least 27% of EU's final energy consumption by 2030, as part of the EU's energy and climate goals for 2030 (European comission, 2014b). On 14 June 2018 the Commission, the Parliament and the Council reached a political agreement (European Commission - Press release Database, 2018) which includes a binding renewable energy target for the EU for 2030 of 32%. To achieve these targets, development and investment on different aspects of renewable techniques is essential.

In this document the anaerobic digestion technic as a common and widespread practice in EU and in the world to treat manure and convert it to high value product, has been studied.

1.3. Anaerobic Digestion

Anaerobic digestion (AD) is a serial multi-stage biological process for decomposition and stabilization of organic matter in the absence of O_2. By the participation of several groups of anaerobic microorganisms, various types of organic matter can be converted into a renewable energy source known as biogas, a mixture containing mainly methane (CH_4) and carbon dioxide (CO_2), which can be used as a replacement for fossil fuel to generate heat or electricity (Pellera and Gidarakos, 2017; Sun et al., 2016). It is widely known that anaerobic digestion is a sustainable, cost-effective technology for waste valorization and energy recovery in the form of biofuel

(Kothari et al., 2014). As clean energy, biogas can replace fossil fuels which generate greenhouse gases via combustion in the household and commercial activities (Yadvika et al., 2004). Moreover, the digestate of anaerobic digestion are rich in nutrients and it can be served as a fertilizer to the crop cultivation. Therefore, enhancing methane production from various waste can obtain more energy to compensate for the deficiency of non-regenerated energy with consumption the same quantity of the substrate (Li et al., 2019). In Europe, more than 17,662 biogas plants were in operation in 2016 with a total installed electricity capacity of 9985 MW (European Biogas Association, 2017).

1.3.1. Description of the process

The process takes place in an enclosed reactor on absence of oxygen, where degradation of organic materials occurs through four consecutive stages, namely hydrolysis, acidification, acetogenesis and methanogenesis. Figure 1.1.

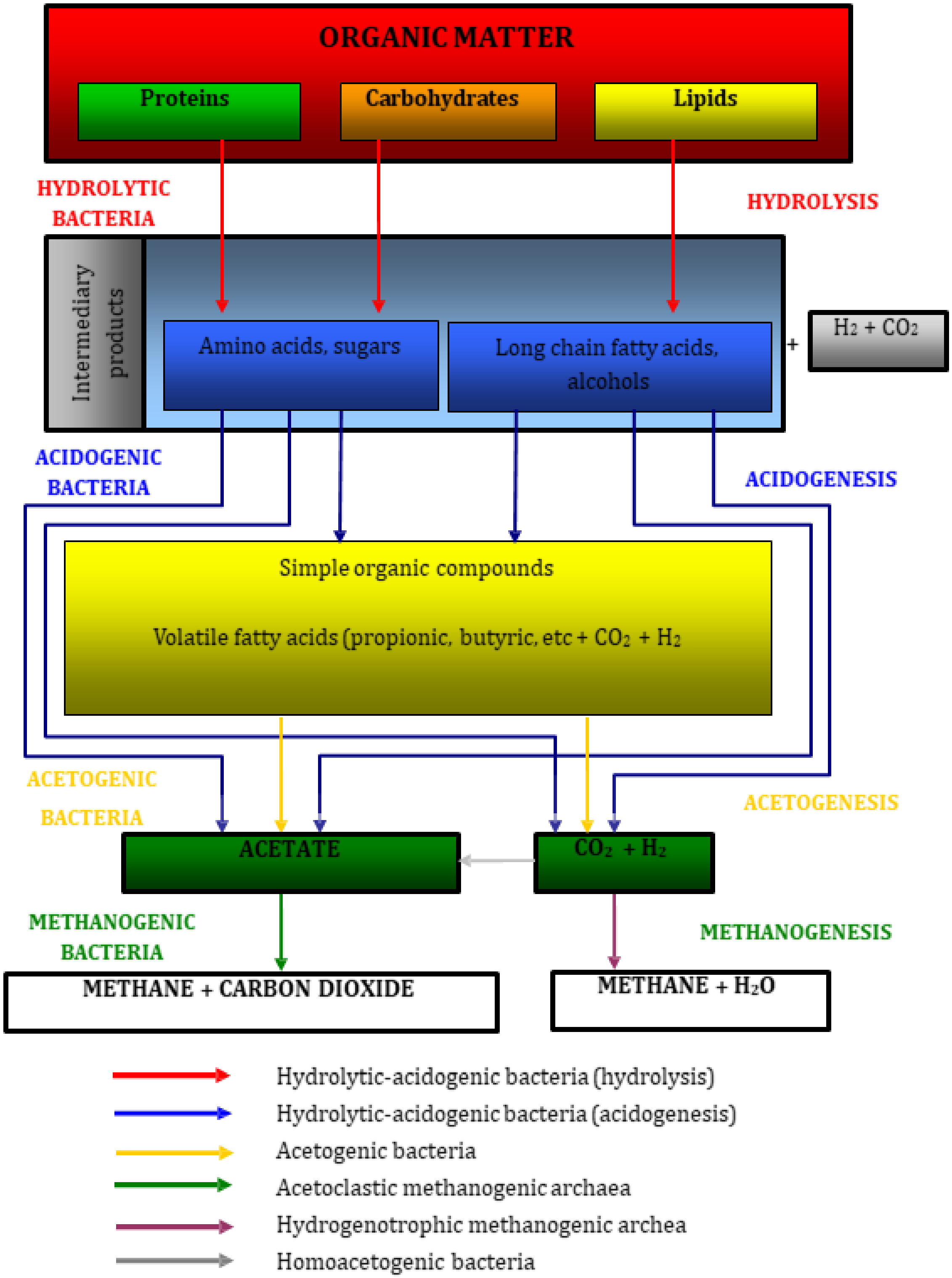


Figure 1. 1 Flow chart of anaerobic digestion (Ponsá et al., 2010)

- **Hydrolysis**

In the first stage, facultative hydrolytic bacteria using extracellular enzymes hydrolyze and fragment undissolved particles and complex molecules (proteins, carbohydrates and lipids) to soluble and simpler compounds (amino acids, sugars, long chain fatty acids, alcohols, CO2 and H2) (Ponsá et al., 2008a).

- **Acidification**

Acidification is also called fermentation which serves intermediate from substrate metabolism as an electron acceptor. In this process, acidogenic fermentation bacteria convert soluble monomers into terminal products, such as volatile fatty acid (VFA), (mainly acetate, propionate and butyrate), alcohols and other products including ammonia, hydrogen and carbon dioxide accompanied by cellular materials generation. Acidogenic bacteria are fast growing compared to other groups used in anaerobic digestion (Li et al., 2019; Ponsá et al., 2008a)

- **Acetogenesis**

In acetogenesis, alcohols, fatty acids and aromatic compounds are degraded to produce acetic acid, carbon dioxide and hydrogen that will be used by methanogenic bacteria in the final anaerobic digestion stage (Ponsá et al., 2008a).

- **Methanogenesis**

During methanogenesis, anaerobic methanogenic microorganisms produce methane from acetate, carbon dioxide and hydrogen. Considering that methanogenic bacteria are slow growing compared to other hydrolytic-acidogenic bacteria, special attention to hydraulic retention time must be given in order to prevent methanogens wash-out. Methanogenesis is a complex phenomenon accomplished by the synergistic action of various mesophilic bacterial species.

Equations 1.1-1.5 show the stages of methane production. (Li et al., 2019; Ponsá et al., 2008a)

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \quad (1.1)$$

$$HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O \quad (1.2)$$

$$4CH_3OH \rightarrow CO_2 + 2H_2O \quad (1.3)$$

$$4HCOO^- + 2H^+ \rightarrow CH_4 + CO_2 + 2HCO_3^- \quad (1.4)$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad (1.5)$$

1.3.2. Anaerobic digestion technologies

Different classifications of anaerobic digestion technologies and systems can be done depending on the: i) number of stages: single-stage or multistage systems; ii) dry matter content: dry or wet systems; and iii) operational temperature: psychrophilic, mesophilic or thermophilic systems.

- **Number of stages**

Most anaerobic systems consist of a single-stage digester, which means that all stages take place in the same reactor. In such situation, environmental conditions (i.e. pH, redox potential, temperature, etc.) may favor the development of certain group of bacteria, but it is important to maintain equilibrium to ensure a balanced degradation process. For this reason, the control of environmental conditions is a key factor, especially regarding methanogenic microorganisms, which are strict anaerobes, with the lowest growth rate and are the most sensitive to sudden changes in environmental conditions. The high capital cost of installing multistage systems has resulted in a reduction in the number of these types of facilities. (Ponsá et al., 2010)

- **Dry matter content**

Regarding dry matter content two different technologies can be considered: wet and dry processes. In wet processes the dry matter content of the feeding and in the digester is maintained between 4-10% by, if needed, diluting the feedstock with water (Hartmann and Ahring, 2005). The dry matter content for dry process systems is between 20-40% and no dilution is needed for feedings (Poggi-Varaldo et al., 1997).

- **Operational temperature**

Anaerobic microorganisms can grow at psychrophilic temperatures (15-19°C). However, low biogas production is achieved for anaerobic digestion at these temperatures and thus industrial anaerobic digestion processes do not normally operate in the psychrophilic range.

In mesophilic systems, anaerobic digestion takes place between 20°-45°C and operates optimally between 37-41°C (Song et al., 2004).

Finally, for optimal thermophilic processes operational temperature must be between 50- 52°C, but in some systems it is possible to reach temperatures as high as 70°C (Song et al., 2004). In general, the higher temperature, the faster the reaction rate and consequently lower retention time and volume required. Thermophilic AD has a rate-advantage over mesophilic digestion as a result of its faster reaction rates and higher-load bearing capacity and, consequently, exhibits higher productivity compared with mesophilic AD. However, the system is more unstable and acidification may occur during thermophilic AD, inhibiting biogas production. Other disadvantages such as decreased stability, low-quality effluent, increased toxicity and susceptibility to environmental conditions, larger investments, poor methanogenis and higher net energy input have also been identified. In addition, this process is more sensitive to environmental changes than the mesophilic process. Although mesophilic systems exhibit better process stability and higher richness in bacteria, they afford low methane yields and suffer from poor biodegradability and disadvantages related to nutrient imbalance (Bowen et al., 2014).

1.3.3. Factors affecting AD process for biogas production

There are some main operating parameters in anaerobic digestion systems. These parameters determine the microbial activity and thus influence/affect the anaerobic degradation efficiency. Process parameters can be split into the so–called environmental parameters (pH, alkalinity, C/N ratio, VFA) and operating parameters (temperature, retention time, organic loading rate).

- **Temperature**

As mentioned before, anaerobic biological activity can be developed for temperatures ranging from 5 to 70°C. However, there are generally two temperature ranges used at the full-scale industrial level providing optimum digestion conditions for methane production: the mesophilic and thermophilic ranges. The mesophilic range is between 20-40°C but the optimum temperature is considered to be 30-35°C. The thermophilic temperature range is between 50-65°C but the processes are normally undertaken at 50-55°C. It is important to keep constant temperature in the digesters and avoid rapid changes of temperature since it could lead to a thermal shock to microorganisms and a consequent stability loss.

- **pH**

The operational pH affects the AD process. The ideal pH range for AD has been reported to be 6.8–7.4. The growth rate of microorganisms is significantly affected by pH changing (Mao et al., 2015). During manure anaerobic digestion, pH value can be affected by the ammonia and VFA concentrations, process instabilities due to high ammonia concentrations often result in VFA accumulation, which leads to a detrimental decrease in pH but also a lower concentration of free ammonia. The interaction of free ammonia, VFAs and pH may lead to an “inhibited steady state”, a condition where the process is somewhat stable but operates with a lower methane yield.

It should be emphasized that both methanogenic and acidogenic microorganisms have optimal pH levels. Methanogenesis is most efficient at pH 6.5–8.2, and the optimal pH is 7.0 (Lee et al., 2009). The growth rate of methanogens is greatly reduced at pH levels below 6.6, and the activity of methanogenic bacteria decreased at a higher or lower pH (Zhang et al., 2009). The optimum pH of acidogenesis was between pH 5.5 and 6.5 (KIM et al., 2003).

- **Alkalinity**

Alkalinity is a direct measure of the buffering capacity of the digester. The optimum range of alkalinity is between 1000-3000 mg CaCO3 L^{-1}, (Pajpai, 2017) but to really ensure the digester stability is recommended to keep alkalinity up to 2.5 g CaCO3 L^{-1}. Alkalinity allows for indirect detection of digester acidification.

- **C/N ratio**

The C/N ratio reflects the nutrient levels of a digestion substrate, and thus, digestion systems are sensitive to C/N ratio. A high C/N ratio is an indicator of rapid consumption of nitrogen by methanogens and results in lower reaction rates and lower gas production while a low C/N ratio may cause inhibition, due to the accumulation of ammonia and pH values exceeding 8.5, which is toxic for methanogenic bacteria. The optimal C/N ratio in anaerobic digestion is approximately between 20 and 35 with a ratio of 25 being the most commonly used (Puñal et al., 2000; Yen and Brune, 2007; T. Zhang et al., 2013).

Insufficient amounts of carbon or nitrogen can limit AD performance in the anaerobic mono digestion of livestock manure or crop straw.

- **Volatile fatty acids (VFA)**

Volatile fatty acids (VFA) concentration in the digester is one of the most important parameters for anaerobic digestion reactors because instability of the system is often marked by a rapid increase in the VFA concentration, which signals methanogenic phase inhibition. carbohydrate and protein hydrolysis are limited by high VFA concentrations. VFAs are expressed as concentration of acetic acid (AcOH) in the feedstock and, depending on the type of material treated, this value can range from 200 to 2000 mg AcOH L^{-1} (Ponsá, 2010).

- **Organic loading rate (OLR)**

OLR represents the amount of volatile solids fed into a digester per day under continuous feeding. With increasing OLR, the biogas yield increases to an extent, but the equilibrium and productivity of the digestion process can also be greatly disturbed. Adding a large volume of new material daily may result in changes in the digester's environment and temporarily inhibits bacterial activity during the early stages of fermentation (Mao et al., 2015). In some literatures, the maximum OLR to avoid of foam formation and system inhibition in manure based digester and under mesophilic condition, is reported to be 3.5 g VS. L^{-1}. d^{-1} (Kougias et al., 2013).

- **Retention time**

The retention time is the minimum time required to complete the degradation of organic matter or the average time that the organic matter remains in the digester (Kothari et al., 2014; Matheri et al., 2016). It is associated with the microbial growth rate and depends on the process temperature, OLR and substrate composition. Two significant types of retention time are herein discussed: SRT, which is defined as the average time that bacteria (solids) spend in a digester, and HRT which is defined by the following equation (Ekama and Wentzel, 2008).

$$HRT = \frac{V}{Q} \qquad (1.6)$$

where V is the reactor volume and Q the influent flow rate in time. An average retention time of 15–30 days is required to treat waste under mesophilic conditions. Decreasing the HRT usually leads to VFA accumulation, whereas, a longer than optimal HRT results in insufficient utilization of digester components (Mao et al., 2015).

1.3.4. Anaerobic co-digestion

Nowadays, it is well known that mono digestion of animal manure produces low biogas yield which will cause negative economic evaluation on investments to treating manure by this process (Zhang et al., 2011). The reason of low biogas production in livestock manure is mainly related to the lack of nutrients and specially easily degradable carbon sources. The biogas yield of the most common livestock manure as sole substrate in digestion is shown in Table 1.1.

Table 1. 1 Biogas production from different livestock manure

Substrate	Methane production ($L.Kg^{-1}VS$)	Reference
Cattle manure	300	(Xavier et al., 2015)
Pig slurry	241	(Yang et al., 2019)
Chicken manure	260	(Molaey et al., 2018)

Therefore, to make this technology more attractive to farmers, an increase in CH_4 yield can be achieved by co-digesting animal manure with different types of co-substrates. Co-digestion of manure waste with other types of wastes, can provide positive synergistic effects and can potentially dilute toxic compounds. These co-substrates should be widely available and cheap, neutral to alkaline and containing low concentration of acid and oils as these together results in the flotation and washing of microorganisms or inhibition of the process by long chain fatty acids accumulation (Silvestre et al., 2014). The co-digestion of different substrates is not only desirable for improving methane recovery rates and reducing life cycle costs, but it also provides better organic load removal efficiencies as an effect of C:N ratio correction, pH balancing and improvement on the buffering capacity of the treatment systems and reducing the treatment costs (Athanasoulia et al., 2014; Grosser et al., 2017). Table 1.2 shows the examples of some achievements in co-digestion processes in different process situations (reactor types and temperature) at manure based bio-reactors.

Table 1. 2 Anaerobic Co-digestion using cow manure and pig manure as the main substrates

Substrates	Condition	Biogas yield (L.Kg^{-1}VS)	References
Cattle manure and olive mill waste	Mesophilic	180	(Goberna et al., 2010)
Cattle manure and cheese whey	Mesophilic	380	(Comino et al., 2012)
Pig manure and glycerol	Mesophilic	780	(Astals et al., 2012)
Pig manure and waste sardine oil	Mesophilic	500	(Ferreira et al., 2012)
Cattle manure and glycerol	Mesophilic	830	(Robra et al., 2010)
Cattle manure and sugar beet by-product	Thermophilic	240	(Fang et al., 2011)

One of the useful wastes to be used as co-substrate are inexpensive and easy accessible agricultural by-products (Xavier et al., 2015). The amount of agricultural waste worldwide is huge and therefore, anaerobic co-digestion of livestock manure and agricultural by products have been widely practiced. Table 1.3 shows the summary of some results obtained in other literature in this regard.

Table 1. 3 Summary of anaerobic co-digestion of animal manure and lignocellulosic material

Manure type	Co-substrate	Condition	Methane yield (L.Kg^{-1}VS)	References
Cattle manure	Palm pressed fiber	Mesophilic	346.2	(Bah et al., 2014)
Cattle manure	Whole stillage	Mesophilic	310	(Westerholm et al., 2012)
Cattle manure	Kitchen waste	Mesophilic	310	(R. P. Li et al., 2009)
Cattle manure	Wheat straw	Mesophilic & Thermophilic	130-210	(Risberg et al., 2013)
Swine manure	Corn stover	Mesophilic	350	(X. Li et al., 2009)
Swine manure	Cotton stalk	Mesophilic	267	(Cheng and Zhong, 2014)

Another substrate which can positively affect anaerobic digestion is other easy biodegradable wastes like cheese whey. Cheese whey has global production of 1.8-1.9×10^8 tons per year (Baldasso et al., 2011), and due to environmental problems caused by deposition of untreated cheese whey as well as its biodegradability potential, many studies were carried out to use cheese whey as co-substrate in the AD process (Dereli et al., 2019; Escalante et al., 2018). Table 1.4 shows the summary of results obtained for anaerobic digestion of cheese whey in other literature.

Table 1. 4 Summary of anaerobic co-digestion of cheese whey

Substrate	Co-substrate	Condition	Methane yield ($L.Kg^{-1}COD$)	References
Cheese whey	-	Mesophilic	230	(Ghaly, 1996)
Diluted cheese whey	-	Mesophilic	424	(Ergu et al., 2001)
Cheese whey	-	Mesophilic	300	(Saddoud et al., 2007)
Cheese whey	Cattle manure	Mesophilic	366-665 ($L.Kg^{-1}VS$)	(Comino et al., 2012)

Chapter 2:

Research Objectives

Considering the environmental impact of deposition of untreated excess amount of livestock waste in the environment as well as taking into account environmental problems of production of huge amount of agricultural waste and dairy industries waste, the main objective of this work is to provide not only a complete study on anaerobic co-digestion of livestock waste using agricultural and dairy industry by-products (Wheat straw & cheese whey) as co-substrates, but also to provide a complete techno-economic study of implementation of these process at full scale. The information provided in this document can be very useful for engineering companies and researchers to carry out preliminary feasibility assessments of the technology when designing full-scale AD plants for farms.

Thus, in order to reach this main objective, the research plans were proposed and are presented in two parts as below:

In the first case study of the research the objectives were:

- To evaluate the anaerobic biodegradability of cattle manure and raw straw using different pre-treatment methods such as (briquetted, alkali, microwave-alkali and thermal pre-treatments) in the batch experiment
- To evaluate anaerobic performance of anaerobic co-digestion of Cattle manure and Wheat straw (raw & briquetted) in the semi-continuous reactors
- To carry out a techno-economic viability assessment of anaerobic co-digestion in small to medium size cattle farms

In the second case study of the research the considered objectives were:

- To evaluate the anaerobic biodegradability of different animal manure (Cow, Goat and Sheep) as well as their corresponding cheese whey in the batch test

- To evaluate anaerobic performance of anaerobic co-digestion of each animal manure with its corresponding cheese whey (Cow manure and Cow cheese whey, Sheep manure and Sheep cheese whey, Goat manure and goat cheese whey) in the semi-continuous reactors.
- To carry out a techno-economic viability assessment of anaerobic co-digestion in small to medium size cattle farms for each scenario

Chapter 3:

Material & Methods

3.1. Inoculum

To obtain the anaerobic biodegradability of the samples, the use of anaerobic inoculum is required since it contains the anaerobic bacteria. Inoculum and its biogas production will be used as blank samples in all the experiment. Inoculum to carry out the AD test in all experiments was collected from a Mechanical-Biological Treatment Plant located in Barcelona (Spain) treating Organic Fraction of Municipal Solid Waste (4500 m3 of capacity, working temperature of 37°C and hydraulic retention time of 21 days). Anaerobic inoculum cannot not be frozen and should be kept at 37°C during one week to remove all remaining biodegradable fractions. Physio-chemical analysis of inoculum in each part of experiment is reported in the corresponding result section.

3.2. Substrates

Raw and briquetted straw were obtained from local providers. Cattle, sheep and goat manure were collected from farms located in Girona (Spain). Since the Goat and Sheep manure have solid structure they were blended to make them in powder form for further usage. Cattle, sheep and goat cheese whey were obtained from local dairy factories located in Girona (Spain). All manures and cheese whey were kept in fridge until their analysis. Physio-chemical analysis of substrates is reported in the corresponding result section.

3.3. Analytical methods

Routine parameters were determined according to standards procedures included in the "Standard methods for the examination of water and waste water" (American public health association, 2017). Results were calculated as a mean of three replicates.

3.3.1. Total solid (TS) and Moisture content (MC):

TS and MC were analyzed calculating the water loss, as shown in Equations 3.1 and 3.2. The sample was oven dried at 105°C for 24 hours.

$$TS(\%) = \frac{A-B}{Sample\ Weight} * 100 \qquad \text{(Equation 3.1)}$$

Where: TS= Total solid content of the sample (%). A = the final weight of dried residue + dish(g); B= weight of dish(g).

$$MC(\%) = 100 - TS \qquad \text{(Equation 3.2)}$$

Where; MC= Moisture content of the sample.

3.3.2. Volatile solid (VS, equivalent to total organic matter, OM):

VS was analyzed by sample ignition at 550°C in the presence of excess air for 2.5 hours,

calculated as equation 3.3 shows.

$$VS\left(\frac{g}{g\ Sample}\right) = \frac{(A-B)}{Sample\ mass(g)} * 100 \qquad \text{(Equation 3.3)}$$

Where; A= final weight of residue + dish before ignition,

B= final weight of residue + dish after ignition.

3.3.3. pH

The pH was measured with an electrometric pH meter (Crison, micropH200) directly in the liquid samples.

3.3.4. Total nitrogen Kjeldahl (TNK)

TNK was determined following the next three principal steps:

i. Sample digestion. This process converts all the organic nitrogen into ammonia. This change is achieved by exposing the sample to concentrated sulfuric acid in the presence of a catalyst at a high temperature.

ii. Distillation. The $N\text{-}NH_4^+$ from an aliquot is transformed into $N\text{-}NH_3$ by distillation in the presence of excess of base into a test tube containing an excess of boric acid at a known concentration.

iii. Titration. The difference between the equivalents of acid initially present and those remaining after distillation equal the equivalent of acid neutralized by ammonia, i.e. the equivalent of ammonia from both the N-organic and the $N\text{-}NH_4^+$ existing in the initial sample. Unlike the $N\text{-}NH_4^+$ content of the sample, the amount of organic nitrogen can be determined.

Total nitrogen Kjeldahl (TNK) was determined using 0.5 g of the sample. The sample was digested for 1.5 hrs. at 400°C using 25 mL of concentrated sulphuric acid in 100 mL Kjeldahl tubes using a Bloc Digester 6 (with twenty tubes capacity) (J.P. Selecta S.A., Barcelona, Spain). To speed up the digestion, a catalyst (Kjeltab®) was added. Each digestion block contained two blank tubes that contained the standard amount of acid described above and a catalyst tablet (Kjeltab®). After allowing the sample to cool, the sample was diluted using deionized water. A Büchi Distillation Unit K-355 (Flawil, CH) was used for sample distillation with an excess of NaOH (35%). The condensate was placed in a conical flask with 100 mL of boric acid (4%) with mixed indicator. A colorimetric assay was used to measure the amount of nitrogen formed by adding, HCl and an acid indicator. TNK was calculated using Equation 3.4.

$$TNK = \frac{(V_i - V_0) * N * 14}{W_{wb}} \qquad \text{(Equation 3.4)}$$

Where: TNK, total N-Kjeldhal (%); V_i, HCl volume consumed (mL) in sample titration; V_0, volume of HCl consumed (mL) in control titration; N, normality of the HCl used in determination; and W_{wb}, sample weight in wet basis (g).

3.3.5. Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is an indirect measurement of the amount of organic matter in a sample. With this test, all organic compounds that can be digested by a digestion reagent can be measured. In this thesis colorimetric method was performed to obtain COD of the samples. To measure the COD, potassium dichromate is used as the oxidant. Potassium dichromate is a hexavalent chromium salt that is bright orange in color and is a very strong oxidant. Between 95-100% of organic material can be oxidized by dichromate. Once dichromate oxidizes a substance it's converted to a trivalent form of chromium, which is a dull green color.

To carry out the COD experiment dilution of sample is required. The dilution ratio is based on TS content of the samples and whether if they can be solved in water easily or not. In general, more solid content will need higher sample dilution ratio. Thus the dilution ratio mostly varies from 1:100 to 1:250 in most cases. In this thesis 1ml or 1 g of the samples were diluted in the 100ml flask and then 2ml of the solution was taken into prepared reactive tubes with the oxidant and sulfuric acid. Digestion was performed on the digester at (150°C) for 2 hours. The amount of trivalent chromium in a sample after digestion was quantified by measuring the absorbance of the sample at a wavelength of 600 nm in a spectrophotometer. It is noteworthy to mention a sample of deionized water as reagent blank has to be digested the same as actual samples. The final COD of the sample will be calculated as shown in Equation 3.5.

$$COD\left(\frac{mg}{L}\right) = Number\ read\ from\ Spectophotometer \times dilution\ ratio\ (flask\ volume)$$

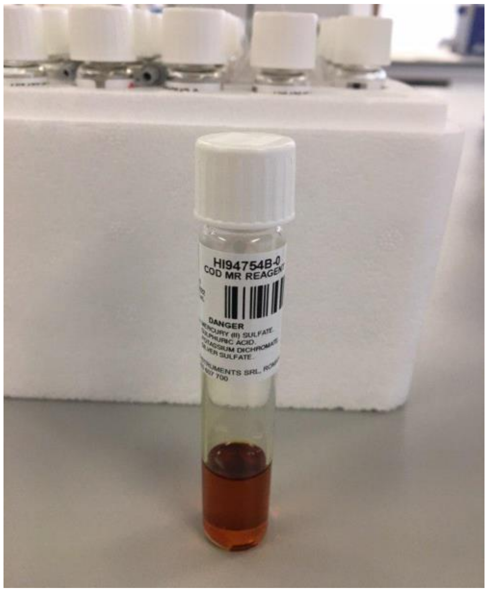


Figure 3. 1 Prepared reactive tubes before digestion

Figure 3. 2 Prepared reactive tubes after digestion

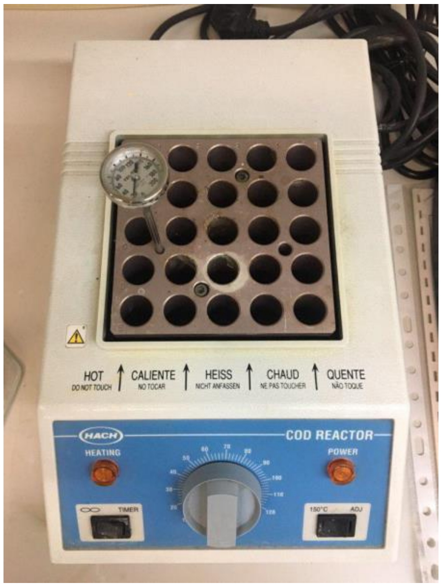


Figure 3. 3 Digester

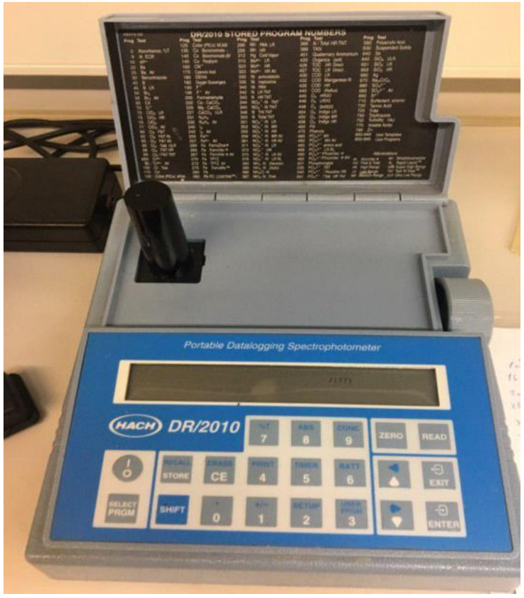


Figure 3. 4 Spectrophotometer

3.3.6. Bulk density (BD)

BD is defined as the weight per unit of volume of sample. BD was calculated on wet basis dividing the sample weight by the sample volume as shown in Equation 3.6**.**

$$BD_W = \frac{W_S}{V_S} \qquad \text{(Equation 3.6)}$$

3.4. Lignocellulosic compounds pretreatment

In order to break down lignin chains in the agricultural residues and increase their biodegradability, different pretreatments have been studied in this thesis.

Figure 3. 5 Example of lignocellulosic biomass (Wheat Straw& Sarment)

3.4.1. Alkali pretreatment.

Alkali pretreatment of straw was performed as described by Zhang et al (Y. Zhang et al., 2013). Briefly, straw treated with 10 g/L NaOH per g of straw at 121ºC for 60 min, and washed using tap water until achieve pH=10. The alkaline pretreated straw was then immersed in 3% (v/v) hydrogen peroxide at 50 ºC for 24 h and washed to below pH=9 and stored at 4 ºC until use.

3.4.2. Microwave-Alkali-Acid pretreatment.

As described by Akhtar (Akhtar et al., 2017), straw samples were placed in 1% NaOH (w/v) per g of straw for microwave pretreatment. Microwave pretreatment of straw was executed for 3 min at 675W, 150 ºC. After microwave pretreatment, biomass was neutralized using distilled water and then dried at room temperature. Dried microwave-alkali pretreated biomass was immersed in 1% (v/v) H2SO4 to achieve a liquid-to-solid ratio of 10:1 (v/w) for 1 h. The treated biomass was washed thoroughly using distilled water until neutral pH, dried overnight in an oven (60 ºC) and then stored in moisture free container for further studies.

3.4.3. Thermal pretreatment.

To perform the thermal pretreatment of samples, a modification of Carvalheiro protocol has been used (Carvalheiro et al., 2005, 2004). The raw straw samples were kept in incubator at 121 ºC for 30 minutes. After incubation, samples were washed with distilled water with liquid-to-solid ratio of 10 g/g. The solid was recovered by filtration, washed and dried at 50 °C until the moisture content was less than 10% (w/w) was.

3.4.4. Briquetting.

Briquetting is a mechanical process in which biomass with a low initial density (around 0.2 kg L^{-1}) has first shredded and then subjected to high pressure, promoting its agglomeration and densification. The resulting product (briquettes) achieved a density of around 1.2 kg L^{-1}.

The produced briquettes had typical shapes of cylinder and cuboid. Generally, the cylindrical briquettes were 70 mm in diameter and 100 mm in length with unit density of 900 kg m^{-3}. The cubic briquettes were almost 12.7 × 12.7 mm in cross section, and 100 mm in length with the unit density around 1000 kg m^{-3}. Theoretically, this process can also alter the chemical structure of the biomass. Firstly, the reduction of the particle size of biomass by shredding process increases its surface area and it can reduce both the degree of polymerization and cellulose crystallinity. In addition, vaporization of liquid content in the lignocellulosic material can be expected during the briquetting process due to the high pressure which can promote hydrolysis of the hemicelluloses and lignin into lower molecular weight carbohydrates.

3.5. Biogas composition

Biogas content was analyzed by gas chromatography (GC) (Agilent 7820A GC System) with a thermal conductivity detector (TCD) and using a PoraPlot Q column (30 m × 0.53 mm × 1.5 µm). The gas chromatography operating conditions were as follows: (a) oven temperature isothermal at 60 °C; (b) injector temperature 60 °C; (c) TCD temperature 150 °C; and (d) carrier gas He at 14 psi pressure. The GC was calibrated with gas standards of known concentration.

Figure 3. 6 Gas Chromatograph (Agilent 7820A GC System)

3.6. Biogas Potential during a fixed time (GBn), Biological Methane Production during a fixed time (BMPn)

The biogas production was determined using the procedure described by Ponsá et al (Ponsá et al., 2008b) At present (and as future trends indicate) almost all digesters work under mesophilic temperatures, being 37°C the most usual. Consequently, the most useful biogas or methane production determinations would be under the same conditions that are industrially used. For that reason, the experiment temperature was established at 37°C. In addition, inoculum was obtained from a digester working at 37°C, so mesophilic populations are already present and no acclimation is needed. When making the mixtures inoculum-sample (waste) the organic loading must be carefully considered. The main problem that can appear along the experiment duration is the medium acidification and inhibition of microorganisms by volatile fatty acids accumulation. This would occur when content of easily hydrolysable organic matter in the sample was excessive. Therefore, different inoculum/sample ratios could be defined to carry out the experiments, since all samples have different composition characteristics. However, in order to define a standard procedure valid for comparing the results of each experiment, a single ratio must be established. Two main points were considered when establishing the most suitable ratio:

i. the sample amount analyzed must be enough for being considered as representative.
ii. No acidification of the media must be assured.

Finally, a ratio of 2/1 inoculum/substrate in volatile solids basis for lignocellulosic residues and COD basis for cheese whey experiment, was assessed as the most suitable for BMP determination. Sealed aluminum bottles of 1 liter of working volume will be used for carrying out the anaerobic tests (Figure 3.5.). The mixture is directly made in the bottles by adding the correspondent amounts of inoculum and sample to finally obtain 600 ml of mixture and around

400 ml of headspace (depending on the bulk density of the mixture) in the bottles. The mixtures were incubated in a temperature-controlled room at 37°C. Before each experiment, the bottles were purged with nitrogen gas to ensure anaerobic conditions. The bottles had a ball valve which can be connected to a pressure digital manometer (SMC model ZSE30, Japan) allowing for the determination of the biogas pressure. The bulk density of the mixture was previously determined (in triplicate) to calculate the headspace volume of the bottles which was assumed constant along the experiment. During the test, the bottles were shaken once a day.

Biogas and methane productions were calculated according to the ideal gas law from the pressure measured in the bottle and considering the headspace volume previously measured. To avoid excessive pressure in the bottle the biogas produced was purged periodically (typically 25-30 times during the experiment). This way pressure was not allowed to reach a value over 3 bar. This contributes to minimize the possible solubilization of carbon dioxide since methane is hardly soluble in aqueous media. Nevertheless, final biogas production at long times should not be affected by this effect. All biogas production tests were carried out in triplicate. The results are expressed as an average with standard deviation. If one of the bottles presented a deviation higher than 20%, it was discarded for the biogas potential calculation.

Figure 3. 7 Set up for anaerobic index determination: sealed aluminum bottles.

A biogas production test containing only inoculum was analyzed in triplicate to be used as a blank. The blank is also useful to have a quantitative measure of inoculum activity. Biogas and methane production from inoculum samples must be subtracted from the biogas and methane production of the waste samples. That would mean that results of GBn and BMPn represent only the biogas or methane produced by degrading anaerobically the organic matter contained in the sample and without considering the remaining organic matter that can content the inoculum.

The procedure to determine GBn and/or BMPn is described below:

i. The volume of biogas or methane produced at 37°C and 1 atm in each experiment is calculated as follows (Equation 3.7.)

$$V_{37^{\circ}C,n} = \frac{\left[B - \left({W}/{BD_w} \right)\right] \times \sum_{i=0}^{n} P_i}{1.032502} \qquad \text{(Equation 3.7)}$$

Where $V_{37°C,n}$ is the volume of biogas (or methane) produced in a bottle after n days (L); B is the bottle working volume (L); W is the total wet weight of the mixture introduced in the bottle (kg); BDw is the wet bulk density of the mixture ($kg \cdot L^{-1}$) ; Pi is the pressure measured after pressure release (bar); n is the days after experiment started; 1.032502 is the atmospheric pressure (bar).

ii. The net volume of biogas (or methane) produced, after subtracting the biogas (or methane) produced by the blank is calculated as follows (Equation 3.8)

$$V_{net\ 37°C,n} = [V_{37°C,n}] - \left[\left(\sum_{i=0}^{3} {V_{37°C\ inoc.,i}}/{W_{inoc,i}}\right)/3\right] \times S_{inoc} \qquad \text{(Equation 3.8)}$$

Where $V_{net\ 37°C,n}$ is the net volume of biogas (or methane) produced in a sample bottle after n days (liters); $V_{37°C\ inoc.,i}$ is the volume of biogas (or methane) produced in each blank triplicate after n days (liters); $W_{inoc,i}$ is the total wet weight of inoculum initially introduced in each blank triplicate (g); S_{inoc} is the wet weight of the inoculums used when making the initial mixture waste-inoculum(g).

iii. The biogas production during n days (GBn) and biological methane potential during n days (BMPn) is finally determined using Equation 3.9

$$GB_n(BMP_n) = \left[\left({V_{net\ 37°C,n}}/{Z}\right) \times \frac{273.15}{310.15}\right] \qquad \text{(Equation 3.9)}$$

Where GBn is the net volume of biogas produced from a waste sample after n days (NLbiogas.kg VS^{-1}); BMPn is the net volume of methane produced from a waste sample after n days (NL methane.kg VS^{-1}); Z is the amount of VS of sample initially loaded in the reactor (kg VS); 310.15 is the temperature measured in Kelvin at which the experiment is carried out (310.15 K) and equivalent to 37°C; 273.15 is the temperature in Kelvin which corresponds to normal conditions (273.15 K) and equivalent to 0°C.

Figure 3.8. shows the example of BMP evolution (average and standard deviation) for 3 different samples of organic fraction of municipal solid waste (OFMSW) from different origin and the blank. (Ponsá et al., 2010)

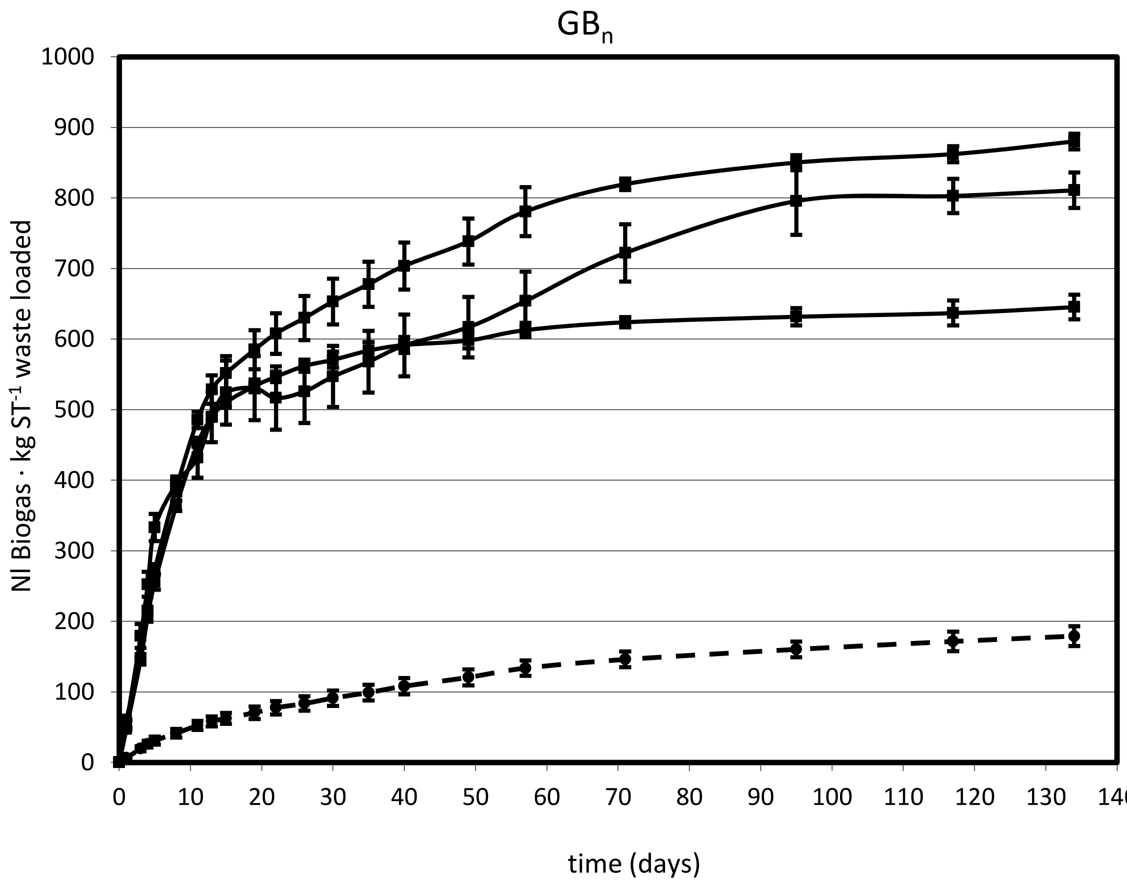


Figure 3. 8 Example of GBn evolution (average and standard deviation) for different samples of OMFSW and blank. (Ponsá, 2010)

3.6.1. Biogas potential biodegradation kinetics modelling

In order to completely characterize the biodegradable organic matter content of a given waste by means of quantitative measures of the easily and slowly biodegradable organic matter and biodegradation kinetic rate constants, the data of cumulative CO_2 produced or mineralized was fitted to the models described by Ponsá (Ponsá, 2010; Ponsá et al., 2011) to the experimental cumulative methane production curves.

i. The maximum biogas production (P) and the maximum biogas production rate (R_{max}) were determined by fitting the modified Gompertz model (Eq. 3.10) described by Ponsá (Ponsá, 2010) to the experimental cumulative methane production curves.

$$M(t) = Pexp\left[-\exp\left(\frac{R_{max}e}{P}(\lambda - \mathrm{t}) + 1\right)\right] \qquad \text{(Equation 3.10)}$$

Where: M is the cumulative of biogas production (NL.Kg^{-1}VS); P is the maximum biogas production potential (NLbiogas.kg^{-1} VS); R_{max} is the maximum biogas production rate (NLbiogas.kg^{-1} VS day^{-1}), $\boldsymbol{\lambda}$ is the lag phase period (days).

ii. To provide a quantitative measure of the different fractions of biodegradable organic matter that is contained in organic wastes, the percentage of carbon mineralized was calculated as the amount of cumulative C-biogas produced at a given time on the basis of the initial TOC (constant value and characterization parameter). The data was fitted to the model proposed by Ponsá et al. (Ponsá et al., 2011) (Eq. 3.10). The objective was to assess the different biodegradable organic fraction by means of a simple, rapid and easily applicable model and also to compare the rapidly and slowly biodegradable fractions in different pretreatments.

$$C_w = C_R \exp(-K_R t) + C_S \exp(-K_S t) + C_1 \qquad \text{(Eq. 3.11)}$$

Where C_W is the remaining carbon of the sample (%) at time t (days), C_R and C_S are the percentages of rapidly and slowly biodegradable fractions, respectively, C_1 is the inert fraction and K_R and K_S are rapid and slow rate constants (day^{-1}), respectively.

Figure 3.9. shows an example of evolution of carbon remaining in the sample of OFMSW, kinetic models fittings, evolution of CR degradation and evolution of CS degradation. (Ponsá, 2010)

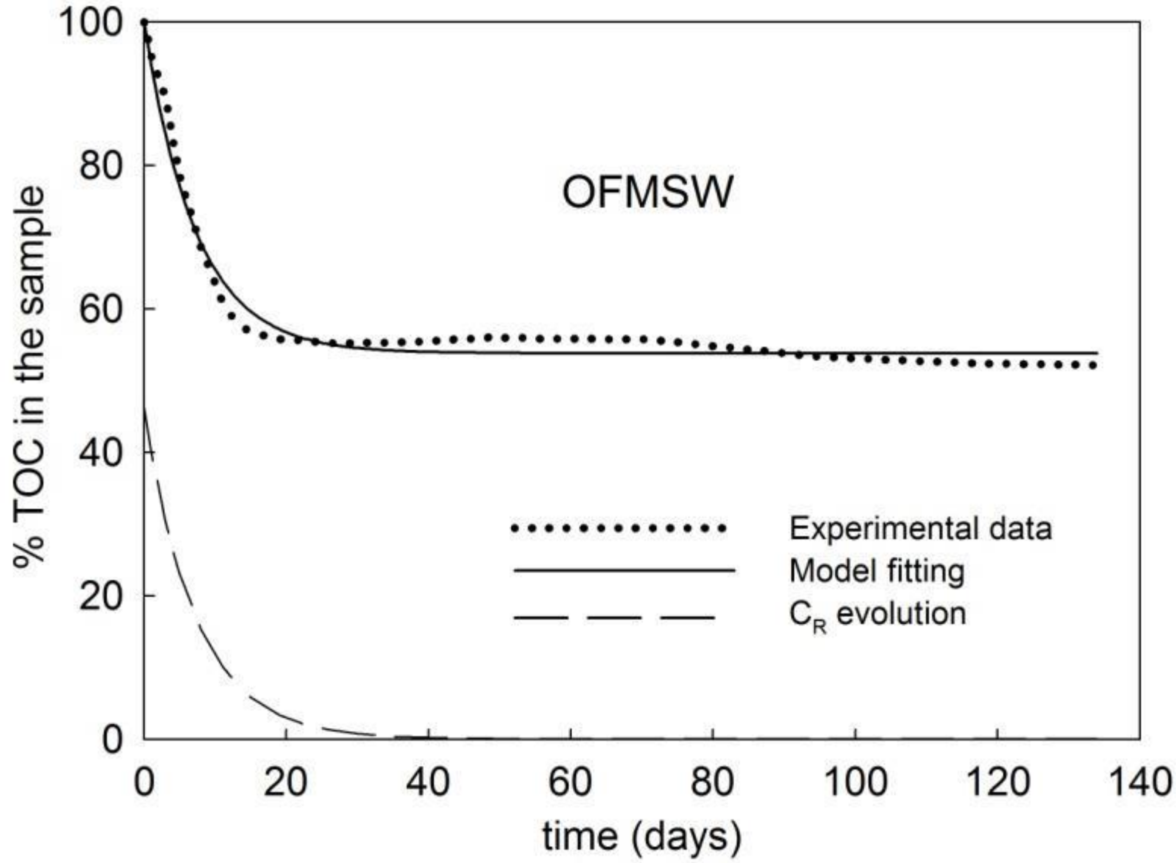


Figure 3. 9 Example of evolution of Carbon remaining in the sample, CR and CS in OFMSW. (Ponsá, 2010)

3.6.2. Statistical methods

One-way ANOVA tests using IBM SPSS 23 were applied to observe statistical differences of biogas productions of each sample in batch test.

3.7. Anaerobic semi-continuous digester configuration and operation

In order to investigate the biodegradability of substrates and their biogas production in the full scale, a pilot scale of the digesters with semi-continuous reactors were designed. Due to the difference of the substrates used in this thesis, two different experiment and system design were carried out. In the first experiment which Wheat straw as a lignocellulosic compound was considered as co-substrate, considering non-soluble solid content of straw, the system was designed for manual feeding and unloading of reactors while in the other experiment in which Cheese whey used as co-substrate the systems were fed and unloaded automatically. In addition, due to higher organic loading rate used in the first experiment, higher reactor volumes were used.

3.7.1. Anaerobic digestion of Wheat straw and Cattle manure in semi-continuous reactors:

Anaerobic co-digestion of cattle manure and cattle manure and raw and briquetted straw was performed using three semi-continuous reactors (5 L) with effective working volume of 4.5 L for a period of 6 months with a Hydraulic Retention Time (HRT) of 25 days. Figure 3.6. shows the experiment set up. The reactors operated under mesophilic conditions (37 ± 0.2 ºC), temperature was controlled by a thermostatically regulated water bath. Mechanical stirring was set to provide a semi-continuous mixing. Extraction and feeding of reactors were performed manually using a syringe. Biogas produced was collected and measured by a gasometer. The gasometer used in this experiment consists of a cylindrical container closed on the upper face and open on the lower one, the container is free to scroll vertically and the lower portion is immersed in a tank consist of 1% solution of Sulphuric acid+ potassium chloride (KCL). The tank therefore floats on the solution and emerges or sinks based on the quantity of gas stored inside. The presence of solution prevents the gas from coming out of the tank and the gas itself is introduced and withdrawn through pipes that emerge from the solution. The presence of KCL prohibits solubilization of the dissolvable gases in the water and thus will lead to more precise gas measurement. Figures 3.6a-3.6c show the schematic structure of the gas meter. The reactors were fed and unloaded manually in daily basis.

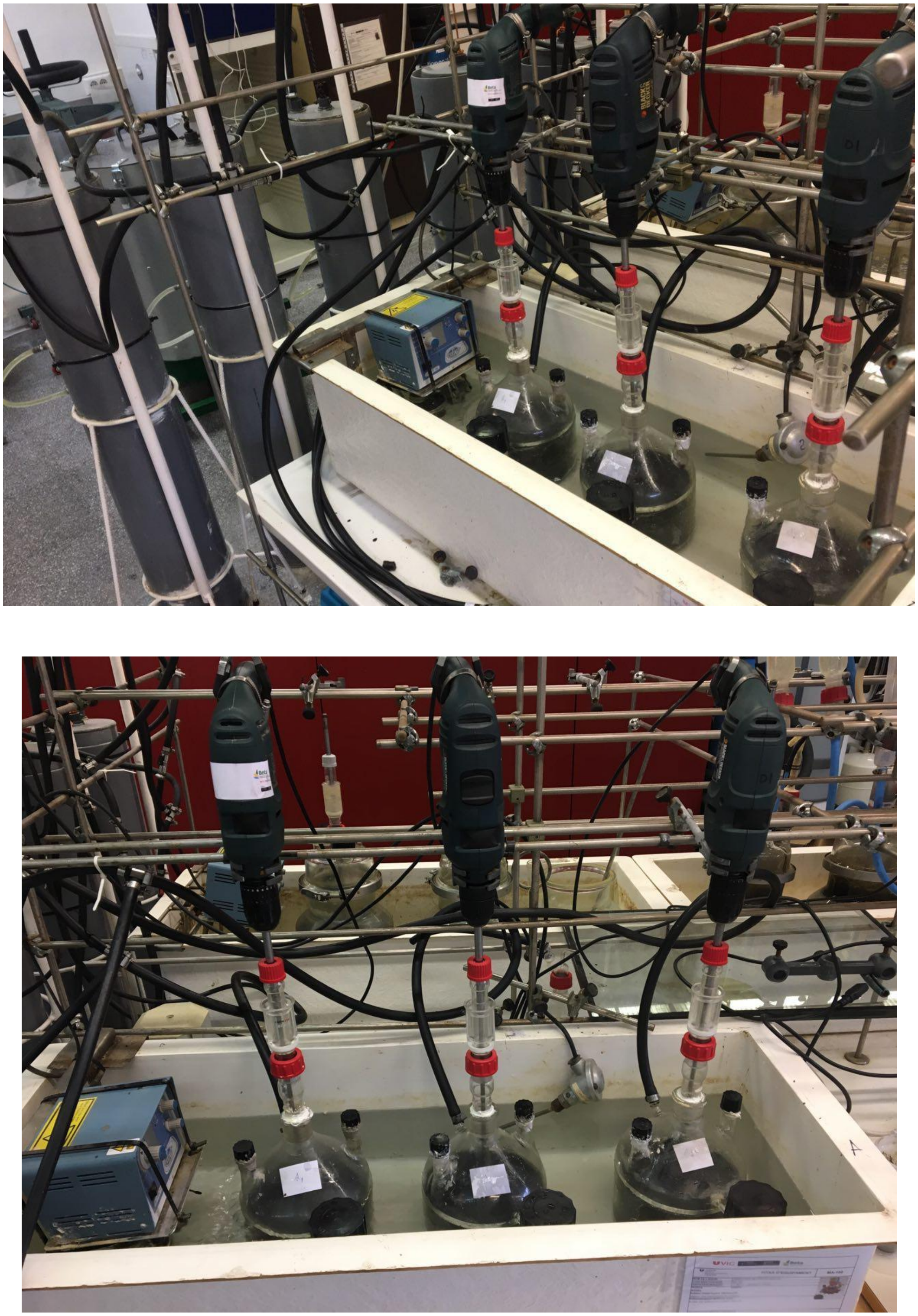


Figure 3. 10 Experiment setup of semi continuous reactors

Figure 3. 11 Gasometer for straw experiment

Figure 3. 12 Syringe for manual feeding

3.7.2. Anaerobic digestion of Cheese whey and animal manure in semi-continuous reactors:

Anaerobic co-digestion of cow manure and cow cheese whey, Goat manure and goat cheese whey, Sheep manure and sheep cheese whey were performed in three different reactors (3L) with working volume of 2.5 Liter for a period of 4 months with a Hydraulic Retention Time (HRT) of 28 days. The reactors operated under mesophilic conditions (37 ± 0.2 ºC), temperature was controlled by a thermostatically regulated water bath. Mechanical automatic stirring was set to provide a semi-continuous mixing with 50rpm every 5 minutes. Figure 3.13. shows the experiment set up. Since the cheese whey is highly biodegradable, thus the feeding solutions have been kept in a fridge during all the experiment where they were connected to feeding pumps by tubes. The solutions were being homogenized by a magnetic stirrer inside the fridge. Biogas produced was collected and measured by a digital gas meter (Ritter MGC-1 V3.4 PMMA) with 120 ml of volume filled with 1.8% HCL (Hydro chloride acid) and volume measuring chamber of 3.3 ml. The reactors were fed and unloaded with automatic pumps in daily basis. In the gas line of every reactor and before gas meter, an expandable air bag was set to maintain the internal pressure of the system during unloading of material and feeding by pumps. pH was monitored continuously during the experiment by a sensor inside the reactors.

Figure 3. 13 Experiment set up for co-digestion of Cheese whey and animal manure

Figure 3. 14 Digital Gas meter

Figure 3. 15 Expandable air bag

Chapter 4:
Results

4.1. Straw as co-substrate in anaerobic digestion of livestock waste

4.1.1. Introduction

Lignocellulosic biomass (second generation biofuels from raw materials based on agricultural waste and non-food crop biomass) is a promising energy source, because it is available in large quantities that will not compete with food production and may contribute to environmental sustainability (they have a more favorable GHG balance) (Demirbas, 2009). Thus their application in anaerobic digestion have lately gained more attention because of their abundant availability and the increased needs for bioenergy. Previous researchers (He et al., 2014; Shen et al., 2018; Zhou et al., 2017) have applied these lignocellulosic materials as substrate in anaerobic digestion with or without pretreatment (Hassan et al., 2017). It should be noticed that the C/N ratio of lignocellulosic materials are more than 50 (Lin et al., 2018), which can act as a suitable co-substrate in mixing with RS that presents high nitrogen content, providing a versatile mixture for anaerobic processes that could be optimized for each fraction to maximize biogas production and VS degradation. Particularly, agricultural wastes throughout the world are approximately 1.5 billion metric tons. Among these residues, wheat straw is the second most abundant agricultural waste in the world and the first in Europe which can be used as biomass for renewable energy production (Ferreira et al., 2013; Risberg et al., 2013). The annual global production of dry wheat in 2004 was estimated at around 529 Tg, being Asia (43%) and Europe (32%) the largest production regions. About 20 Tg of dry wheat (4% of global production) is lost as waste (Kim and Dale, 2004). Although lignocellulosic wastes such as straw have high potential to be used for producing bio-energy, they have some barriers to achieve this purpose which lead them to not be widely used in AD. The complex structure of the plant material (lignin and cellulose) causes a decrease in biodegradability and biogas yield (Yang et al., 2015; Zheng et al., 2014). Thus, pre-treatment of lignocellulosic materials were widely practiced for AD processes.

4.1.2. Material and Methods

The procedures and analysis for AD of straw as co-substrate have been carried out as follow:

4.1.2.1.Inoculum and substrates

The physicochemical characteristics of the inoculum, the raw manure (RM) and the raw & briquetted straw (RS & BS respectively) used in the experiments are summarized in Table 4.1. The Total Organic Carbon (TOC) content of straw and cattle manure were estimated according to literature (McKendry, 2002; Wang et al., 2018; Wu et al., 2010; Yue et al., 2017).

Table 4. 1 Characterization of the substrates and inoculum

Substrate	**TS (%)**	**VS (%TS)**	**%TOC (%TS)**	**TKN (g/L)**	**COD (g/L)**
Inoculum	4.0 ± 0.1	54.0 ± 0.1	31.0 ± 0.1	n.a.	29.4 ± 0.9
Cattle manure	4.0 ± 0.1	69.0 ± 0.1	36.0 ± 0.1	2.3 ± 0.3	44.4 ± 5.4
Raw Straw	91.0 ± 0.4	94.0 ± 0.4	45.0 ± 0.1	4.9 ± 0.6*	na
Briquetted straw	90.0±0.1	89.0±0.1	51.0±0.1	5.9±1.2	na

* Unit is (g/Kg)
na: not analyzed

4.1.2.2.Straw pretreatment

Substrate pretreatment is a common step in processing lignocellulosic feedstock whose materials, such as hemicellulose and cellulose are turned into soluble compounds. Pretreatment methods such as chemical treatments, alkalization, Fenton and ozonation, thermal, biological, ultrasound and microwave irradiation have been studied before (Grosser et al., 2017; Neshat et al., 2017) However, chemical treatments are costly and implies limited implement at full scale systems, on the contrary briquetting (which is a mechanical process in which biomass with a low initial density is first shredded and then submitted to high pressure, promoting its agglomeration and densification) is considered a feasible alternative to be implemented at full scale from an economic and operational point of view. Briquetting can solve problems in relation to logistics of using raw straw in anaerobic co-digestion processes. For example, straw low bulk density, typically between 40-80 $kg \cdot m^{-3}$, implies significant increase in the handling, storage and transportation costs (Rijal et al., 2012). Therefore, densification technologies such as the pelleting and briquetting has been suggested as potential processes to solve these logistic issues. According to Singh et al. (Singh et al., 2010), when lorries are used to transport biomass, savings around 46% of the transport costs (in terms of US\$ t^{-1} km^{-1}) can be achieved if biomass is briquetted instead of baled. From an energy point of view, there will be savings in diesel consumption by transport as well, since the trucks can transport higher amounts of straw due to higher density obtained by briquetting. From Singh et al. (Singh et al., 2010), it can be calculated that 0.83 L of diesel can be saved per kg of straw when the mean transport distance is 50 km, corresponding to approximately savings at around 8.3 kWh kg^{-1} straw. According to Xavier et al. (Xavier et al., 2015) it has been estimated that the total energy consumption for the wheat straw briquetting process in a commercial setup is about 100 kWh t^{-1} while energy produced from the briquetted straw during their AD experiment corresponded to 1100 kWh t^{-1}. As a result, the use of briquetted straw for anaerobic co-digestion results in a positive net energy output since less than 10% of the energy produced from the straw would be used for briquetting.

During densification, the moisture in the biomass forms steam under high pressure and temperature, which may hydrolyze the hemicellulose and lignin into lower molecular carbohydrates, lignin products, sugar polymers and other derivatives (Xavier et al., 2015). Therefore, particle size reduction through shredding and the application of high pressure and temperature during briquetting process could both accelerate the hydrolysis and acidogenesis of the biomass, achieving a faster and higher CH4 yield. Only few studies have been found dealing with AD of briquetted materials. Wang et al. (Wang et al., 2016) studied the effects of densification on AD for producing biogas. In their experiments they studied corn stover in forms of pellet and briquettes. They observed that the biogas production from briquetted corn stover was slightly higher than the un briquetted. However, that improvement was not statistically significant. Another study about AD of cattle manure with briquetted and shredded wheat straw has been carried out by Xavier et al (Xavier et al., 2015). Their results showed that in terms of final methane yield, no significant differences were found between briquetted and shredded wheat straw. In this thesis also Alkali pre-treatment, Micro-Alkali-Acid and Thermal pretreatment of straw using the treatment methods described in section 3.4.1-3.4.3 were investigated. The briquetted straw obtained from local biomass briquette providers located in Barcelona, Spain. Figures 4.1-4.3. Show the result of each sample after pretreatment.

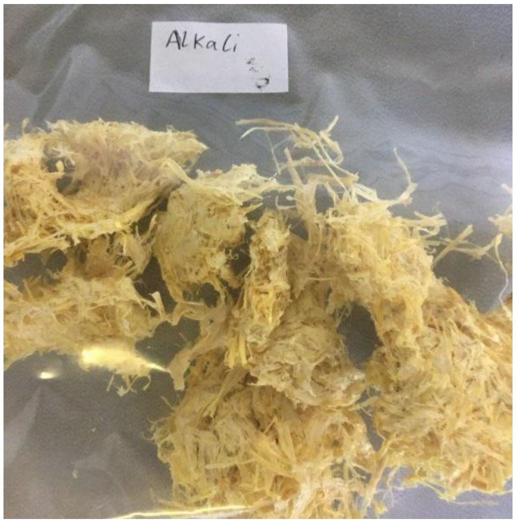


Figure 4. 1 Alkali pretreated straw

Figure 4. 2 Microwave pretreated straw

Figure 4. 3 Thermal pretreated straw

Figure 4. 4 Briquetted straw

4.1.2.3. Initial set up for Biogas potential test of Straw (GBn):

Anaerobic biodegradability of wheat straw as a lignocellulosic waste with different types of pretreatments were investigated in this study. The experiment was carried on based on the procedure described in section 3.6; 6g of raw straw samples (raw & pre-treated) were mixed with 594ml of inoculum in 1L aluminum bottles to achieve VS inoculum/VS substrate of 2/1. The bottles were purged with nitrogen and sealed quickly in order to remove the oxygen. In case of cattle manure 170ml of cattle manure was mixed with 430ml of inoculum to have VS inoculum/VS substrate of 2/1. 600ml of only inoculum was set as the blank sample and 5g of Glucose in 594ml of inoculum was considered as the control sample. The bottles pressures were measured daily until there was no special biogas production.

4.1.2.4.Initial set up for Biogas production test of straw (raw & briquetted) in semi-continuous reactors:

To obtain relevant data to perform the techno-economic assessment of co-digestion processes, anaerobic co-digestion of RM mixed with (i) RS and (ii) BS was performed and compared with the mono-digestion RM. The tests were performed in semi-continuous reactors (5 L) with an effective working volume of 4.5 L for a period of 7 months, three reactors were set up (one for the mono-digestion process of RM, one for the co-digestion of RM mixed with RS and one for the co-digestion of RM and BS). The operational conditions were as follow: HRT of 25 days, mesophilic conditions (37 ± 0.2 ºC, temperature was controlled by a thermostatically regulated water bath) and mechanical stirring (1 minutes of stirring at 50 rpm every 30 minutes). Biogas produced was measured by means a gasometer (MiliGascounter, RITTER). The reactors were fed and unloaded in daily basis. Figure 1 shows the experimental set up.

During the first HRT (25 days) the three reactors were fed directly with RM (180 mL/d). The Organic Loading Rate (OLR) at this stage for the three reactors were 1.1 kg $VS{\cdot}m^{-3}{\cdot}d^{-1}$. The first reactor was fed only with RM during the whole experiment, therefore, the OLR of this reactor was kept constant at 1.1 kg $VS{\cdot}m^{-3}{\cdot}d^{-1}$. This reactor was used as control to compare the mono-digestion process with the co-digestion process (reactors two and three). The daily feed of RM was also kept constant into reactors two and three during the whole experiment, however, from the second HRT to the end of the experiment, RS (reactor 2) and BS (reactor 3) were added in the feeding mixture. Thus, the OLR was increased regularly by adding higher amounts of RS or BS. From the second to the forth HRT (from day 26 to day 100) the co-digestion reactors worked with an OLR of 2.0 kg $VS{\cdot}m^{-3}{\cdot}d^{-1}$. After that, the OLR was increased to 2.6 kg $VS{\cdot}m^{-3}{\cdot}d^{-1}$ for another two HRT (day100 to the day 150). Finally, the experiment finished with an OLR of 3.6 kg $VS{\cdot}m^{-3}{\cdot}d^{-1}$.

4.1.3. Results and Discussion

4.1.3.1.Biogas potential & Kinetic parameters results

Table 4.2. and Figure 4.5 show the biogas potential assay of all analyzed samples. The cumulative amount of biogas produced ranged from 326 to 866 NLbiogas Kg^{-1} VS. The samples with the highest biogas production corresponded, in decreasing order, to the alkali pretreated, microwave pretreated, raw straw, thermal pretreated and briquetted straw. The amount of biogas produced by raw straw, briquetted straw and thermal pre-treated straw was very similar among them (differences not statistically significant). Alkali and microwave pretreatments showed a clear improvement in biogas production from raw straw as their cumulative biogas productions were 866 and 652 NLbiogas Kg^{-1} VS respectively, which show an increase of 155% and 92% when comparing to what was achieved from raw straw. These results support other studies carried out by Akhtar et al, Cheng and Zhong, and Li et al. (Akhtar et al., 2017; Cheng and Zhong, 2014; X.

Li et al., 2009) about decreasing lignin content, increasing cellulose and glucose content and improving AD efficiency after applying microwave-alkali and alkali pretreatment. Mancini et al. (Mancini et al., 2018) also studied the Increased biogas production from wheat straw by applying chemical pretreatments and their result show that Alkali pretreatment is the most effective one by increasing the methane production up to 15% which support the result obtained in this thesis.

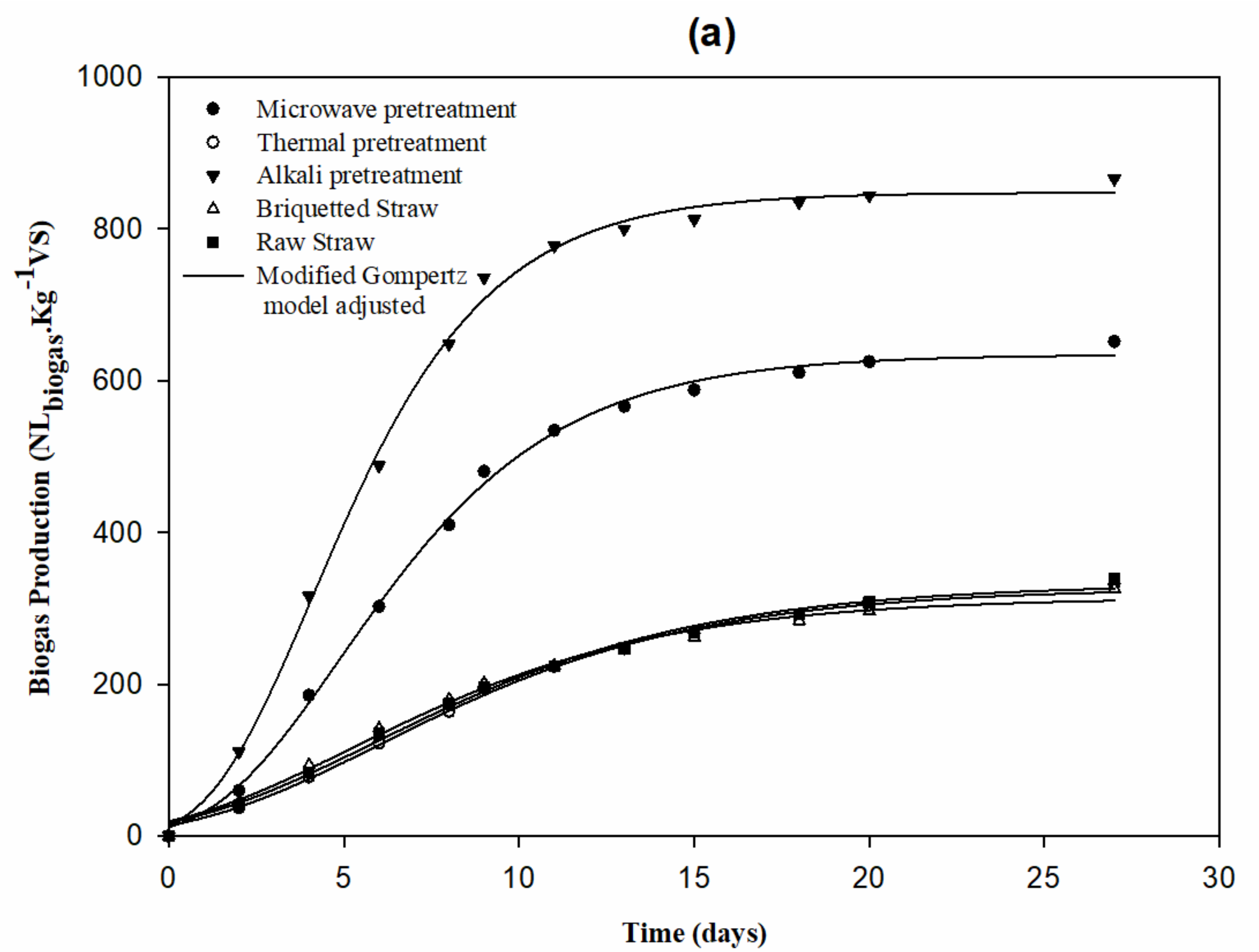


Figure 4. 5 Cumulative biogas production of Straw samples (raw and pretreated) in batch test

The anaerobic biodegradation kinetic parameters of the analyzed samples are also shown in Table 4.2. and Figure 4.6. The decay model used allows the determination of three organic carbon fractions: C_R (rapid degradable carbon), C_S (slowly degradable carbon) and C_I (non-degradable carbon). The applied kinetic model identifies that organic matter only follows one biodegradation kinetic, meaning that all organic fractions behave the same and all the biodegradable carbon is slowly biodegradable carbon, considering that K_S is lower than 0.15 d^{-1} with the exception of Alkali pretreatment which has rapidly biodegradable carbon with K_R of 0.16 d^{-1}. According to the model, straw pretreated with alkali presented the highest biodegradable organic matter percentages (95.28%), which means a successful digestion of lignin into simpler degradable compounds. After the alkali pretreated straw, the order obtained for the straw according to carbon removal was: microwave (79.16%), thermal (39.50%), raw straw (39.27%) and briquetted straw (35.28%). Mancini et al. (Mancini et al., 2018) also studied the kinetic parameter of the pretreated straw and in their result Alkali pretreatment showed the best improvement in kinetic parameters by increasing the maximum biogas production rate up to 118%. Their results support the results obtained in this thesis.

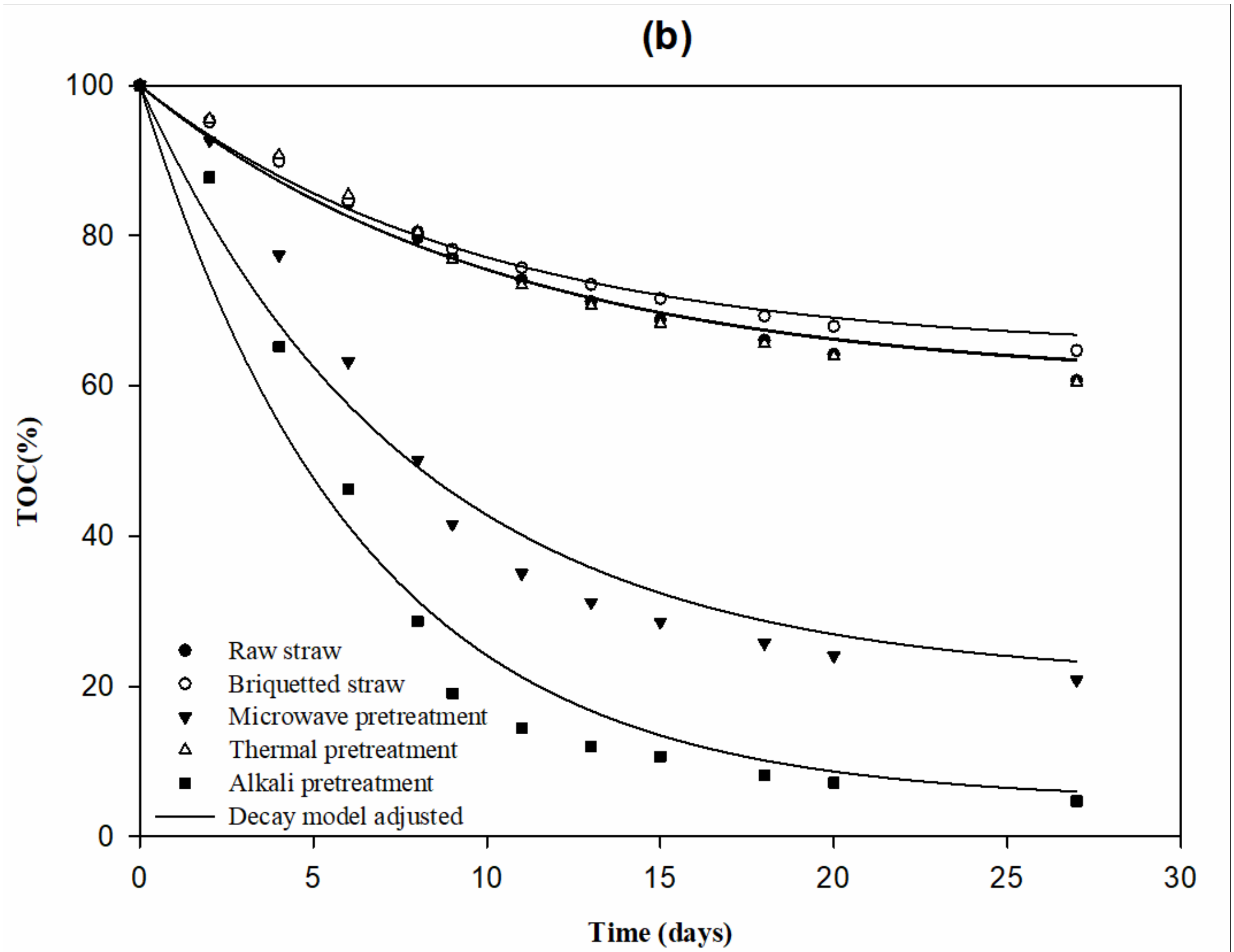


Figure 4. 6 Total organic carbon reduction of Straw samples (raw and pretreated) during biodegradation.

Table 4. 2 Biogas production and Kinetic parameters of the samples

	Biogas potential test (NL_{biogas} Kg^{-1} VS)	% Difference from Raw Straw	Gompertz model	Biodegradation Kinetic modeling					
			Maximum biogas production (P) (NL_{biogas} Kg^{-1} VS)	R_{MAX} (NL_{biogas} Kg^{-1} VS d^{-1})	$\%C_R$	$\%C_S$	$\%C_I$	K_R (d^{-1})	K_S (d^{-1})
Raw Straw*	339 ± 18	0	332.9 ± 8.5	22.6	0.00	39.2	60.7	0.00	0.10
Briquetted Straw*	326 ± 16	- 4%	310.8 ± 13.2	22.7	0.00	35.2	64.7	0.00	0.10
Microwave pretreated straw	652 ± 33	+ 92%	634.5 ± 7.0	66.2	0.00	79.0	20.8	0.00	0.13
Thermal pretreated straw*	332 ± 11	- 2%	327.2 ± 6.9	23	0.00	39.4	60.5	0.00	0.10
Alkali pretreated straw	866 ± 20	+ 156%	847.8 ± 8.3	108	95.2	0.0	4.7	0.16	0.00

*Raw straw, briquetted straw, thermal pre-treated straw and cattle manure biogas production are not statistically different (P>0.05)

4.1.3.2.Biogas production of raw & briquetted straw in semi-continuous reactors

Table 4.3 shows the performance of the semi-continuous reactors with the working conditions of each reactor and the feeding and effluent physio-chemical characteristics. Figures 4.7 and 4.8 represent the biogas production of the bioreactors during the whole experiment at different OLR for co-digestion of cattle manure and raw straw and cattle manure and briquetted straw respectively. The biogas production per amount of VS in reactor one (mono-digestion of RM) was constant around d 0.23 m^3_{biogas} kg^{-1} VS and the biogas production of reactors two and three (co-digestion of RM and RS/BS) showed an increase in biogas production ranging from 0.25 to 0.35 m^3_{biogas} kg^{-1} VS depending on the ratio of RM:RS/BS, the higher the straw ratio the higher the biogas production.

The volume of RM was maintained constant in the three reactors (180 mL/day) during the whole experiment, thus the increase in OLR for the co-digestion reactors was the result of increasing the RS and BS content in the feeding. After the start-up of the reactors (first retention time), from days 26 to 75, biogas production in co-digestion reactors two and three, working at an OLR=2.0 kg $VS \cdot m^{-3} \cdot d^{-1}$, was 0.40 $L_{biogas}/L_{reactor} \cdot d$ (0.3 m^3_{biogas} Kg^{-1} VS). On the contrary, the mono-digestion process in reactor 1 (RM), working at an OLR=1.1 kg $VS \cdot m^{-3} \cdot d^{-1}$ produced only 0.12 $L_{biogas}/L_{reactor} \cdot d$ (0.24 m^3_{biogas} Kg^{-1} VS). As the operational conditions in reactor one did not change during the whole experiment the biogas production remained constant until the end of the test. During the fourth and five retention time, the OLR was increased from 2.0 to 2.6 in reactors two ant three, and the specific biogas production (volume of biogas per volume of reactor per day) of both systems increased to 0.67 $L_{biogas}/L_{reactor} \cdot d$ (0.32 m^3_{biogas} Kg^{-1} VS). In the last and final retention time of the experiment, when the OLR was increased to 3.6, the specific biogas productions increased to 1.11 $L_{biogas}/L_{reactor} \cdot d$ (0.35 m^3_{biogas} Kg $^{-1}$VS) and 1.10 $L_{biogas}/L_{reactor} \cdot d$ (0.34 m^3_{biogas} Kg^{-1}VS) respectively. At this OLR, and due to the high amount of straw fed into the reactor operational problems such as pipe clogging and agitation failures occurred mainly in reactor two working with RS, thus the experiment was stopped. This can be explained by analyzing the VS removal percentages in the effluents of RM + RS and RM + BS which were 80.0% and 46.3%, respectively (Table 4.3). VS removal correspond on one hand to the VS converted to biogas, and on the other hand, to the VS accumulation inside the reactors. With similar biogas production, the difference in VS removal is explained due to higher VS accumulation inside the co-digestion RM + RS reactor. This VS accumulation can be explained because of the low density of RS favours its accumulation inside the reactor, causing operational and maintenance problems such as foaming, pipe clogging, pumps and agitation malfunction or reduction of reactors useful volume. The same behaviour was not observed in the RM + BS reactor. When BS is disgregated inside the reactor, it forms a more homogeneous mixture, leading to a more homogeneous digestate extraction preventing the solid accumulation and preventing operational problems with agitators and digestate extraction systems. Same operational improvements may be expected at full scale when digesting BS instead of RS reducing its associated maintenance costs.

The increase in specific biogas production per volume of reactor is mainly due to the increase in the OLR, most of the cattle slurries have a TS concentration ranging from 2 to 5%, hence, if the slurry is mono-digested the OLR inside the digester is kept below its optimum value meaning that the AD reactor is underused and part of its energy potential recovery is lost. By adding a lignocellulosic co-substrate such as RS or BS, the OLR can be increased (maintaining the HRT and the reactor size), thus, maximizing the use of the reactor capacity making the whole system more profitable for farmers.

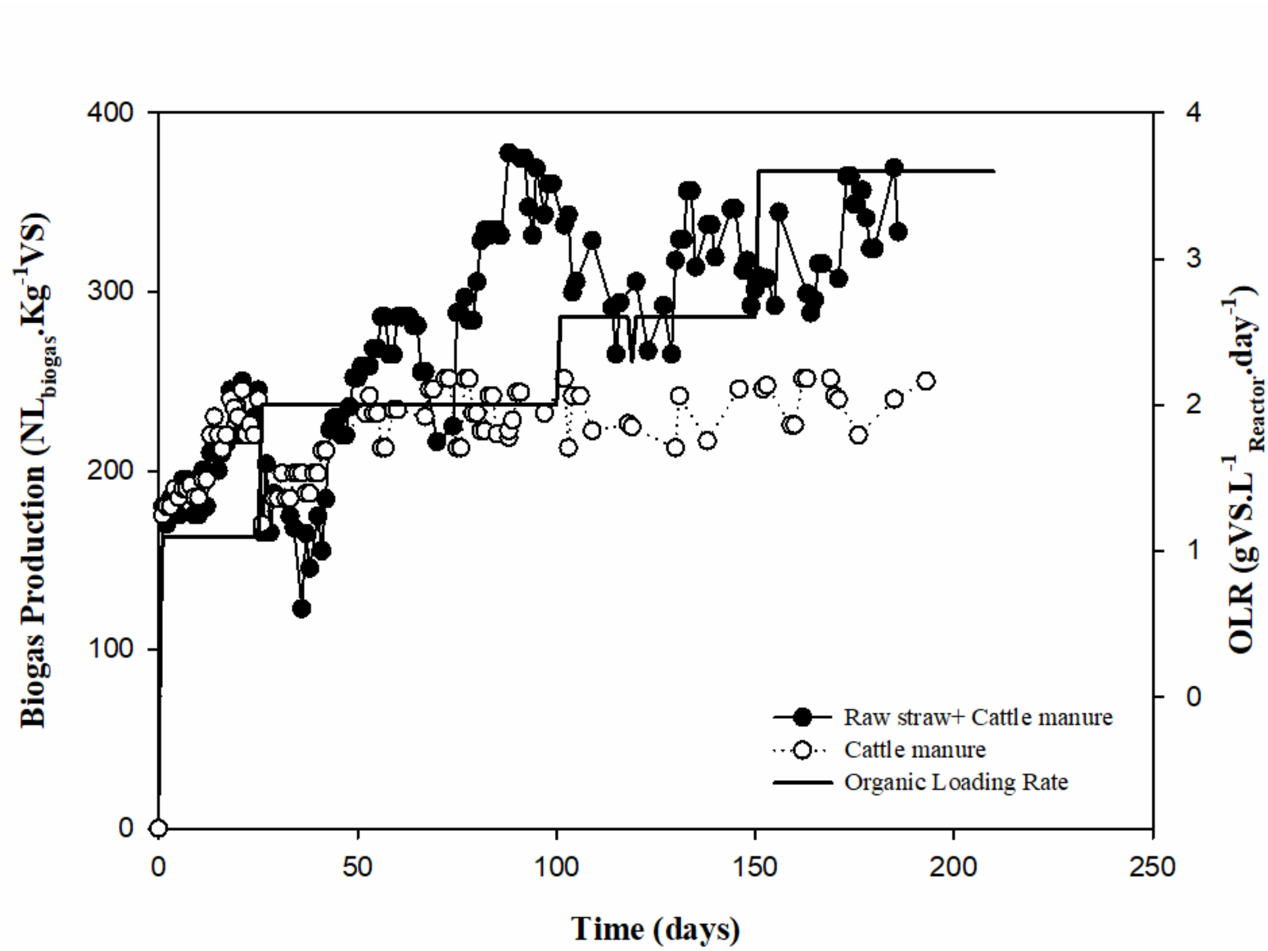


Figure 4. 7 Cumulative Biogas production of Raw Straw in semi-continuous reactors

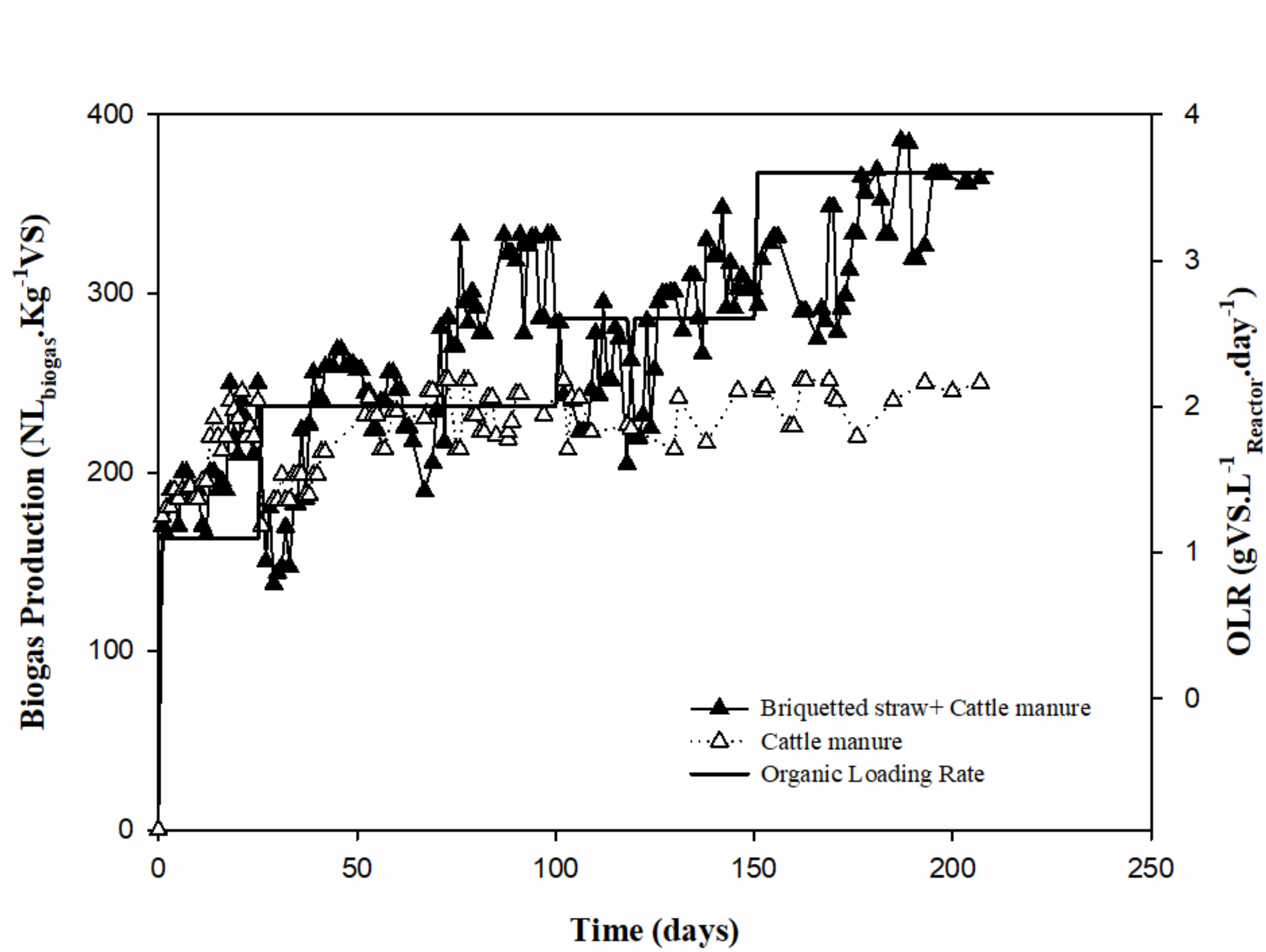


Figure 4. 8 Cumulative Biogas production of Briquetted Straw in semi-continuous reactors

Table 4. 3 Performance of semi-continuous reactors in each OLR and Characterization of the effluents in the last retention time

	RM			RM + RS			RM + BS		
	Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3
AD working conditions									
HRT (d)	25	25	25	25	25	25	25	25	25
OLR (kg $VS/m^3_{reactor}$ d)	1.1	1.1	1.1	2.0	2.6	3.6	2.0	2.6	3.6
Temperature (ºC)	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2
Feeding material									
Manure (mL/d)	180	180	180	180	180	180	180	180	180
Straw (g/d)	0	0	0	5.0	8.0	13.5	5.5	8.5	14.0
TS (%)	3.0 ± 0.1	3.0 ± 0.1	3.0 ± 0.1	6.3 ± 0.3	7.7 ± 0.3	10.0 ± 0.3	6.5 ± 0.4	7.8 ± 0.4	9.7 ± 0.4
VS (% dry matter)	69.0 ± 0.1	69.0 ± 0.1	69.0 ± 0.1	78.6 ± 0.3	81.5 ± 0.3	84.7 ± 0.3	77.1 ± 0.4	79.3 ± 0.4	81.3 ± 0.4
TKN (g/L)	2.3 ± 0.1	2.3 ± 0.1	2.3 ± 0.1	0.30 ± 0.03	0.30 ± 0.02	0.30 ± 0.03	0.30 ± 0.02	0.30 ± 0.01	0.30 ± 0.02
pH	7.9 ± 0.3	8.2 ± 0.2	8.1 ± 0.3	7.8 ± 0.4	8.3 ± 0.1	7.8 ± 0.2	8.0 ± 0.5	8.2 ± 0.2	7.9 ± 0.4
Outlet from AD									
TS (%)	na	na	2.3 ± 0.2	na	na	3.2 ± 0.3	na	na	5.9 ± 0.2
VS (% dry matter)	na	na	60.2 ± 0.2	na	na	67.2 ± 0.3	na	na	71.8 ± 0.2
TKN (g/L)	na	na	2.3	na	na	2.4	na	na	2.4
Total ammonia (g/L)	na	na	1.2	na	na	0.9	na	na	0.9
pH	7.7 ± 0.5	7.8 ± 0.3	8.2 ± 0.4	8.0 ± 0.2	7.8 ± 0.4	8.2 ± 0.2	7.9 ± 0.5	7.9 ± 0.4	7.8 ± 0.3
VS removal (% dry matter)	na	na	33.1	na	na	80.0	na	na	46.3
Biogas									
Biogas production rate (L_{biogas}/d)	0.54 ± 0.04	0.54 ± 0.04	0.54 ± 0.05	1.8 ± 0.3	3.0 ± 0.1	5.0 ± 0.4	1.8 ± 0.3	2.8 ± 0.2	4.9 ± 0.4
Biogas yield (L_{bigoas}/kg VS_{added})	235 ± 15	230 ± 15	240 ± 15	300 ± 15	320 ± 20	345 ± 20	300 ± 12	320 ± 25	340 ± 30
Specific biogas prodution ($L_{bigoas}/L_{reactor}$ d)	0.12 ± 0.01	0.12 ± 0.01	0.12 ± 0.01	0.40 ± 0.06	0.67 ± 0.02	1.11 ± 0.08	0.39 ± 0.06	0.67 ± 0.04	1.10 ± 0.08
% CH_4	61 ± 2	62 ± 1	61 ± 3	62 ± 2	59 ± 5	61 ± 4	60 ± 3	62 ± 2	61 ± 4

na*: not analyzed

4.2. Cheese whey as co-substrate in anaerobic digestion of livestock waste

4.2.1. Introduction

The dairy industry plays an economically important part in the agricultural sector in most industrialized and many developing countries. Dairying improves food security and represents a source of employment and income to millions of smallholder families (Escalante et al., 2018) and More than 80% of the produced milk in developing countries comes from small producers (production of milk under 500 L/d) (Anthony Bennett, Frederic Lhoste, Jay Crook, 2005). This dairy chain generates residual liquid fraction well-known as Cheese whey(CW), which represents in volume approximately 90% of the milk employed and is considered either a resource of interest or a concentrated wastewater requiring treatment, depending on the different points of view (Dereli et al., 2019; Escalante et al., 2018). Cheese whey characterization depends on the milk quality used (goat, cow, sheep and buffalo), which may vary depending on animal breed, feed, health and lactation stage (de Wit, 2001). CW has an elevated organic load that varies in the range of 45– 65 g/kg for volatile solids (VS) and 68–94 g/L for chemical oxygen demand (COD) (Dareioti and Kornaros, 2015; Gelegenis et al., 2007; Jasko et al., 2011; Riggio et al., 2015; Saddoud et al., 2007). CW disposal is still regarded as a challenging issue for environmental protection as it can cause an excess of oxygen consumption, impermeabilization, eutrophication, toxicity, etc. in the receiving environments. The volume of effluents produced in the cheese manufacturing industry has increased with the increase in cheese production (Prazeres et al., 2012; Zhou et al., 2019). Currently, the global production of cheese whey is estimated to be approximately $1.8–1.9×10^8$ tons per year (Baldasso et al., 2011). The polluting power of whey has led countries such as United States, Canada, Australia, New Zealand, and the European Union, to introduce strict environment protection legislation. Such a legislative framework - against improper disposal of whey and in favor of its recycling-encouraged the dairy industry to explore other approaches and opportunities for the management of dairy effluents (Smithers, 2008). Anaerobic digestion is a well-known process to treat CW residues. Considering the highly biodegradable nutrients of CW, it absorbs many attractions for small and medium dairy enterprises to implement AD plant instead of other costly treatment processes. It is reported in many studies that AD of whey as sole substrate can harm the system due to low alkalinity content and the rapid acidification of cheese whey that can exhaust the buffering capacity, leading to a drop in pH, volatile fatty acids (VFA) accumulation and subsequent reactor failure (Ergu et al., 2001; Janczukowicz et al., 2008). To address this problem many studies have used the co-digestion of cheese whey with different feedstock mainly animal manures to enhance the C/N ratio, increase alkalinity and buffering capacity of system, improve efficiency and investigate synergistic effects of system (Comino et al., 2012; Escalante et al., 2018; Maragkaki et al., 2017; Rico et al., 2015; Vivekanand et al., 2018; Zhou et al., 2019). For example, Saddoud et al. (Saddoud et al., 2007) digested CW in a membrane reactor, reaching a methane yield of 0.3 m^3 CH4.kg^{-1} COD and varying organic load rate (OLR) from 3 to 19.78 kg COD.m^{-3}.d^{-1}. Comino et al. (Comino et al., 2012) used a stirred reactor to digest CW mixed with cattle slurry for an OLR of 2.65 kg VS.m^{-3}.d^{-1}, obtaining a methane yield of 0.34 m^3 CH4.kg^{-1} VS.. According to Escalante (Escalante-Hernández, Jaimes-Estévez et al., 2017) the application of AD to treat CW depends on the a) physicochemical composition of CW (organic matter, reduced alkalinity, and rapid acidification tendency), b) inoculum source (high buffer capacity), and c) reactor configuration.

To the best of our knowledge although many aspects of AD of cheese whey has already been studied, techno-economic studies of its full-scale implementation are very scarce, especially in small to medium farms. Thus, the aims of this study are: (i) determine the best co-digestion ratios of CW and manure to ensure biogas production and the stability of the process and (ii) to carry out a techno-economic viability assessment of anaerobic co-digestion in small to medium size farms.

4.2.2. Material and Methods

The procedures and analysis for AD of straw as co-substrate have been carried out as follow:

4.2.2.1.Inoculum and substrates

Inoculum to carry out the AD laboratory tests (batch and semi-continuous tests) was collected from a Mechanical-Biological Treatment Plant located in Barcelona (Spain) treating Organic Fraction of Municipal Solid Waste. Cattle, sheep and goat manure were collected from farms located in Girona (Spain). Due to high solid content of Goat and Sheep manure, they were blended to make them in powder and later, the TS concentration was adjusted to 4% to carry out the semi-continuous tests. Cattle, sheep and goat cheese whey were obtained from local dairy factories located in Girona (Spain). All manures and cheese whey were kept in fridge until their analysis. The physicochemical characteristics of the inoculum, raw manures (RM) and the different cheese whey used in this study are summarized in Table 4.4.

Table 4. 4 Characterization of the substrates and inoculum

Substrate	TS (%)	VS (%TS)	TKN (g/L)	COD (g/L)	pH
Inoculum	2.3 ± 0.1	48.8 ± 0.3	n.a*.	16.45 ± 2.5	8.7 ± 0.1
Cow manure	4.0± 0.4	72.0 ± 0.5	2.3 ± 0.3	55.8 ± 0.7	8.2 ± 0.2
Goat manure	55.5 ± 0.4	89.4 ± 0.4	1.2 ± 0.1	31.0 ± 0.1**	8.1 ± 0.2
Sheep manure	40.0 ± 2.0	72.7 ± 3.0	3.7 ± 1.5	21.7 ± 0.1**	7.7 ± 0.2
Cow cheese whey	6.9 ± 0.1	92.0 ± 0.1	na*	90.6 ± 1.5	4.2 ± 0.2
Goat cheese whey	7.6 ± 0.4	93.0 ± 0.5	na*	108.5 ± 2.9	4.3 ± 0.2
Sheep cheese whey	8.3 ± 0.7	94.0 ± 0.5	na*	117.0± 8.3	4.5 ± 0.2

***** na: not analyzed

****** COD (g/L) of manure solutions with 4% TS for goat and sheep manure

4.2.2.2.Initial set up for Biogas potential test of CW (GBn):

Anaerobic biodegradability of different animal manure and different cheese whey were investigated in this study. The experiment was carried on based on the procedure described in section 3.6; in case of animal manures, 53ml of cattle manure, 7g of sheep manure and 3g of goat manure were mixed with 547ml, 500ml and 590ml of inoculum respectively in 1L aluminum bottles to achieve inoculum/COD substrate of 2/1. In contrary for the cheese whey, 55ml of cow cheese whey, 47ml of sheep cheese whey and 45ml of goat cheese whey were mixed with 530ml, 553ml and 555ml of inoculum respectively in order to achieve COD inoculum/ COD substrate of 2/1. The bottles were purged with nitrogen and sealed quickly in order to remove the oxygen. 600ml of only inoculum was set as the blank sample and 1.2g of Glucose in 600ml of inoculum was considered as the control sample. The bottles pressures were measured daily until there was no special biogas production

4.2.2.3. Initial set up for Biogas production of animal manure and cheese whey in semi-continuous reactors:

To obtain relevant data to perform the techno-economic assessment of co-digestion processes, anaerobic co-digestion of each RM mixed with its corresponding CW was performed. The biogas production from the semi-continuous tests have been used as base scenario for the techno-economic study (chapter 5). The tests were performed in semi-continuous reactors (3 L) with an effective working volume of 2.5 L for a period of 5 months. Three reactors were set up, one for co-digestion of goat manure and goat cheese whey (R_1), one for the co-digestion of Cow manure and cow cheese whey (R_2), and one for co-digestion of sheep manure and sheep cheese whey (R_3). The operational conditions were as follow: HRT of 28 days, mesophilic conditions (37 ± 0.2 ºC, temperature was controlled by a thermostatically regulated water bath) and mechanical stirring (1 minute of stirring at 50 rpm every 30 minutes). Biogas produced was measured by means of a gasometer (Ritter MGC-1 V3.4 PMMA). The reactors were fed and unloaded automatically in daily basis. Due to high solid content of Goat and Sheep manure and also to keep the system operating under wet condition, Sheep and Goat manure were diluted to achieve a solution of 4% of total solid.

Surveys carried out at different cheese makers reported CW productions ranging from 10 to 30% of liquid manure produced at farm, therefore, ratios ranging from 10 to 30% RM:CW (v:v) where tested. The experiment was carried out in 4 different stages, in the first stage each reactor was fed with only manure as the sole substrate for one HRT. In the second stage (one HRT), the reactors were fed with 90% or RM and 10% CW (v:v), in the third stage (one HRT) the reactors were fed with 80 % RM and 20 % CW (v:v) and the last stage (2 HRT) corresponded to a mixing ratio of 70 % RM and 30 % CW (v:v). During this study the mixing ratio (RM:CW) was established as fixed parameter, thus, different OLR are observed between reactors due to different initial COD of manures and CW. In R1 the OLR increased from 1.11 Kg COD.$m^{-3}d^{-1}$ during the first stage (only manure) to a maximum of 1.95 Kg COD.$m^{-3}d^{-1}$ in stage number 4. In R2 the OLR increased from 2.00 Kg COD.$m^{-3}d^{-1}$ during the first stage (only manure) to a maximum of 2.38 Kg COD.$m^{-3}d^{-1}$ in stage number 4. Lastly, in R3 the OLR increased from 0.78 Kg COD.$m^{-3}d^{-1}$ during the first stage (only manure) to a maximum of 1.81 Kg COD.m^{-3}d in stage number 4.

4.2.3. Results and discussion

4.2.3.1.Biogas potential test results

Anaerobic biodegradability of different livestock manure (Cow, Goat and Sheep) and their cheese whey (Cow, Goat and Sheep) were investigated in this study. The data obtained in this experiment, were fitted to the modified Gompertz model provided by Ponsá (Ponsá, 2010). Table 4.5. and

Figure 4.9 show the biogas potential assay of all analyzed samples. The cumulative amount of biogas produced for manures ranged from 140 to 240 NL_{biogas} Kg^{-1} COD. The samples with the highest biogas production corresponded, in decreasing order, to the Goat manure, Sheep manure and Cow manure. In case of different cheese whey, the cumulative amount of biogas produced ranged from 530 to 622 NL_{biogas} Kg^{-1} COD which belong in decreasing order to Cow cheese whey, Sheep cheese whey and Goat cheese whey respectively. All types of cheese whey showed to be highly digestible in anaerobic digestion process and their biogas production were substantially higher than their corresponding manure.

From the maximum biogas production rate of model (R_{max}) it can be also concluded that almost 90% of the total biogas production for all samples was achieved during the first 9-12 days of the experiment. This data can be useful for upscaling the system.

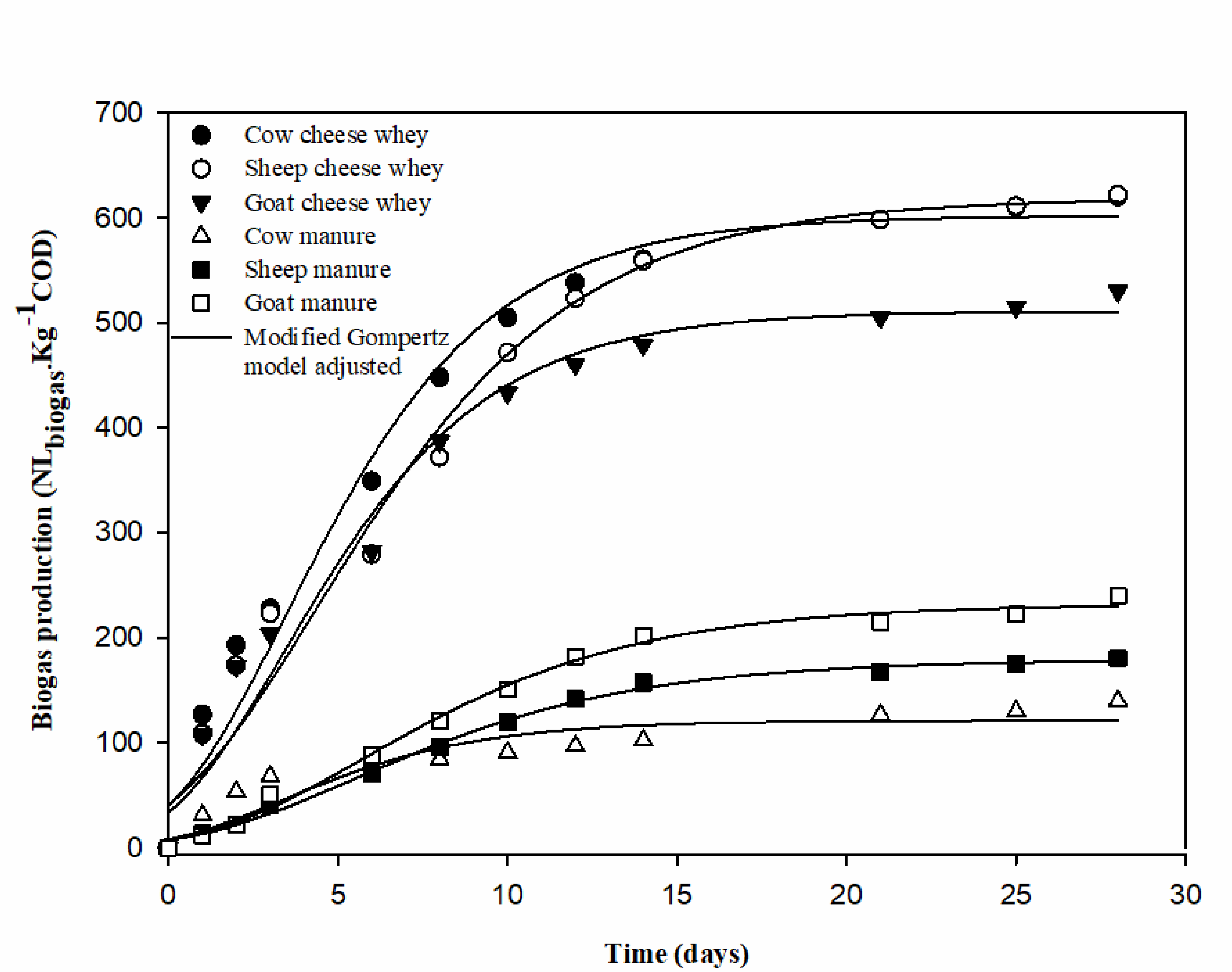


Figure 4. 9 Cumulative biogas production of different animal manure and cheese whey in batch test

Table 4. 5 Biogas production of the different manures and cheese whey

	Biogas potential test	Gompertz model	
	(NL_{biogas} Kg^{-1} COD)	Maximum biogas production (P) (NL_{biogas} Kg^{-1} COD)	R_{max} ($NL_{biogas}.Kg^{-1}COD.d^{-1}$)
Cow manure	140 ± 10	121 ± 10	13.5
Sheep manure	180 ± 20	179 ± 3	14
Goat manure	240 ± 20	232 ± 5	18.3
Cow Cheese whey	620 ± 10	602 ± 19	64
Sheep Cheese whey	622 ± 15	619 ± 24	52.3
Goat Cheese whey	530 ± 10	511± 18	54.8

4.2.3.2.Biogas production of different cheese whey and manure in semi-continuous reactors:

Table 4.6 shows the performance of the semi-continuous reactors with the working conditions of each reactor and the feeding and outlet characteristics. Figures 4.10-4.12. represent the biogas production of the bioreactors during the whole experiment at different stage of the experiment. It should be noticed that the fourth stage of the experiment was performed for two hydraulic retention time in order to achieve more reliable results at maximum mixing ratio. The volume of manure was decreased in each stage of experiment while the volume of cheese whey increased. Thus the raise in the biogas production was a result of increasing cheese whey.

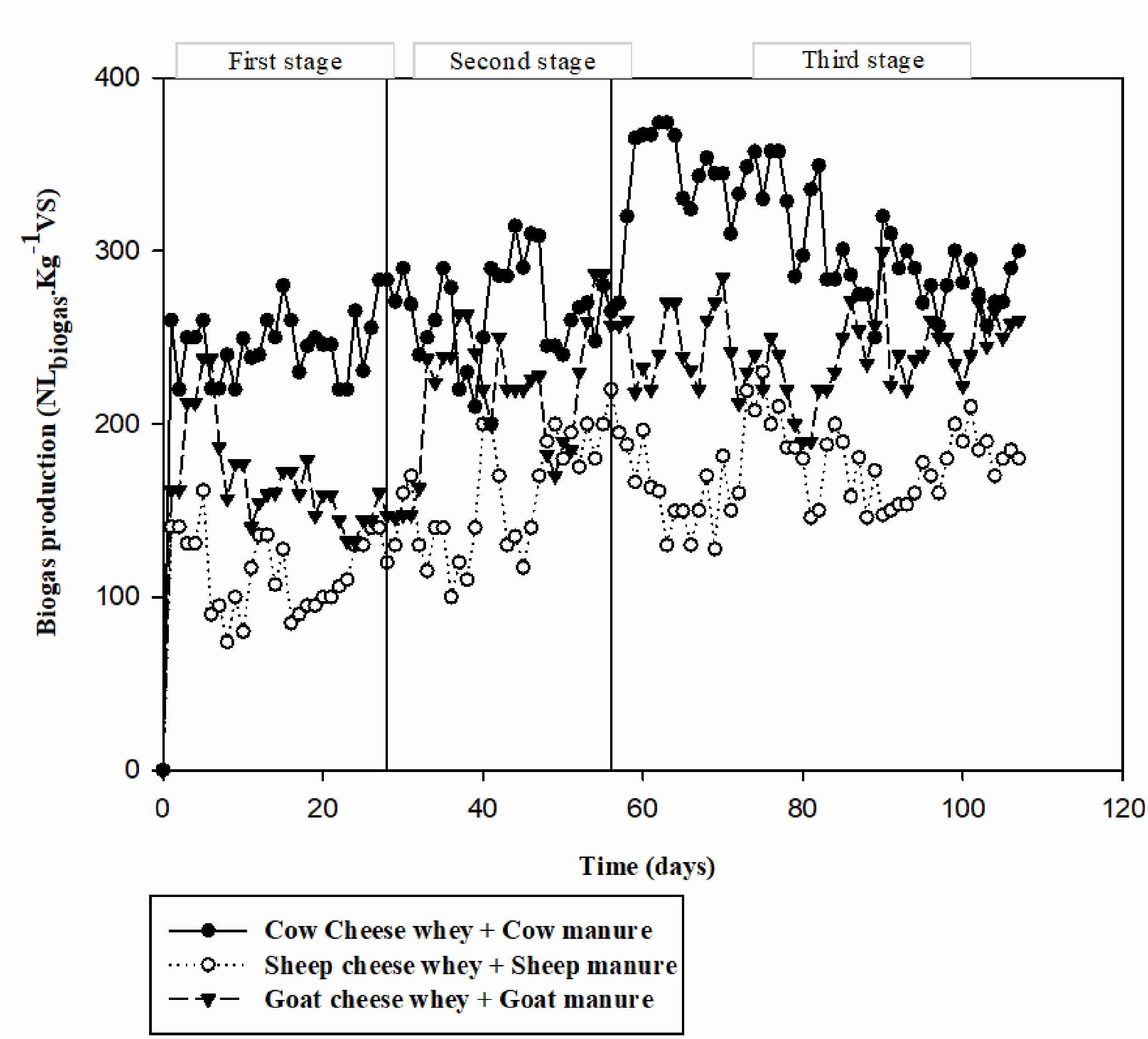


Figure 4. 10 Cumulative Biogas production of cheese whey and manure (Goat, Cow & Sheep) in semi-continuous reactors

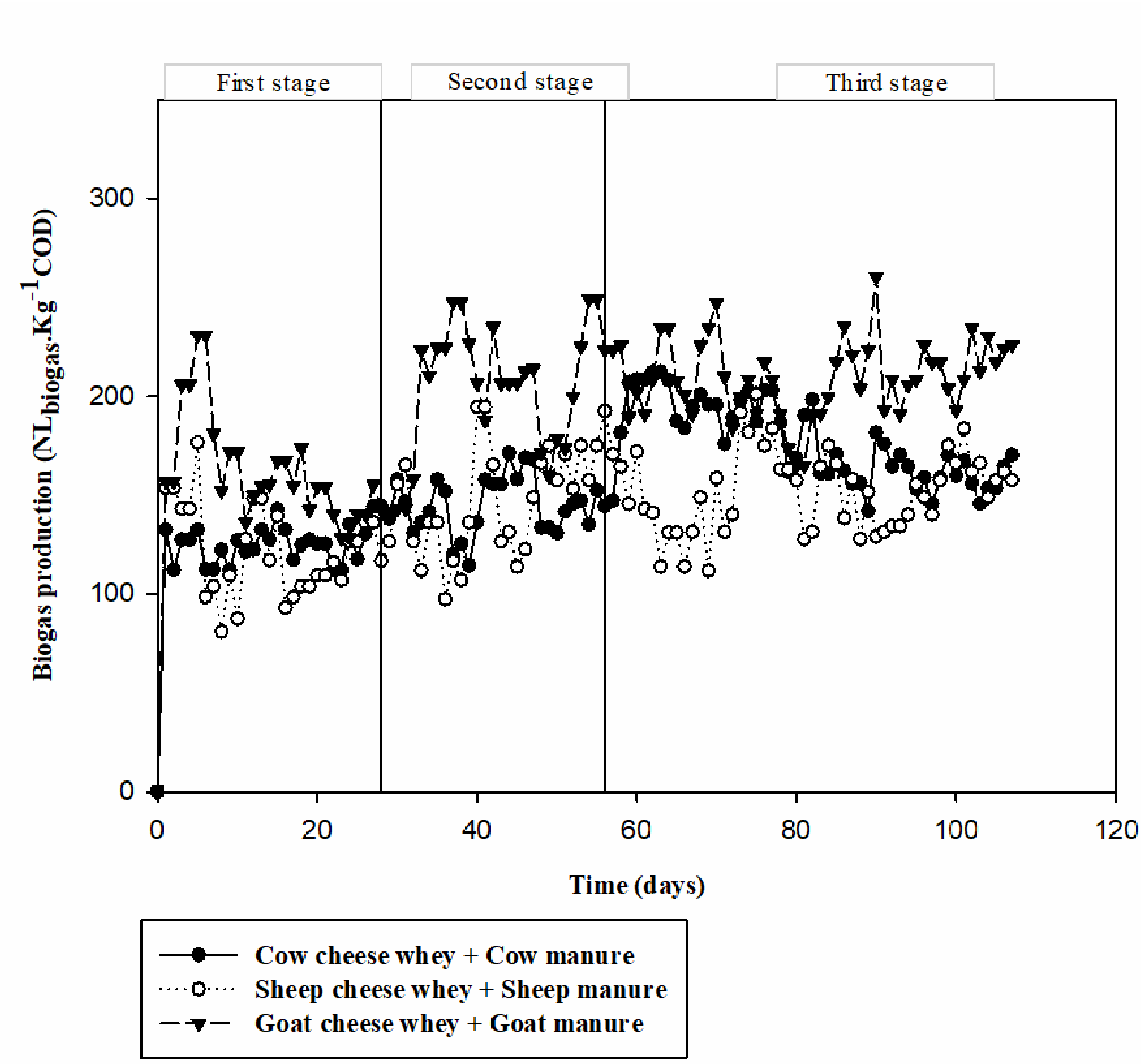


Figure 4. 11 Cumulative Biogas production (NL. Kg-1COD) of cheese whey and manure (Goat, Cow & Sheep) in semi-continuous reactors

During the first stage of the experiment in which the reactors were fed only with RM, the specific biogas production for R_1, R_2 and R_3 was 0.15 $L_{biogas}/L_{reactor}.d$ (142 $L_{biogas}.Kg^{-1}$ COD), 0.19 $L_{biogas}/L_{reactor}.d$ (96 $L_{biogas}.Kg^{-1}$ COD) and 0.08 $L_{biogas}/L_{reactor}.d$ (103 $L_{biogas}.Kg^{-1}$ COD) respectively. In the second stage (mixing ratio 90:10 RM:CW), the specific biogas production of R_1, R_2 and R_3 was 0.25 $L_{biogas}/L_{reactor}\cdot d$ (160 $L_{biogas}\cdot Kg^{-1}$ COD), 0.30 $L_{biogas}/L_{reactor}\cdot d$ (125 $L_{biogas}\cdot Kg^{-1}$ COD) and 0.15 $L_{biogas}/L_{reactor}\cdot d$ (121 $L_{biogas}\cdot Kg^{-1}$ COD), respectively. During the third stage (mixing ratio 80:20 RM:CW) the specific biogas production increased to 0.39 $L_{biogas}/L_{reactor}\cdot d$ (208 $L_{biogas}\cdot Kg^{-1}$ COD), 0.36 $L_{biogas}/L_{reactor}\cdot d$

(145 $L_{biogas}\cdot Kg^{-1}$ COD) and 0.22 $L_{biogas}/L_{reactor}\cdot d$ (134 $L_{biogas}\cdot Kg^{-1}$ COD) respectively showing an increase up to 56%, 20% and 46% of specific biogas compared to the second stage of experiment. In the final stage of the experiment (mixing ratio 70:30 RM:CW), the specific biogas productions obtained were 0.46 $L_{biogas}/L_{reactor}\cdot d$ (211 $L_{biogas}\cdot Kg^{-1}$ COD), 0.48 $L_{biogas}/L_{reactor}\cdot d$ (178 $L_{biogas}\cdot Kg^{-1}$ COD) and 0.31 $L_{biogas}/L_{reactor}\cdot d$ (154 $L_{biogas}\cdot Kg^{-1}$ COD) for R_1, R_2 and R_3 respectively, which corresponded to an increase in biogas production of 18%, 33% and 40% compared to the third stage.

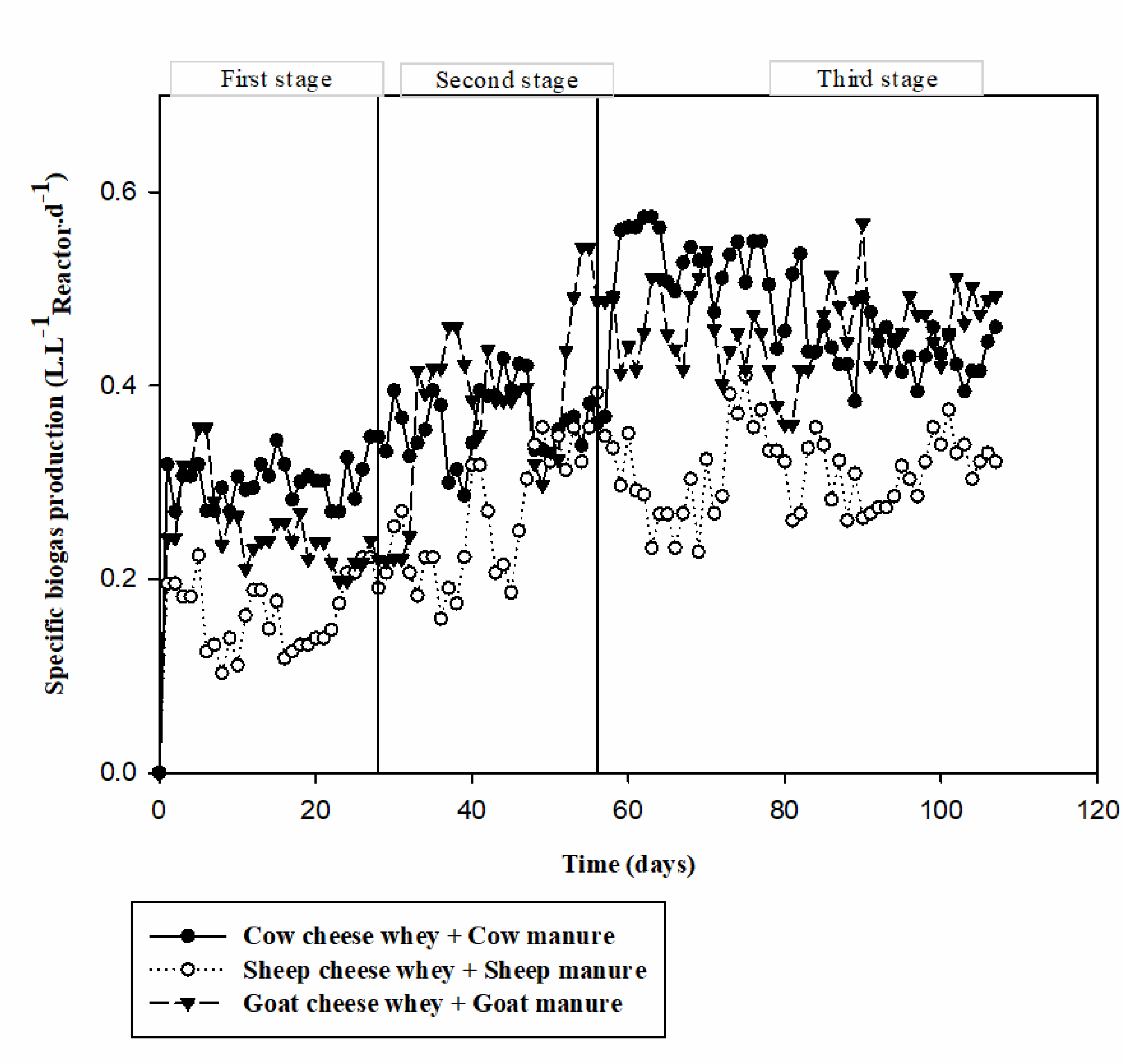


Figure 4. 12 Specific biogas production of cheese whey and manure (Goat, Cow & Sheep) in semi continuous reactors

One of the main issues when working with CW is its acidity, as seen in Table 4.6, the pH of inlet co- digestion feedstock decreased to values ranging from 4.2 to 5.7 compared with RM which has a pH around 8. During the whole experiment the reactor was kept at optimal pH conditions, however the pH decreased progressively when increasing the CW ratio, and in the last mixing ratio 70:30 RM:CW the pH decreased to 7, indicating that the maximum buffer capacity of the system is reached which means that higher ratios of CW are not recommended as they could lead to higher pH drop and finally to reactor failure. It is noteworthy that the results obtained in the semi-continuous reactors are far from the results obtained in the batch experiment. This could be explained by the fact that due to high biodegradability of CW and the low degradability of RM, the anaerobic bacteria was not digesting the whole degradable fraction of RM leading to lower biogas production than expected. A better acclimation of the reactor should be carried out in order to maximize the biogas production in co-digestion systems. The results obtained in this study are supporting the results of other studies which carried out by Kavacik and Tapaloglu, Rico et.al and Comino et.al (Comino et al., 2012; Kavacik and Topaloglu, 2010).

Table 4. 6 Performance of semi-continuous reactors in each stage of experiment and characterization of the effluents in the last retention time

		R_1				**R_2**				**R_3**			
		Stage 1	Stage 2	Stage 3	Stage 4	Stage 1	Stage 2	Stage 3	Stage 4	Stage 1	Stage 2	Stage 3	Stage 4
AD working conditions													
	HRT (d)	28	28	28	28	28	28	28	28	28	28	28	28
	OLR (Kg COD/$m^3_{reactor}$ d)	1.11	1.39	1.67	1.95	2	2.13	2.26	2.38	0.78	1.12	1.47	1.81
	OLR (kg VS/$m^3_{reactor}$ d)	1.28	1.31	1.54	1.67	1.03	1.16	1.28	1.4	1.04	1.22	1.4	1.57
	Temperature (ºC)	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2	37.0 ± 0.2
Feeding material													
	Manure (mL/d)	90	81	72	63	90	81	72	63	90	81	72	63
	Cheese whey (mL/d)	0	9	18	27	0	9	18	27	0	9	18	27
	TS (%)	4.0 ± 0.1	4.4 ± 0.1	4.7 ± 0.1	5.1 ± 0.1	4.0 ± 0.1	4.2 ± 0.3	4.6 ± 0.3	5.1 ± 0.3	4.0 ± 0.1	4.4 ± 0.4	4.8 ± 0.4	5.2 ± 0.4
	VS (% dry matter)	89.4 ± 0.3	84.0 ± 0.1	85.6 ± 0.1	87.0 ± 0.1	0.72 ± 0.5	75.2 ± 0.3	78.2 ± 0.3	80.7 ± 0.3	72.7 ± 0.3	76.7 ± 0.4	79.9 ± 0.4	82.6 ± 0.4
	COD (g/L)	31 ± 0.5	38.7 ± 0.5	46.5 ± 0.5	54.3 ± 0.5	55.8 ± 0.7	59.3 ± 1.5	62.8 ± 1.5	66.2 ± 1.5	21.7 ± 0.5	31.3 ± 1.5	40.8 ± 1.5	50.3 ± 1.6
	Total ammonia (g/L)	0.31 ± 0.05	0.33 ± 0.05	0.33 ± 0.05	0.35 ± 0.05	1.04 ± 0.02	1.02 ± 0.02	1.01 ± 0.02	1.01 ± 0.03	0.37 ± 0.04	0.38 ± 0.08	0.40 ± 0.05	0.43 ± 0.04
	pH	8.2 ± 0.2	5.7 ± 0.2	5.5 ± 0.2	5.6 ± 0.2	8.0 ± 0.2	5.3 ± 0.2	5.5 ± 0.2	5.4 ± 0.2	7.8 ± 0.2	4.2 ± 0.5	4.4 ± 0.4	4.5 ± 0.4
Outlet from AD													
	TS (%)	3.11 ± 0.3	na	na	3.41 ± 0.3	2.73 ± 0.1	na	na	2.53 ± 0.3	3.1 ± 0.1	na	na	2.44 ± 0.3
	VS (% dry matter)	80 ± 0.5	na	na	77.24 ± 0.5	58 ± 0.5	na	na	58.61 ± 0.5	64 ± 0.5	na	na	65.80 ± 0.5
	COD (g/L)	20.15 ± 1.2	23.2 ± 1.5	21.2 ± 1.5	19.0 ± 1.5	33.48 ± 0.7	25.0 ± 2.0	24.1 ± 2.0	23.4 ± 2.0	17.36	22.5 ± 2.0	23.6 ± 2.0	23.7 ± 2.0
	Total ammonia (g/L)	0.33 ± 0.02	0.36 ± 0.03	0.38 ± 0.02	0.40 ± 0.02	1.01 ± 0.05	1.0 ± 0.05	0.98 ± 0.05	1.09 ± 0.05	0.35 ± 0.03	0.37 ± 0.06	0.40 ± 0.06	0.38 ± 0.06
	pH	8.1 ± 0.2	8.0 ± 0.5	7.7 ± 0.3	7.2 ± 0.4	8.2 ± 0.2	8.1 ± 0.2	7.5 ± 0.4	7.0 ± 0.2	7.7 ± 0.3	7.9 ± 0.5	7.5 ± 0.4	7.1 ± 0.3
	VS removal (% dry matter)	30	na	na	40.8	45	na	na	62.1	32	na	na	65.5
	COD removal (%)	35	40	54.6	65	40	53.8	61.5	64.0	20	27.8	42.1	52.7
Biogas*													
	Biogas production rate (L_{biogas}/d)	0.39 ± 0.05	0.63 ± 0.1	0.98 ± 0.1	1.15 ± 0.1	0.48 ± 0.05	0.75 ± 0.07	0.90 ± 0.07	1.20 ± 0.07	0.2 ± 0.02	0.38 ± 0.08	0.55 ± 0.08	0.78 ± 0.08
	Biogas yield (L_{bigoas}/kg VS_{added})	123 ± 15	165 ± 25	222 ± 25	243 ± 25	186 ± 10	247 ± 15	266 ± 15	313 ± 15	77 ± 15	110 ± 20	138 ± 20	175 ± 20
	Biogas yield (L_{bigoas}/kg COD_{added})	142 ± 15	160 ± 20	208 ± 20	211 ± 20	96 ± 15	125 ± 20	145 ± 20	178 ± 20	103 ± 10	121 ± 15	134 ± 15	154 ± 15
	Specific biogas prodution (L_{bigoas}/$L_{reactor}$ d)	0.15 ± 0.04	0.25 ± 0.04	0.39 ± 0.04	0.46 ± 0.04	0.19 ± 0.02	0.3 ± 0.02	0.36 ± 0.03	0.48 ± 0.05	0.08 ± 0.02	0.15 ± 0.03	0.22 ± 0.04	0.31 ± 0.04
	% CH_4	58 ± 1	63 ± 2	60 ± 1	61 ± 3	59 ± 2	63 ± 2	59 ± 5	60 ± 4	59 ± 1	62 ± 3	64 ± 2	61 ± 4

na*: not analyzed

Chapter 5:

Techno-Economic Assessment

5. Techno-Economic assessment:

In order to investigate economic feasibility of implementation of full scale anaerobic digestion plant in a farm, the economical assessment was deeply studied for all the studied feedstock at lab scale. Figure 5.1. shows the schematic structure of the studied plant. Thus, the study is divided to two main case study as follow:

1- Techno-Economic assessment of implementation of AD plant in a farm, treating cattle manure and using straw (raw & briquetted) as co-substrates.

2- Techno-Economic assessment of implementation of AD plant in the dairy farms, treating animal manure and using cheese whey as co-substrate.

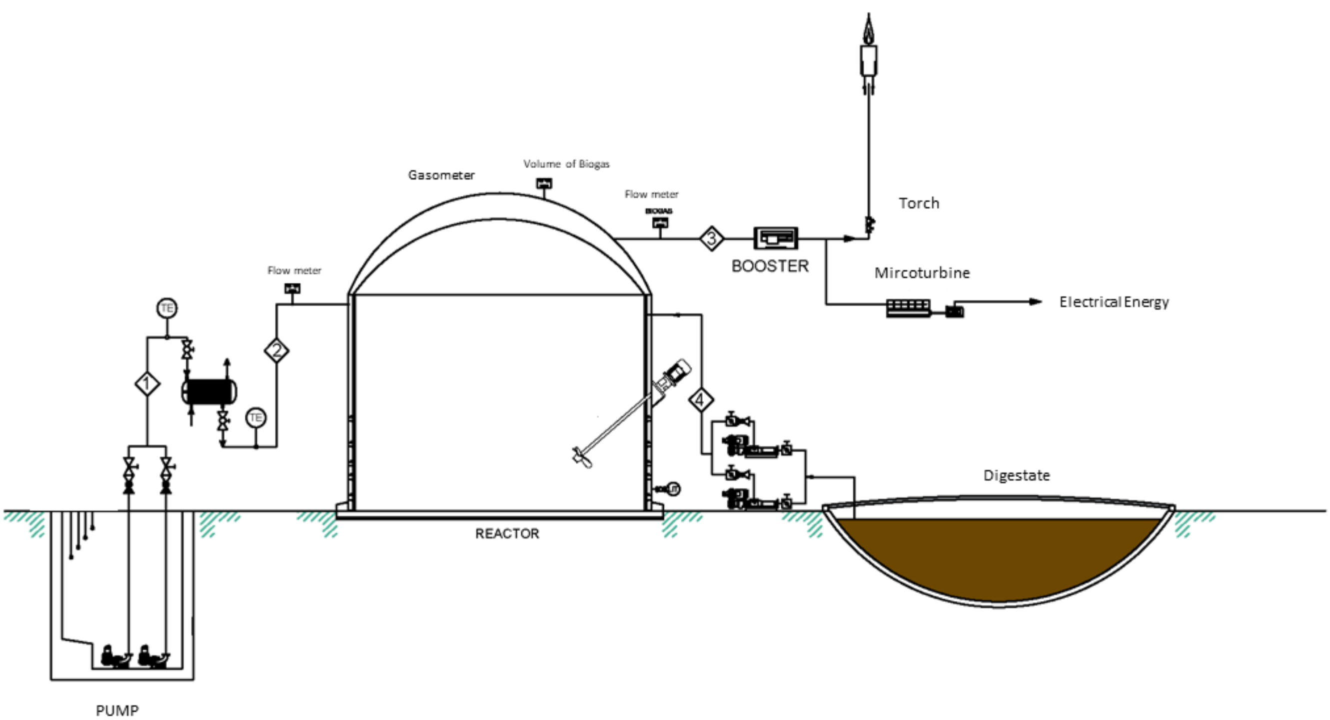


Figure 5. 1 Schematic structure of the AD plant in real scale

5.1. Base scenario

5.1.1. Farm and Anaerobic Digester facility description

An economic assessment for the implementation of an anaerobic mono digestion and co-digestion process (at first case study with RS or BS and in the second case study with cheese whey) at real scale has been carried out using La Fageda dairy farm (Girona, Spain) as the base scenario. La Fageda has 250 heads of dairy cattle. Every year, an amount close to 15,250 m^3 of LCFM are produced containing an amount of 611.4 t/year of total solids (including manure and bedding material). Currently the RM is stored in a tank and after a solid/liquid separation the solid fraction is composted and the liquid fraction is directly applied in surrounding arable land.

Farming stages and specially milk processing stages are energy intensive processes, for example huge energy demand (both calorific and electricity) is expected during milk pasteurization, homogenation and fermentation processes, La Fageda has an average electricity consumption of 283,421 Kwh/month and average heat consumption of 448,523 MJ/month. Thus, a techno-economic assessment to evaluate the potential of partially substitute the current energy consumption based of fossil fuels for green energy coming from anaerobic digestion has been carried out. To this end, an economic assessment has been performed under different mono-digestion and co-digestion conditions. Taking into consideration the results obtained in the lab, the following operational conditions were considered for each case study.

- For the first case study related to use of straw as co-substrate, to treat the amount of RM generated yearly in La Fageda a reactor of 1052 m^3 is needed. Base on the results obtained in the lab tests HRT of 25 days was considered and system operates under wet conditions (TS=4%) and mesophilic temperature (37ºC). When mono-digestion of only RM is used as feedstock, the OLR is 1.1 kg $VS.m^{-3}.d^{-1}$. On the other hand, in co-digestion different amounts of straw to achieve an

- OLR of 1.5, 1.7 and 2 kg $VS.m^{-3}.d^{-1}$ will be needed. It is noteworthy that higher OLR tested at lab scale (2.6 and 3.6 kg $VS·m^{-3}·d^{-1}$) have not been contemplated in this techno-economic assessment in order to keep the total amount of VS in the feed <10% which means that the system is still able to work in wet conditions and same pumps, stirring devices, etc. can be used.
- In the second case study for using cheese whey as co-substrate, to treat the amount of RM generated yearly in La Fageda a reactor of 1174 m^3 is needed. Base on the results obtained in the lab tests HRT of 28 days was considered and system operates under wet conditions (TS=4%) and mesophilic temperature (37ºC). When mono-digestion of only RM is used as feedstock, the OLR is 2.0 kg $COD·m^{-3}·d^{-1}$. On the other hand, in co-digestion assessment different amounts of cheese whey to achieve the optimum proportion of cheese whey in the feed (10%, 20% or 30%) will be needed.

5.1.2. Cost and Revenue analysis

The capital and operating costs of systems for each case study and different scenarios are shown in Table 5.1 and Table 5.2. To evaluate the capital costs (CAPEX) of the proposed system, a national SME company that is a provider of AD systems was inquired. The capital costs of the AD facility include mainly the cost of: (i) AD reactor and ancillary equipment such as pumps, mixings device and also the energy recovery system among others, (ii) valves and tubes, (iii) electrical installation and control, (iv) engineering services and (v) Civil works. The price for valves and tubes and electrical installation and control, as well as engineering services are in the low range of available market prices, therefore higher prices could be expected from other suppliers. Regarding energy recovery, two systems have been evaluated: (i) heat recovery (using a ‘Dunphy Energy, Domogreen Comet” biogas boiler, heat recovery efficiency equal to 80%) and (ii) heat and power recovery (using a “Micropower Europe CAPSTONE C30” micro-turbine, electricity recovery efficiency equal to 26% and heat recovery efficiency equal to 50%).

Table 5. 1 Capital and operating costs of the anaerobic digestion system for RM + straw with heat & power and heat recovery systems

	OLR= 1.1 kg VS·m^{-3}$_{reactor}$		OLR= 1.5 kg VS·m^{-3}$_{reactor}$				OLR= 1.7 kg VS·m^{-3}$_{reactor}$				OLR= 2 kg VS·m^{-3}$_{reactor}$			
	Heat & power recovery	Heat recovery	Heat & power recovery		Heat recovery		Heat & power recovery		Heat recovery		Heat & power recovery		Heat recovery	
	RM	RM	RS	BR	RS	BR	RS	BR	RS	BR	RS	BR	RS	BR
Capital costs (€)														
Reactor price, energy recovery system & ancillary materials*	528,100	416,800	526,800	526,800	415,600	415,600	526,800	526,800	415,600	415,600	526,800	526,800	415,600	415,600
Valves and tubes	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000
Electrical installation and control	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000
Engineering services	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000	15,000
Civil works	7,000	7,000	7,000	7,000	7,000	7,000	7,000	7,000	7,000	7,000	7,000	7,000	7,000	7,000
Operating costs														
Straw cost														
Monthly Raw straw cost (€/year)	-	-	8,034	-	8,034	-	12,096	-	12,096	-	18,180	-	18,180	-
Monthly briquetted costs (€/year)	-	-	-	10,426	-	10,426	-	15,696	-	15,696		23,592	-	23,592
Energy cost														
Internal AD electricity consumption (€/year)	396	396	396	396	396	396	396	396	396	396	396	396	396	396
Other cost														
Maintenance Cost (€/year)	7,200	7,200	14,400	7,200	14,400	7,200	14,400	7,200	14,400	7,200	14,400	7,200	14,400	7,200
Insurance (€/year)	1,168	945	1,168	1,168	945	945	1,168	1,168	945	945	1,168	1,168	945	945

Table 5. 2 Capital and operating cost of the anaerobic digestion system for RM + CW with heat & power and heat recovery systems

	Heat & power recovery			Heat recovery		
	RM + 10% CW	RM + 20% CW	RM + 30% CW	RM + 10% CW	RM + 20% CW	RM + 30% CW
Capital costs (€)						
Reactor price, energy recovery system & ancillary materials*	611,100	664,800	733.800	499,900	553,600	622,600
Valves and tubes	15,000	15,000	15,000	15,000	15,000	15,000
Electrical installation and control	20,000	20,000	20,000	20,000	20,000	20,000
Engineering services	15,000	15,000	15,000	15,000	15,000	15,000
Civil works	7,000	7,000	7,000	7,000	7,000	7,000
Operating costs						
Internal AD electricity consumption (€/year)	396	396	396	396	396	396
Maintenance Cost (€/year)	7,200	7,200	7,200	7,200	7,200	7,200
Insurance (€/year)	1,336	1,444	1,582	1,114	1,221	1,359

To evaluate the operational costs (OPEX) of the proposed system, the following operational costs are considered: (i) internal energy consumption (heat & electricity), (ii) co-feedstock purchase (RS or BS for first case study) and (iii) insurance and maintenance/daily operation costs:

- Internal energy consumption: considers the electricity consumption consumed by the daily AD operations (e.g. pumps and mixing). The total estimated internal electricity consumption of the AD system is equal to 330 KWh/month and the electricity cost used is the average price paid during 2018 by La Fageda farm (0.1 ± 0.03 €). No heating costs have been considered, however it is considered that part of the heat recovered from the AD system is used to maintain the reactor at 35 -37 ºC and therefore, the net heat production to be used in other farm processes is reduced accordingly.
- Co-substrate purchased:

- **First case study, Straw as co-substrate:**

  Two different co-substrates have been used in the analysis (RS and BS). No straw on-farm production is considered in the base scenario, thus, the purchase of these feedstock to an external provider is considered. For RS (in baled form), the average price used in this base scenario is the average price at farm gate in Catalonia which is 43 €/t. Prices for BS were obtained directly from national providers with a current price of 56 €/t at the farm gate. The amount of purchased straw (raw or briquetted) depends on the desired OLR, thus, 15.6 t_{straw}/month, 23.4 t_{straw}/month and 35.2 t_{straw}/month will be needed to achieve the desired OLR of 1.5, 1.7 and 2 kg $VS \cdot m^{-3} \cdot d^{-1}$ respectively.
- **Second case study, Cheese whey as co-substrate:**

  One of the objectives of this study is to treat all cheese whey produced by the cheese production line in a farm in the scale of La Fageda. Furthermore, cheese whey is a residue and in case of need of more cheese whey to increase the proportion of whey in the feedstock, it will be sent to the farm free of charge. Thus in the second case study no cost for co-substrate purchase was considered.

- Maintenance and daily operation cost were estimated as yearly hours of work equivalents (Blumenstein et al., 2016). For the mono-digestion of RM, co-digestion of RM + BS and also for the co-digestion of RM + cheese whey, 720 yearly hours equivalents have been considered with an annual Operation and maintenance costs of 7,200 €/year. For the co-digestion of RM + RS in the first case study, more maintenance requirements have been considered due more frequent AD operations related to avoid pipe clogging, foam accumulation, etc. and 1,440 yearly hours equivalents have been considered with an annual Operation and maintenance costs of 14,400 €/year.

Regarding revenues, only revenues coming from energy recovery (only heat or heat & power) have been considered in this study. Regarding heat recovery, it is considered that all net heat produced (after consuming the necessary energy to keep the reactor at mesophilic temperature) is used to substitute heat consumption at farm/milk processing facilities. Therefore, heat revenues come from avoided costs of current heat needs of the farm and milk processing facilities. Heat costs per MJ were obtained directly from farm utility bills. Electricity revenues works in a different way; it has been considered that the produced electricity is sold to the grid mix. The base average electricity selling price in Spain used in this study is equal to 65.09 €/MWh (average price for October 2018, it varies on a daily basis). However, according to the national energy commission (CNE), in Spain the production of renewal electricity has financial support under several circumstances. If the installation system were renewal energy is produced has a maximum power of 499 KWh and a maximum usage of 4235h per year, it will be considered as premium renewable energy and will receive an extra price of 74.64 €/MWh. As a result, the final electricity selling price is 0.14 ± 0.03 €/KWh.

Neither additional costs nor revenues/savings for the post-treatment/use of the digestate have been taken into account. The rationale behind that is that both RM and digestates will be applied to agricultural soil without further treatment, therefore, costs and/or revenues associated with this stage will be the same with or without installing the AD system at farm.

5.1.3. Assumptions and limitation of the study

The techno-economic assessment carried out in this study has tried to consider all important input and output parameters affecting the final results, however several assumptions and some limitations must be highlighted:

- The techno-economic assessment is performed for small to medium cattle dairy farms, this type of farms usually use the animals slurry as fertilizer/soil amendment, in this study, it is considered that the digestate from the AD process is also used directly as fertilizer/soil amendment in the same way of raw slurry, therefore, no extra cost/revenue has been considered.
- In the heat & power recovery system scenario it is not considered any biogas desulphuration process before using the biogas in the microturbine. The selected microturbine is able to work with H_2S concentrations up to 2,000 ppm_v. If higher concentrations are expected a desulphuration process should be included.
- A detailed study of transportation cost of RS and BS is not carried out, average prices at the farm gate from official sources and external providers has been used to carry out the study Sensitivity analysis.

There are relevant parameters that can affect the results of the economic assessment, thus, several different sensitivity assessments have been carried out to evaluate these parameters in each case study and scenario as follow:

5.1.4. Sensitivity analysis of first case study (Straw as co-substrate)

For the use of raw or briquetted straw, as the co-substrates in the farm, five different parameters which have the most effect on techno-economic study have been considered. The five sensitivity assessments are: (i) Farm size, (ii) Straw prices, (iii) Electricity prices, (iv) alternative pre-treatments and (v) discount rate.

- Farm size: The economic viability of the AD in small to medium farms is highly size-dependent mainly because of AD energy revenues are not able to offset CAPEX cost. The AD reactor and the energy recovery system (microturbine or boiler) have a fixed costs and variable costs mainly related to the reactor size. Four different budgets were prepared for the SME Engineering company for different reactor sizes (100, 200, 400 and 1052 m^3) including all ancillary equipment and a linear regression model was carried out determine the reactor costs for different reactor sizes. Equations 5.1 and 5.2 show the obtained linear regressions to determine the reactor cost for (i) AD heat & power recovery systems (including micro-turbine costs) and (ii) AD heat recovery systems (including biogas boiler costs) respectively:

$$Reactor\ price\ (€) = 329.05 * Reactor\ size + 181{,}815 \quad (5.1)$$

$$Reactor\ price\ (€) = 329.05 * Reactor\ size + 70{,}605 \quad (5.2)$$

La Fageda can be considered a medium size dairy farm, therefore, in this sensitivity analysis a farm of 100 cattle heads have been studied.

- straw price: The base scenario considers that the straw (raw or briquetted) is bought to an external provider. In that scenario is considered that the straw is an on-farm by-product. The production of straw on-farm has an approximate cost of 16.5€/t (Nolan et al., 2010) instead of the average buying price of 43€/t. Also a sensitivity analysis has been performed to find the maximum price of purchased RS and BS that makes the AD system still profitable.

- Electricity price: Electricity price is a parameter that highly influence the final economic performance of the system. The sensitivity analysis has been performed to find the minimum price of electricity (revenue) that makes the system profitable.

- Alternative pre-treatments: A part from briquetting, several other pre-treatments leading to higher biogas production from straw have been studied at lab-scale. No information was found about the price at full-scale to obtain this pre-treated straw, therefore, a sensitivity assessment to find the maximum price of the pre-treated straw that makes the system profitable has been carried out for alkali and microwave pre-treatments.

- Discount rate: Net Present Value (NPV) has been used as a method to evaluate the economic viability of the AD system. The discount rate is a parameter that highly affect the final results of the NPV, in the base scenario a discount rate of 6% was chosen and in this sensitivity scenario discount rates from 5% to 10% have been assessed.

5.1.5. Sensitivity analysis for second case study (Cheese whey as co-substrate)

The same as section 5.2.1. The parameters which have the most influence on economic assessment of implementation of AD plant using cheese whey as co-substrate were investigated and are as follow:

- Type of farm’s animal and farm size in each scenario:

  In the base scenario, Lafageda as a farm which has 250 heads of cattle was considered for the economic assessments. However, in the lab scale, anaerobic biodegradability of Sheep manure and Sheep cheese whey as well as Goat manure and Goat cheese whey were investigated. Therefore, another economic study was carried out to investigate the economic performance of farms having goat and sheep as livestock and also the minimum heads of Cattles, Goats and Sheeps which makes the implementation of AD plant in a dairy farm treating animal manure and their corresponding cheese whey, profitable. It is noteworthy that the change in reactor size and therefore capital cost, follows the equations 5.1 and 5.2 described in section 5.2.1.

  In case of farms of having Sheep and Goat as livestock, the daily manure production of 1.44 $Kg.d^{-1}$ and 1.55 $Kg.d^{-1}$ were considered for Sheep and Goat respectively (J. A. Ogejo et al., 2010)

- Electricity price: The same as section 5.2.1. Electricity price is a parameter that can affect the economical indexes of system. Therefore, a sensitivity analysis to find the maximum electricity price in which they system will be profitable was investigated.
- Discount rate: In the base scenario of this study, Discount rate was considered 7% and in this sensitivity scenario discount rates from 6% to 10% have been assessed.
- Biogas production: In this study, biogas production obtained in semi-continuous experiment is used for economic assessments. However, in the batch tests, higher amount of biogas production is obtained. Since higher biogas production can be translated to higher energy production and therefore better economic feasibility, thus another sensitivity analysis using data of batch experiment is carried out for this case study.

5.2. *Economic Indexes*

Net present value (NPV): NPV is a method to evaluate the economics of a project and is calculated as the sum of the initial investment and the present value of all future cash flows at a particular discount rate (Chau et al., 2009). NPV can be represented by Equation 5.3:

$$NPV = \sum_{t=1}^{n} (CI - CO)_t \, (1 + i_0)^{-t} \qquad (5.3)$$

where: CI is the cash inflow, CO is the cash outflow, t is the year, i_0 is the discount rate (7% in this study); and n is the life span of the project (25 years). A discount rate of 7% has been assumed by taking into account a risk-free rate of 2.5% (the proxy used is the rate of a three-month U.S. Treasury bill) and a 3.5% risk premium for a total return expectation of 7%.

Internal rate of return (IRR): Project IRR plays a crucial role in assessing the financial feasibility and viability of the project before making an investment decision. By definition, project IRR is the discount rate at which the NPV of the project is zero (Delivand et al., 2011). The IRR can be represented by the following equation:

$$(CI - CO)_t (1 + IRR)^{-t} = 0 \qquad (5.4)$$

Investment payback period (IPP). IPP refers to the period of time required to recover the investment funds (reach break-even point). It can be resulted by sum of annual cash flows over time until achieve to a positive value.

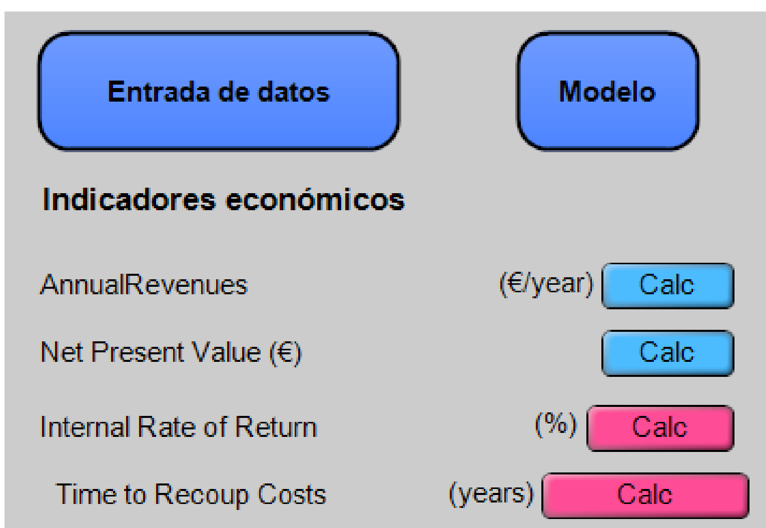
The following data (i) biogas production (0.30 ± 0.02 $m^3.kg^{-1}$VS for co-digestion of RM + RS/BS and 0.23 ± 0.01 $m^3.Kg^{-1}$ VS for mono-digestion of RM in the first case study and a biogas production of 0.178 m^3_{biogas} kg^{-1} $_{COD}$ for 30% proportion of CW in the feedstock, 0.145 m^3_{biogas} kg-

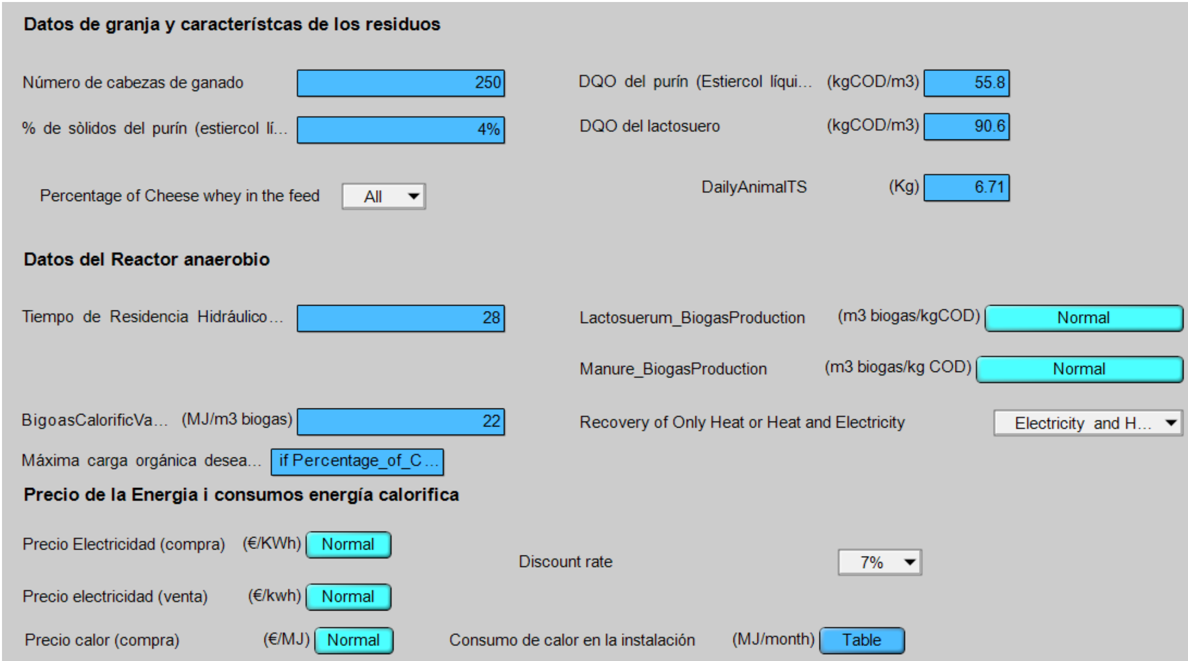
[1] $_{COD}$ and 0.125 m^3_{biogas} kg^{-1} $_{COD}$ for 20% and 10% of CW respectively and 0.096 m^3_{biogas} kg^{-1} $_{COD}$ for the RM in the second case study), (ii) electricity buying price (0.10 ± 0.03 €/KWh), (iii) electricity selling price (0.14 ± 0.03) and (iv) heat avoided cost (0.025 ± 0.005 €/MJ) used to model the economic performance. The economic performance has an associated uncertainty, therefore, it has also been modelled the probability to get positive NPV taking into account this uncertainty (using a normal distribution and the standard deviation of the selected parameters).

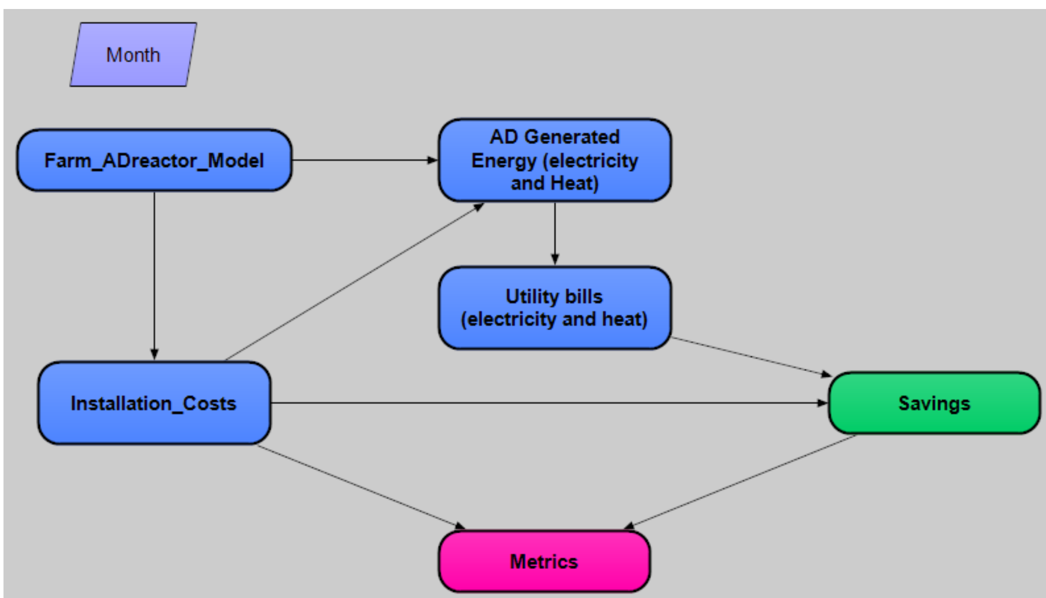
5.2.1. Modeling of economic feasibility of AD systems using analytica software

Analytica free 101 (Lumina Decision Systems) has been used to simulate and design the full plant model to evaluate the economic feasibility using the data obtained in the lab experiments. Figures below show the relations of parameters for modeling the system. It is noteworthy that the model is similar for both case studies being the main difference in the use of either VS or COD to calculate the OLR of the system.

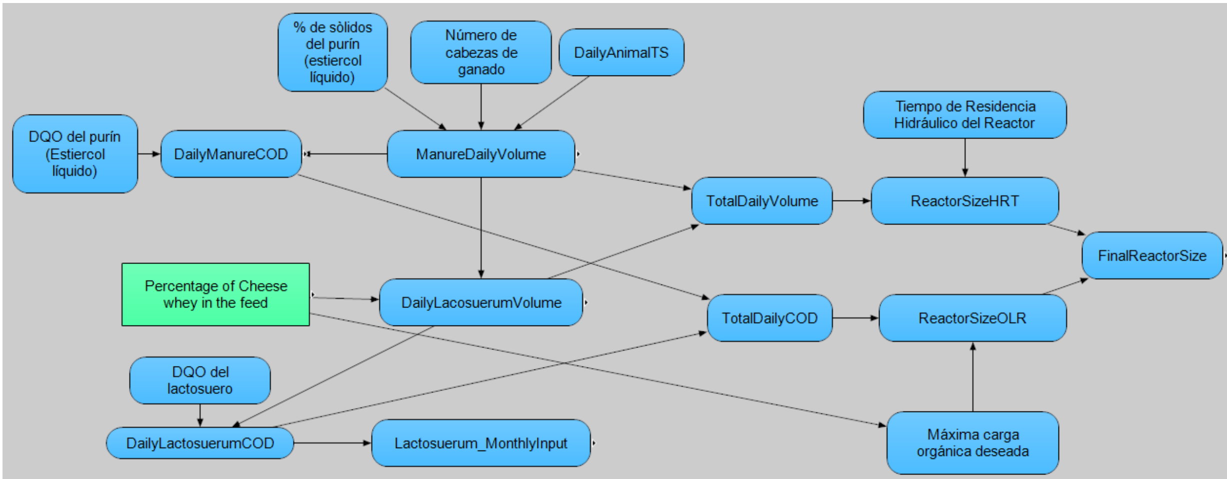
I. In the beginning general relations between input data and final calculations is modeled.




Datos de granja y característcas de los residuos
Número de cabezas de ganado
250
% de sòlidos del purín (estiercol lí...
4%
DQO del purín (Estiercol líqui... (kgCOD/m3)
55.8
DQO del lactosuero (kgCOD/m3)
90.6
Percentage of Cheese whey in the feed
All
DailyAnimalTS (Kg)
6.71
Datos del Reactor anaerobio
Tiempo de Residencia Hidráulico...
28
Lactosuerum_BiogasProduction (m3 biogas/kgCOD)
Normal
Manure_BiogasProduction (m3 biogas/kg COD)
Normal
BigoasCalorificVa... (MJ/m3 biogas)
22
Recovery of Only Heat or Heat and Electricity
Electricity and H...
Máxima carga orgánica desea...
if Percentage_of_C...
Precio de la Energia i consumos energía calorifica
Precio Electricidad (compra) (€/KWh)
Normal
Discount rate
7%
Precio electricidad (venta) (€/kwh)
Normal
Precio calor (compra) (€/MJ)
Normal
Consumo de calor en la instalación (MJ/month)
Table

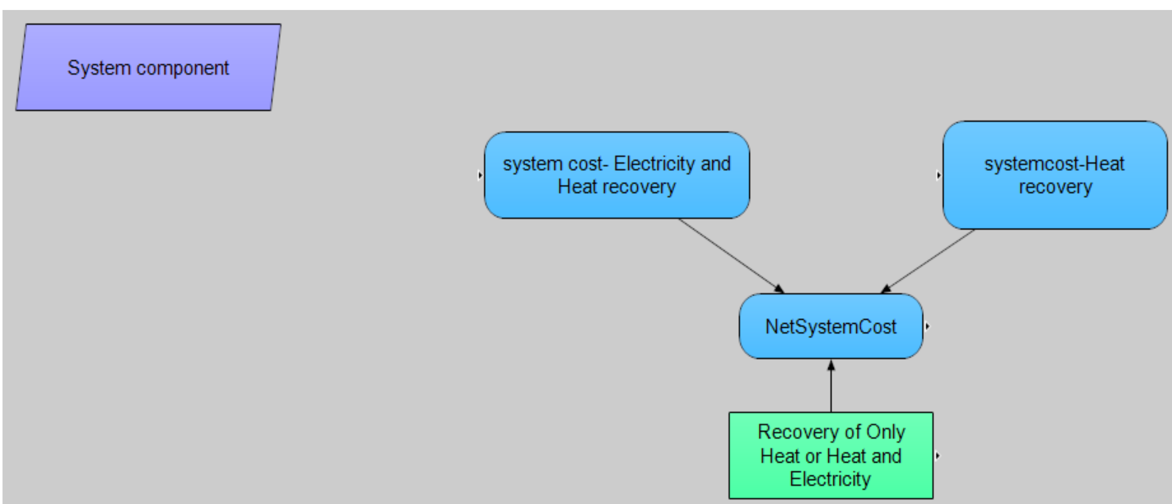

Month
Farm_ADreactor_Model
AD Generated Energy (electricity and Heat)
Utility bills (electricity and heat)
Installation_Costs
Savings
Metrics

II. Farm and AD data are modeled as follow

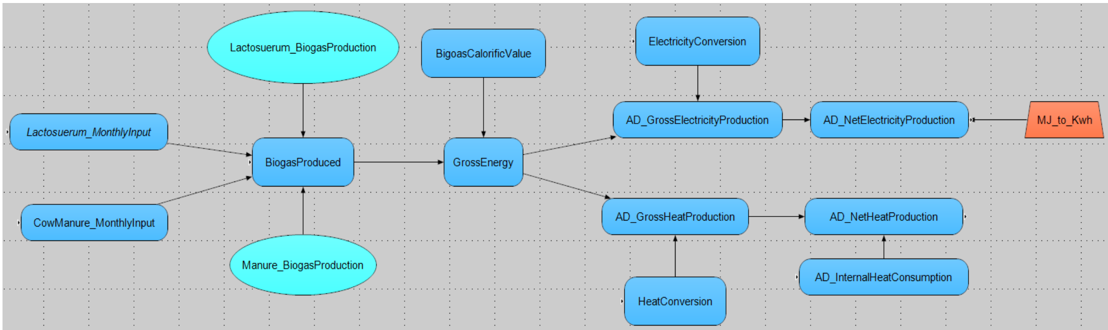


*In the calculation of reactor size, there is usually difference between calculating the reactor size based on HRT or OLR. Thus, the bigger reactor size is considered.

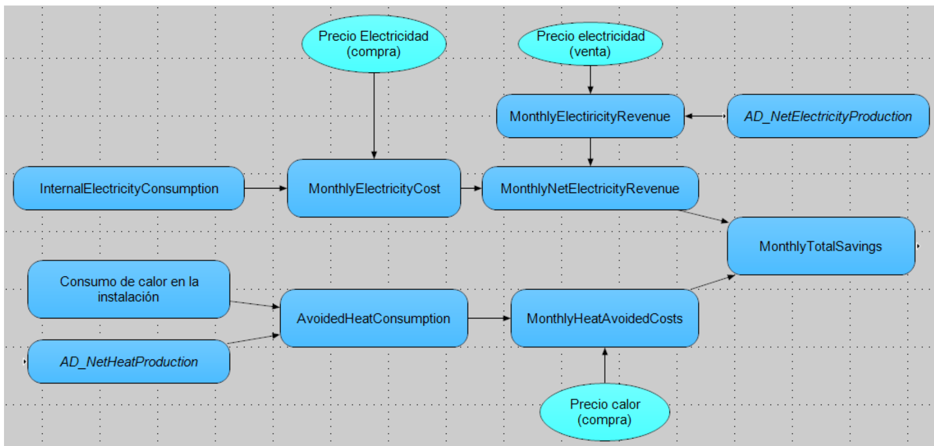
III. The system installation cost varies base on the design of the energy recovery system (heat & power recovery or only heat recovery).



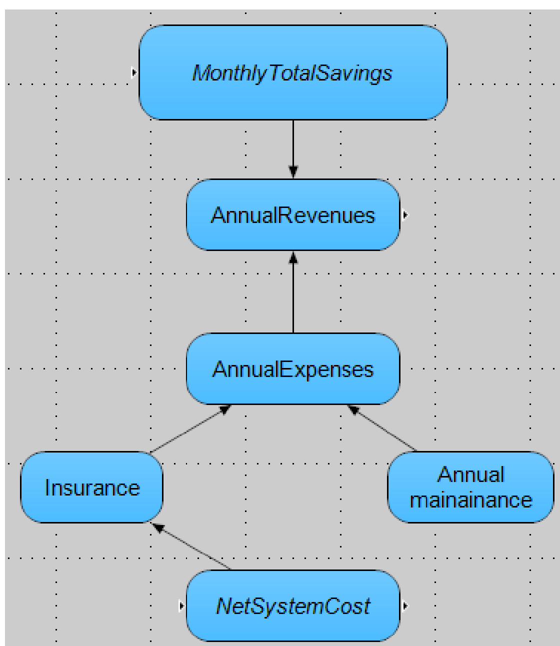
IV. The generated energy from AD is calculated as follow



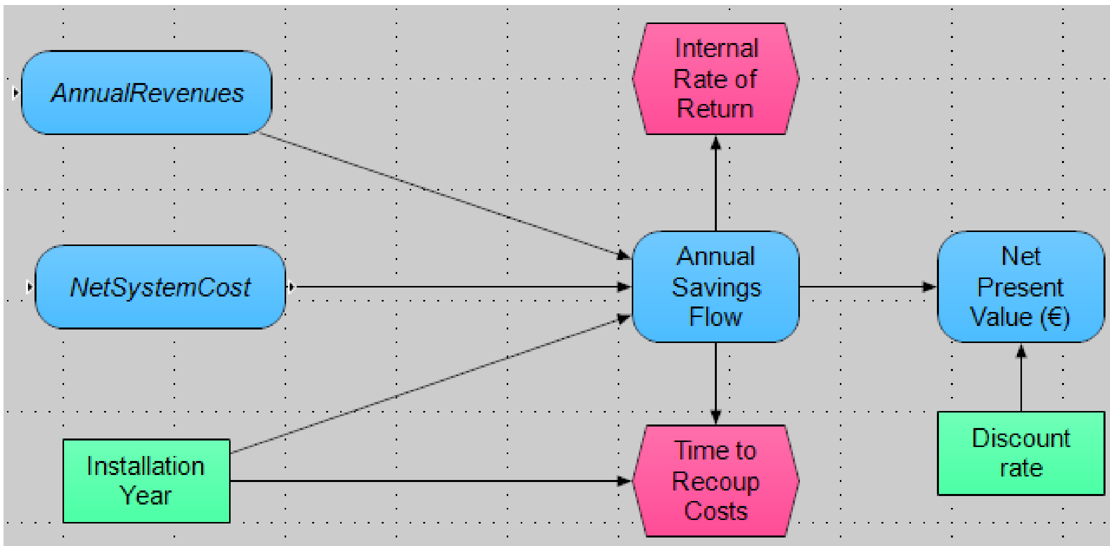
V. Utility bills (heat and electricity) are important factors of calculations



VI. The revenues and saving have been calculated



VII. Base on the given life span of system, annual saving flow, net system cost and annual savings, other metrics were calculated



5.3. *Analysis of economic indices*

5.3.1. *First case study (straw as co-substrate)*

5.3.1.1.Base scenario

Table 5.3 and Figures 5.2 and 5.3 show the results of the base scenario economic assessment. In this scenario mono-digestion of RM (OLR = 1.1 kg $VS \cdot m^{-3} \cdot d^{-1}$) and co-digestion of RM with RS or BS (OLR of 1.5, 1.7 and 2 kg $VS \cdot m^{-3} \cdot d^{-1}$) have been evaluated for a system with heat & power energy recovery and only with heat recovery. As no significant differences in biogas production were achieved in lab test (batch and continuous reactors) the same biogas production per kg VS has been considered in both RM + RS or RM + BS co-digestion processes. For the RM mono-digestion economic assessment a biogas production of 0.23 m^3_{biogas} kg^{-1} VS has been used (average from lab semi-continuous reactor 1 working at an OLR of 1.1 kg $VS \cdot m^{-3} \cdot d^{-1}$) and for the RM + RS/BS co-digestion economic assessments a biogas production of 0.30 m^3_{biogas} kg^{-1} VS has been used for an OLR of 2 kg VS·m^{-3}·d^{-1} (average from lab semi-continuous reactor 2 and 3 at an OLR of 2 kg VS·m^{-3}·d^{-1}), for the OLR of 1.5 and 1.7 kg VS·m^{-3}·d^{-1} the biogas production per VS has been inferred from the previous biogas productions taking into account the average manure and straw VS composition in the feed (0.28 and 0.29 m^3_{biogas} kg^{-1} VS for an OLR of 1.5 and 1.7 respectively).

Table 5. 3 Economic performance of system at base scenarios

	OLR=1.1 kg VS·m^{-3}$_{reactor}$		OLR=1.5 kg VS·m^{-3}$_{reactor}$				OLR=1.7 kg VS·m^{-3}$_{reactor}$				OLR=2 kg VS·m^{-3}$_{reactor}$			
	Heat & power recovery	Heat recovery	Heat & power recovery		Heat recovery		Heat & power recovery		Heat recovery		Heat & power recovery		Heat recovery	
	RM	RM	RM + RS	RM + BR	RM + RS	RM + BR	RM + RS	RM + BR	RM + RS	RM + BR	RM + RS	RM + BR	RM + RS	RM + BR
Biogas production														
Biogas production (m^3.Kg^{-1} VS)	0.23	0.23	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Total biogas production (m^3/month)	8,681	8,681	12,920	12,920	12,920	12,920	15,050	15,050	15,050	15,050	18,260	18,260	18,260	18,260
Energy production														
Biogas calorific value (MJ·m^{-3}$_{biogas}$)	22	22	22	22	22	22	22	22	22	22	22	22	22	22
Gross generated energy (MJ)	191,000	191,000	284,200	284,200	284,200	284,200	331,200	331,200	331,200	331,200	401,800	401,800	401,800	401,800
Net electricity production (kwh/month)	13,790	0	20,520	20,520	0	0	23,920	23,920	0	0	29,020	29,020	0	0
Net heat production (MJ/month)	32,370	89,660	78,950	78,950	164,200	164,200	102,500	102,500	201,800	201,800	137,800	137,800	258,300	258,300
Revenues														
Electricity sell price (€/KWh)	0.14	-	0.14	0.14	-	-	0.14	0.14	-	-	0.14	0.14	-	-
Heat avoided costs (€/MJ)	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025
Electricity revenues (€/year)	23,172	0	34,476	34,476	0	0	40,188	40,188	0	0	48,744	48,744	0	0
Heat avoided costs (€/year)	9,710	26,904	23,688	23,688	49,260	49,260	30,744	30,744	60,552	60,552	41,328	41,328	77,496	77,496
Total revenues (€/year)	32,484	26,508	49,728	49,728	38,436	38,436	58,440	58,440	44,460	44,460	71,508	71,508	53,508	53,508
Net revenue (€/year)*	24,120	18,360	34,170	38,970	25,480	30,290	420,880	46,480	32,720	36,320	55,940	57,730	43,570	45,360
Economic Indices														
NPV	NG**	NG**	NG**	NG**	NG**	NG**	NG**	43360	NG**	18,460	164,300	187,200	111,200	134,000
IRR (%)	0.25	NG**	3.48	4.87	2.67	4.43	5.94	6.91	5.27	6.48	9.36	9.81	8.82	9.38
IPP (years)	25	INF***	18	15	19	16	14	13	15	14	11	11	11	11

* Net revenue = Total revenue - OPEX cost (from table 5.1)
**NG: Negative
***INF: The investment will not be recovered during the assessed period of time

- <u>mono-digestion of RM</u>

Total yearly revenues from heat & power and heat recovery are 32,484€/year and 26,508€/year respectively, however, the net revenues (subtracting the OPEX) per year are 23,718€/year and 17,964€/year. These positive yearly cash flows are not able to offset the CAPEX cost in the lifespan of the installation (25 years), this is translated in negative NPV and IRR meaning that the investment will result in a net loss for the farmer. The IPP in case of heat & power energy recovery is 25 years. If the installed energy recovery system considers only heat recovery, the investment will not be recovered in this timeframe. From this analysis it is clear that either a big reduction in CAPEX is needed to make the system viable or on the contrary and increase in biogas production with its concomitant increase in revenues is needed.

- <u>Co-digestion of RM and RS or BS</u>

In order to increase biogas production in this second base scenario, the use of straw in its raw or briquetted form as co-substrate is considered. By adding straw, the OLR was increased from 1.1 kg $VS \cdot m^{-3} \cdot d^{-1}$ (only RM) to 1.5, 1.7 and 2 kg $VS \cdot m^{-3} \cdot d^{-1}$, in these situations the monthly biogas production increased 49%, 73% and 110% respectively compared with the sole digestion of RM. The increase in OLR is not associated to a relevant increase in CAPEX, however it is associated to an increase in OPEX costs (mainly due to the purchase of RS or BS) therefore, the increase in revenues due to the higher biogas production must offset the costs of purchasing the straw.

At an OLR of 1.5 kg $VS \cdot m^{-3} \cdot d^{-1}$ (addition of 15.57 t_{straw}/month) any of the tested scenario became positive, neither the use of RS or BS nor the two assessed energy recovery systems (heat & power recovery and heat recovery). The net revenue increased by 10,000 to 15,000€/year, however the low obtained IRR, ranging from 3.4 to 4.4, makes the system not profitable (NPV<0) at a discount rate of 6%. At an OLR of 1.7 kg $VS \cdot m^{-3} \cdot d^{-1}$ (addition of 23.43 t_{straw}/month) the obtained IRR are slightly above 6 for the use of BR and slightly below 6 for the RS meaning that at this OLR the NPV became positive for the BR. However, as it is shown in Figure 5.2 and 5.3, when evaluating the results considering the uncertainty of the data (e.g. biogas production, selling price of electricity, etc.) either with RS or BS the cumulative probability to obtain NPV>0 ranges from 45 to 55% respectively. On the contrary, at an OLR of 2 kg $VS \cdot m^{-3} \cdot d^{-1}$ (addition of 35.23 t_{straw}/month) the NPV in all scenarios is above 0 indicating that the AD system will be profitable and that the projected earnings generated by the system - in present euros - exceeds its anticipated costs. Figures 4.2 and 4.3 show that at this OLR the cumulative probability to obtain positive NPV ranges from 80 to 85 % for the heat & power recovery system (for RS and BS respectively) and from 70 to 75 % for the heat recovery system (for RS and BS respectively). When comparing the energy recovery system, it is noteworthy to mention that although the capital costs of the heat recovery system are 19% less than the heat & power energy recovery system, this second system presents better economic ratios due to capability of generating electricity and selling it to the market at higher prices. It is also worth mentioning that in this base scenario, to achieve positive results with the heat recovery system, the farm shall be able to use all the net heat produced in the AD system. If the heat production is higher than the heat consumption at farm, the excess heat will be lost, reducing the overall economic sustainability of the system. In addition, as a general comparison, using briquetted straw presents higher economic ratios than raw straw which can be explained by the fact that BS is associated to lower maintenance costs that are able to offset the higher purchasing costs of using BS.

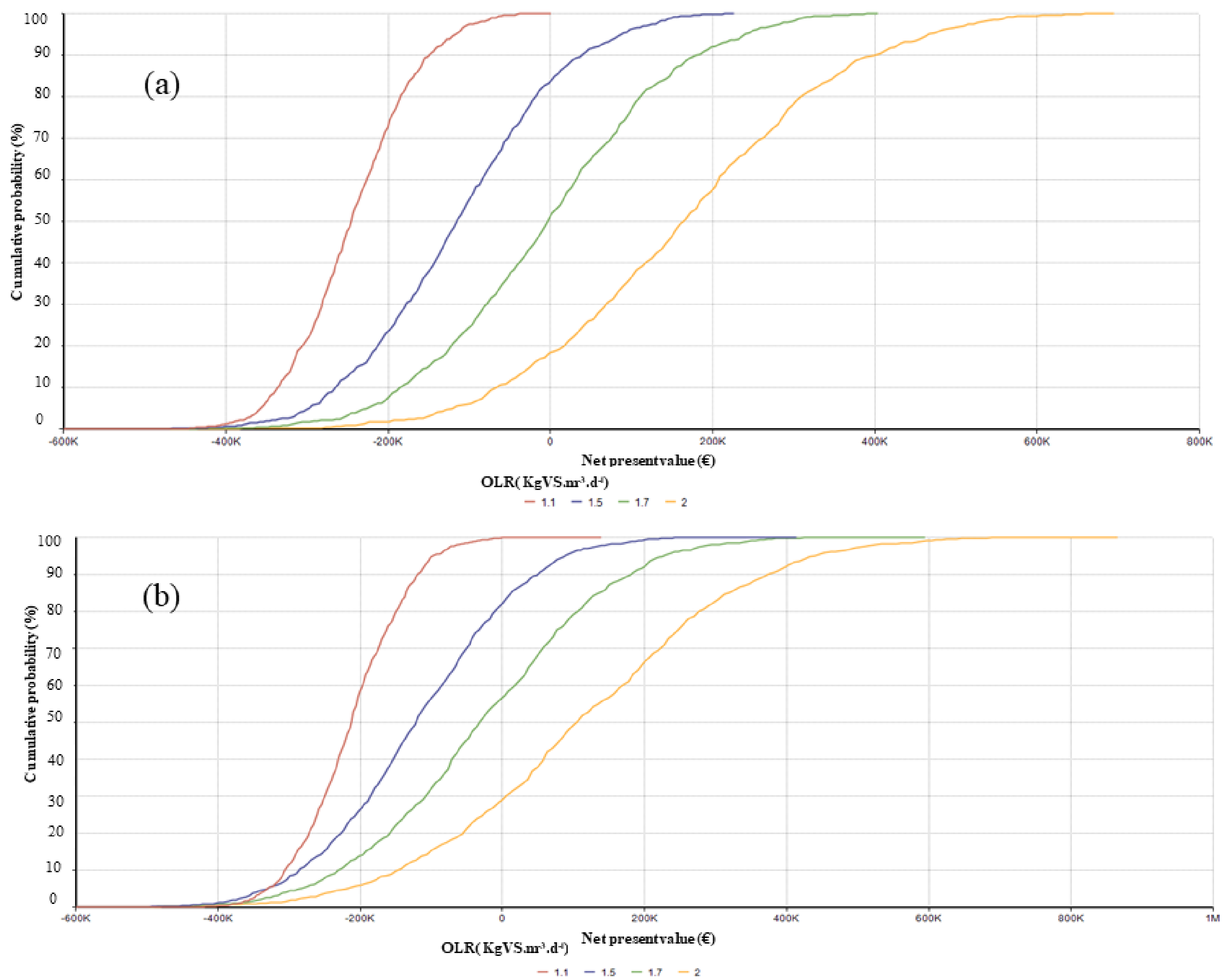


Figure 5. 2 Cumulative probability of net present value for (a) raw straw and total energy recovery, (b) RS and heat recovery

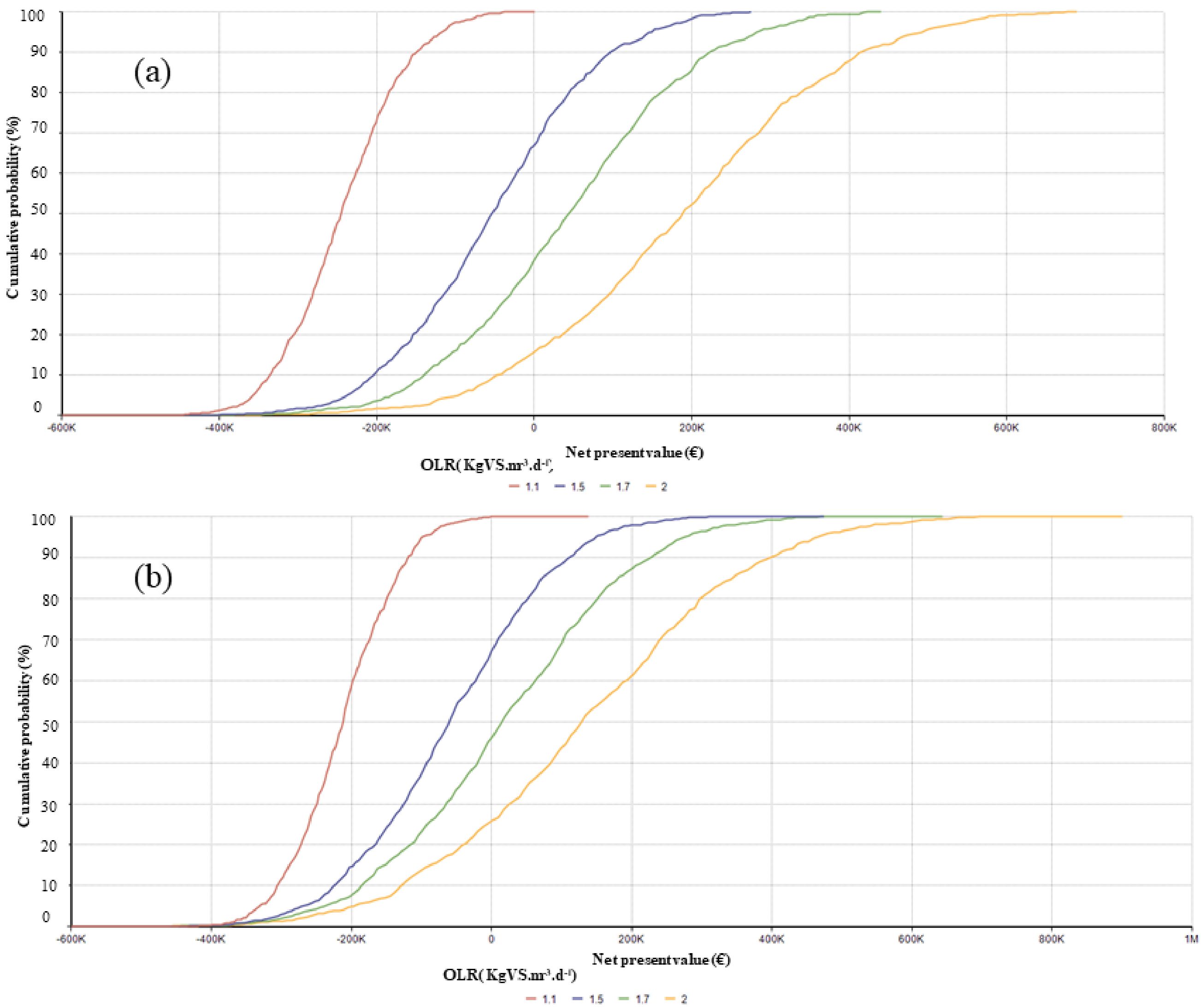


Figure 5. 3 Cumulative probability of net present value for (a) BS and total energy recovery (b) BS and heat recovery

5.3.1.2.Sensitivity analysis

The importance of the critical variables on the economic ratios of the project has been evaluated through a sensitivity analysis. If not explicitly mentioned, the sensitivity scenarios are carried out with a co-digestion system working at an OLR of 2 kg $VS \cdot m^{-3} \cdot d^{-1}$ (best possible results obtained in the base scenario). A sensitivity analysis for (i) size of the farm (adult cattle heads), (ii), straw price, (iii) electricity price, (iv) discount rate and (v) alternative straw pre-treatment has been performed. The result of sensitivity analysis is shown in Table 5.4.

Table 5. 4 Sensitivity analysis of each scenario in which NPV≥0

Economical parameters	Base scenario: OLR=2 kg $VS \cdot m^{-3}_{reactor}$			
	Electricity and Heat recovery		Heat recovery	
	RM + RS	RM + BR	RM + RS	RM + BR
Base scenario				
Farm size (number of adult cattle heads)	160	180	185	156
Electricity selling price (€/KWh)	0.11	0.10	-	-
Straw buying price (€/t)	73	77.6	63.5	67.5
Final price of straw after pretreatment (€/t)				
Alkali pre-treatment	282	286	198	202
Microwave-Alkali pre-treatment	197	201	173	177

- <u>Farm size:</u>

Anaerobic digestion systems are highly affected from economies of scale making it more difficult to be implemented at small farms. The influence of farm size has been investigated to find the minimum farm size (in adult cattle heads) that makes the whole system profitable. The results show that the minimum herd size in which a profitable anaerobic co-digestion (RM + BS) system can be installed with a heat & power energy recovery system is 160 adult cattle heads with a CAPEX costs of 459,600€ (from equation 5.1) and a yearly revenue of 34,040€/year. If only heat recovery is installed, the total number of cattle heads needed to make the system profitable is 156 with an initial investment of 342,900€ (from equation 5.2) and a yearly revenue of 25,350€/year. If the herd size is smaller, the proposed co-digestion system will turn into a net loss for the farmer and the implementation of other type of low-cost digesters could be envisaged.

- <u>Straw price</u>

In the base scenario it was considered that there was not on-farm production of straw, however it is common that this by-product is produced on-farm. thus, a sensitivity assessment of the co-digestion system including the price of on-site production of straw instead of buying it to an external provider has been carried out. The production of RS has an approximate cost for the farm of 16.5 €/t (Nolan et al., 2010) instead of the buying cost of 43€/t considered in the base scenario. Obviously, the decrease in OPEX due to the RS on-farm production has a huge impact on the assessed economic indices. For electricity & heat recovery system using on-farm produced RS, a NPV of 307,500 € an IRR of 12.17 % and an IPP of 9 years are obtained. When considering only heat recovery a NPV of 87,800€, an IRR of 10.8% and an IPP of 10 years are obtained.

Around 4.7 t of wheat straw are produced per hectare and year (Nolan et al., 2010). therefore, the use of on-site produced straw can be a limitation in many small/medium farms if not enough land is cultivated, in that sense, it is noteworthy to highlight that if straw is produced on-farm, the system it is also profitable (NPV of 92,590€ and 67,680 € for heat & power and heat recovery) at an OLR of 1.7 kg $VS \cdot m^{-3} \cdot d^{-1}$ which means less yearly straw requirements (from 422.76 t/year to 281.16 t/year). At an OLR of 1.5 kg $VS \cdot m^{-3} \cdot d^{-1}$, although the NPV is negative (cumulative probability of 65% of NPV<0), the yearly revenues are 30,530€ and 39,210€ with an IRR of 4.4 to 4.9% for heat and heat & power recovery respectively. In this sensitivity scenario only the use of on-farm produced RS is considered, on-site production and use of BS is not considered because of the lack of data about the extra CAPEX cost of buying a briquetting machine and OPEX energy cost for briquetting the straw.

Another sensitivity scenario to find the maximum buying price of straw (either RS or BS) that makes the system profitable (NPV>0) for an AD system working at an OLR of 2 kg $VS \cdot m^{-3} \cdot d^{-1}$ has been carried out. On one hand, for a heat & power recovery system, the maximum price of straw should be 73 €/t for RS and 77.6 €/t for BS. On the other hand, for a heat recovery system the maximum straw prices should be 63.5 €/t and 67.5 €/t for RS BS respectively.

- Electricity prices:

Electricity selling price is a parameter that highly influence the final economic performance of the system. The sensitivity analysis has been performed by finding the minimum electricity price that makes the system profitable (NPV $\geq$ 0). Briefly, for an OLR of 2 kg $VS \cdot m^{-3} \cdot d^{-1}$, the minimum electricity selling price that makes the system profitable is 0.11 €/KWh. As explained in section 2.2.1.2, currently green electricity produced from AD is subsidized under several circumstances (installations with maximum power of 499 KWh and operation less than 4,235h/year) with an extra revenue of 74.65 €/MWh. Current market electricity prices ranges from 60 to 70 €/MWh, thus, without subsidies the electricity production from AD process would not be profitable under any of the assessed scenarios.

- Discount rate:

Discount rate plays and important role in any economic study and can change dramatically the results obtained in any NPV analysis. In the base scenario the discount rate was considered 6%, however, different discounts rates from 5 to 10 are common in many investment situations (e.g. stock market). Figure 4.4 shows the NPV of RM, RM + RS and RM +BS systems. In almost all co-digestion situations a discount rate of 9 still makes this system profitable (unless the RM + RS with heat recovery system which is profitable with a discount rate of 8.8), however at a discount rate of 10 the system will become in a net loss for the farmers. On the contrary negative NPV are obtained even at a discount rate of 5 for mono-digestion systems.

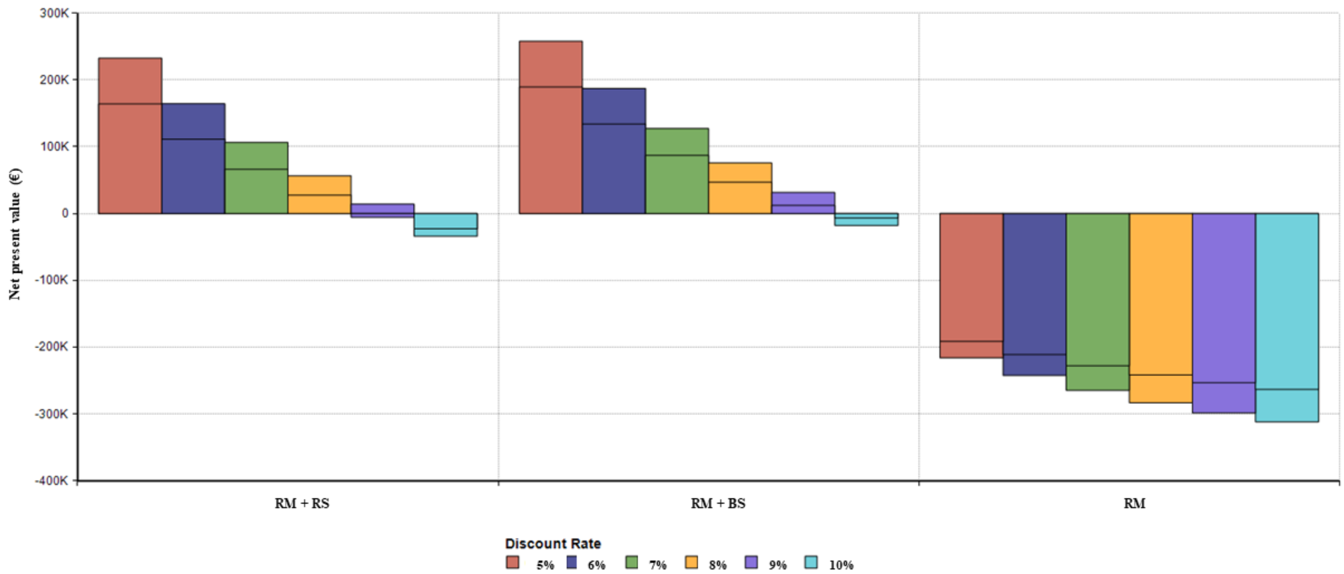


Figure 5. 4 NPV of different scenarios at different discount rates

- <u>Alternative straw pre-treatments:</u>

Although briquetting can reduce transportation, storage and maintenance costs, this pre-treatment was not able to increase biogas production compared to raw straw. On the contrary, alkali and microwave pre-treatments have demonstrated a high efficiency in increasing the biogas production. However, these pre-treatments are energy and/or chemical usage intensive and are not widely applied at industrial scale. Consequently, the main factor affecting the NPV is going to be the final price of the pre-treated straw. The sensitivity analysis has been performed by finding the maximum price of the pre-treatment that makes the system profitable (NPV $\geq$ 0). The electricity selling price and the heat costs are kept the same as in the base scenario. The results are shown in Table 5.4.

The profitability of the system will be positive for prices ranging from 173.3€/t to 286.9€/t of pre-treated material. As a general rule, the higher the biogas production the system will be heading towards electricity recovery instead of heat recovery. It should also be mentioned that since there was no significant difference in biogas production of thermal pre-treated straw and raw and briquetted straw, the sensitivity analysis was not applied for this type of pre-treatment.

5.3.2. Second case study (Cheese whey as co-substrate)

5.3.2.1.Base scenario

For the base scenario, AD of RM and cow cheese whey using data obtained in the semi-continuous experiment was considered. Mono digestion of RM and co-digestion of RM with Cow cheese whey (proportions of 10%, 20% and 30%) have been evaluated for a system with heat & power energy recovery and only with heat recovery. For the RM mono-digestion economic assessment, a biogas production of 0.096 $m^3_{biogas}\,kg^{-1}{}_{COD}$ has been used and for the RM + CW co-digestion economic assessments, a biogas production of 0.178 $m^3_{biogas}\,kg^{-1}{}_{COD}$ for the 30% proportion of CW in the feedstock, 0.145 $m^3_{biogas}\,kg^{-1}{}_{COD}$ and 0.125 $m^3_{biogas}\,kg^{-1}{}_{COD}$ for the 20% and 10% of CW respectively have been used (average from lab semi-continuous reactor). Table 5.5 and Figure 5.5 show the results of the base scenario economic assessment.

Mono digestion of raw manure

Total yearly revenues from heat & power and heat recovery are 20,892€/year and 16,248€/year respectively, however, the net revenues (subtracting the OPEX) per year are 12,450€/year and 8,024€/year respectively. These positive yearly cash flows are not able to offset the CAPEX cost in the lifespan of the installation (25 years), this is translated in negative NPV and IRR meaning that the investment will result in a net loss for the farmer. The investment will not be recovered in this timeframe for both heat & power recovery and heat recovery. From this analysis it is clear that either a big reduction in CAPEX is needed to make the system viable or on the contrary and increase in biogas production with its concomitant increase in revenues is needed.

Table 5. 5 Economic performance of system with different proportion of CW

	RM + 30% CW		RM + 20% CW		RM + 10% CW		RM	
	Heat & power recovery	Heat recovery	Heat & power recovery	Heat recovery	Heat & power recovery	Heat recovery	Heat & power recovery	Heat recovery
Biogas production								
Biogas production ($m^3.Kg^{-1}$ COD)	0.178	0.178	0.145	0.145	0.125	0.125	0.96	0.96
Total biogas production (m^3/month)	21,190	21,190	14,310	14,310	10,360	10,360	6,740	6,740
Energy production								
Biogas calorific value ($MJ \cdot m^{-3}_{biogas}$)	22	22	22	22	22	22	22	22
Gross generated energy (MJ)	466,200	466,200	314,900	314,900	227,900	227,900	148,300	148,300
Net electricity production (kwh/month)	33,670	0	22,740	0	16,460	0	10,710	0
Net heat production (MJ/month)	142,900	282,800	78,520	173,000	43,810	112,200	11,010	55,490
Revenues								
Electricity sell price (€/KWh)	0.14	-	0.14	-	0.14	-	0.14	-
Heat avoided costs (€/MJ)	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025
Electricity revenues (€/year)	56,568	0	38,208	0	27,648	0	17,988	0
Heat avoided costs (€/year)	42,876	84,840	23,556	51,888	13,140	33,648	3,304	16,644
Total revenues (€/year)	99,048	84,444	61,368	51,492	40,392	33,252	20,892	16,248
Net revenue (€/year)*	90,270	75,880	52,720	43,080	31,860	24,940	12,450	8,024
Economic Indices								
NPV	312,900	249,200	NG**	NG**	NG**	NG**	NG**	NG**
IRR (%)	12.05	11.68	5.88	5.48	1.53	0.97	NG**	NG**
IPP (years)	9	9	14	15	21	23	INF***	INF***

* Net revenue = Total revenue - OPEX cost (from table 5.2)
**NG=Negative

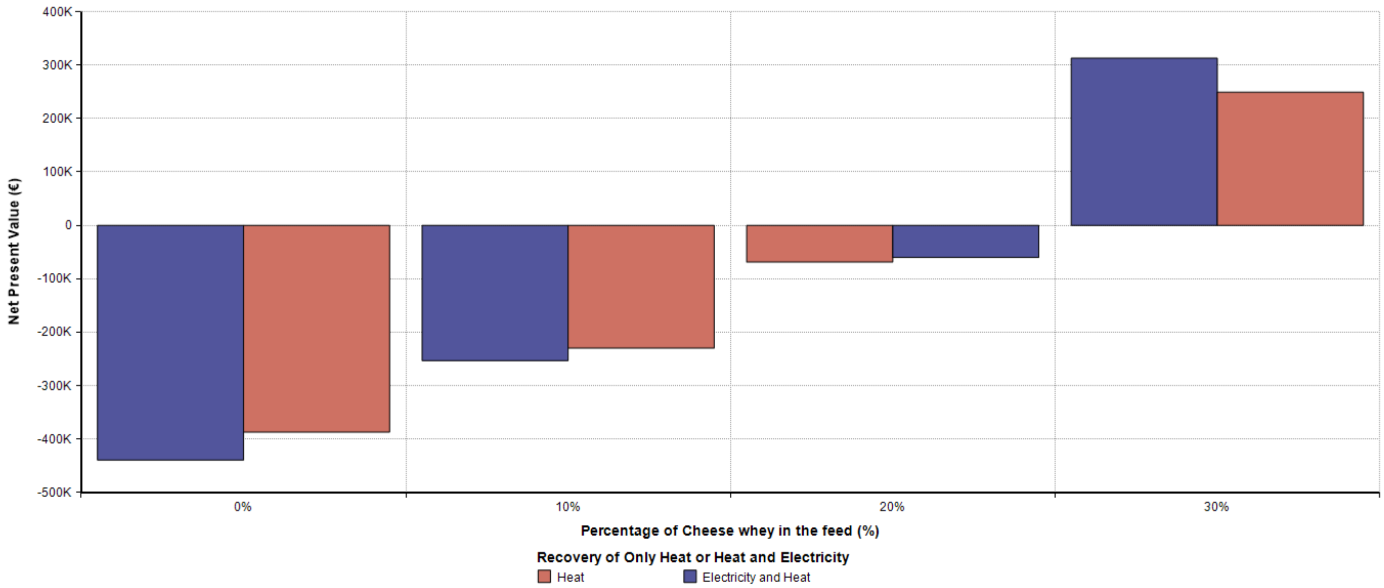


Figure 5. 5 Economic performance of AD system at different proportions of cheese whey

<u>Co-digestion of RM and cheese whey</u>

The result of economic assessment considering the data of biogas production obtained at semi-continuous reactors of this document in all proportions of cheese whey, is shown in Table 5.5 and Figure 5.5. These results show that the system is profitable only in CW proportion of 30% (215.64 m^3CW/month) in the feed with a positive net present value for both total energy recovery system and heat recovery system respectively. Furthermore, the other proportions of cheese whey in the feed using the data obtained in semi-continuous experiment of this study will cause a negative Net Present Value and the investment is not profitable.

In order to increase biogas production, the use of cheese whey as co-substrate is considered. By adding cheese whey, the OLR was increased from 2.0 kg $COD \cdot m^{-3} \cdot d^{-1}$ (only RM) to 2.13, 2.26 and 2.38 kg $COD \cdot m^{-3} \cdot d^{-1}$ (10%, 20% and 30% cow cheese whey respectively), in these situations the monthly biogas production increased 5.4%, 38.1% and 48% respectively compared with the sole digestion of RM. The increase in OLR is not associated to a relevant increase in OPEX, however it is associated to an increase in CAPEX costs (mainly due to the increase in reactor size and thus reactor price) therefore, the increase in revenues due to the higher biogas production must offset the capital costs.

At an OLR of 2.13 kg COD·m^{-3}·d^{-1} (addition of 55.92 m^3_{CW}/month, equal to 10% cheese whey in the feed) all the tested scenarios became negative. At an OLR of 2.26 kg COD·m^{-3}·d^{-1} (addition of 125.76 m^3_{CW}/month equal to 20% cheese whey in the feed) the obtained IRR are slightly less than 7% for both total energy recovery and heat recovery. On the contrary, at an OLR of 2.38 kg COD.m^{-3}·d^{-1} (addition of 215.64 m^3_{CW}/month and equal to 30% cheese whey in the feed) the NPV in all scenarios is well above 0 indicating that the AD system will be profitable and that the projected earnings generated by the system - in present euros - exceeds its anticipated costs.

Figures 5.6a and 5.6b show that at this scenario the cumulative probability to obtain positive NPV is 98.5 % for heat & power recovery and 90% for heat recovery system when 30% of feedstock is cow cheese whey. On the other hand, for 20% of cheese whey in feedstock, the cumulative probability of NPV is negative at 74% and 70% of situations for heat & power recovery and heat recovery system respectively. In all other proportions of cheese whey in the feedstock, the NPV is negative. When comparing the energy recovery system, it is noteworthy to mention that although the capital costs of the heat recovery system are almost 12% less than the heat & power energy recovery system, this second system presents better economic ratios due to capability of generating electricity and selling it to the market at higher prices. It is also worth mentioning that the same as section 5.4.1 to achieve positive results with the heat recovery system, the farm shall be able to use all the net heat produced in the AD system. If the heat production is higher than the heat consumption at farm, the excess heat will be lost, reducing the overall economic sustainability of the system. These results indicate the profitability of investment on AD plant using cheese whey as co-substrate.

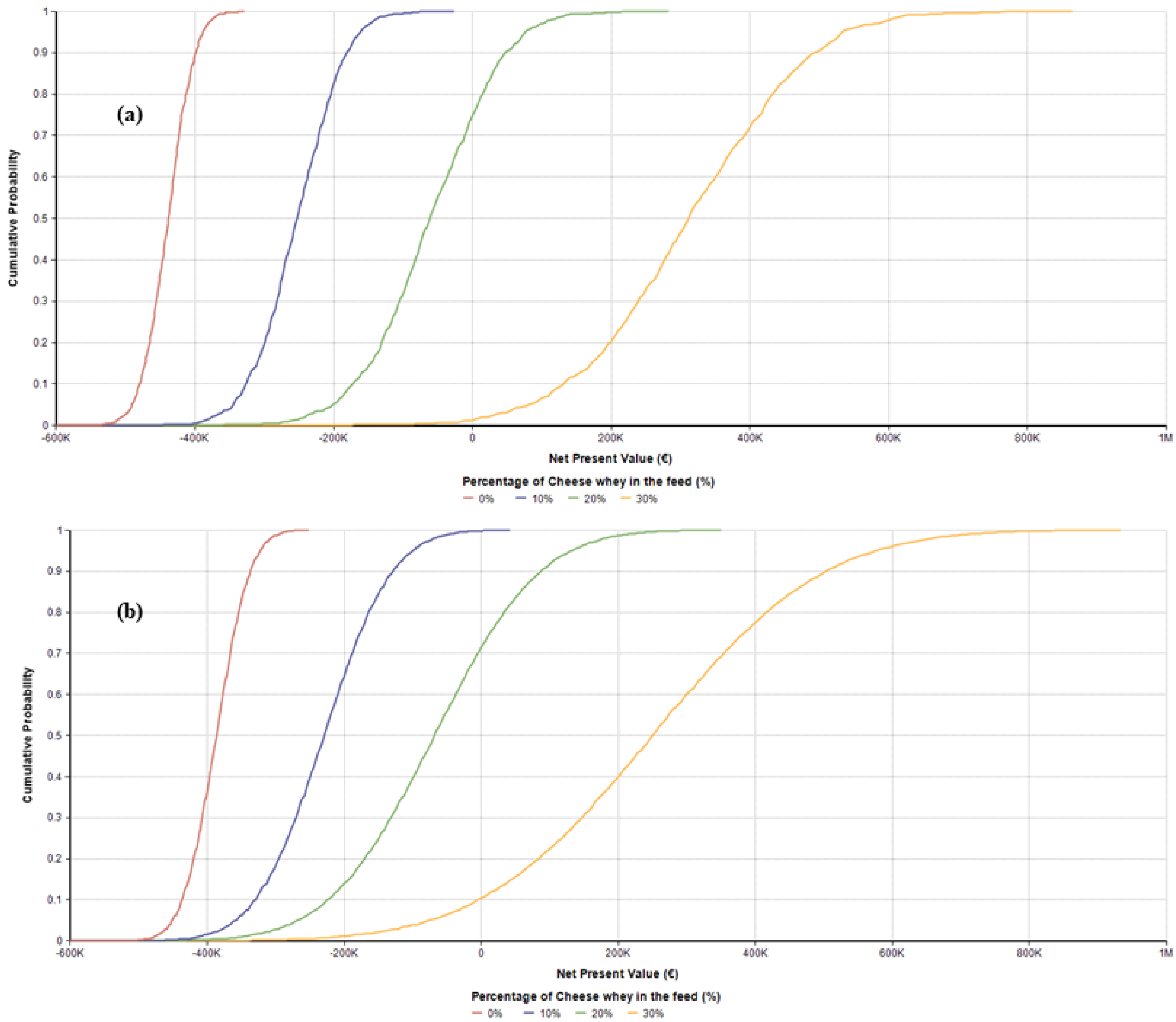


Figure 5. 6 Cumulative probability of net present value for all CW proportions at (a) Heat and power recovery, (b) Heat recovery
Sensitivity analysis

5.3.2.2.Sensitivity analysis

The importance of the critical variables on the economic ratios of the project has been evaluated through a sensitivity analysis. If not explicitly mentioned, the sensitivity scenarios for co-digestion of cow manure + cow cheese whey are carried out with a system working at an OLR of 2.38 kg COD.$m^{-3}\cdot d^{-1}$ and 30% of cheese whey in the feed considering the technical design of system for recovery of heat and electricity (best possible results obtained in the base scenario). A sensitivity analysis for (i) electricity price, (ii) discount rate and (iii) size of the farm and other types of animals and (iv) biogas production has been performed.

Electricity selling price: The result of sensitivity analysis show that the minimum price of selling electricity in which positive net present value can be obtained is 0.08€/KWh. This price is far from the current market prices (0.14€/KWh) and thus it is not expected that change in the electricity market, effect the profitability of system. However, it must be taken into account that the electricity selling price in this study is subsidized due to financial aid of government (74.64€/KWh) and with the real current electricity market prices (65.09€/KWh) the system is not profitable.

Discount rate: The same as section 5.4.1.2. discount rate plays and important role in any economic study and can change dramatically the results obtained in any NPV analysis. In the base scenario the discount rate was considered 7%, however, different discounts rates from 5 to 10 are common in many investment situations (e.g. stock market). Figure 5.7 shows the NPV of RM (0% cheese whey in the feed) and RM + CW systems at different proportions. The results show that even at discount rate of 5% the AD of RM and RM + 10% will have a net loss for the farmers as the NPV is negative. On the other hand, if the system has 20% of cow cheese whey in the feedstock, the NPV becomes positive at discount rate of 5% and almost positive at a discount rate of 6% (5.88) which is slightly below zero. Regarding AD of RM and 30% of CW the system is profitable at all ranges of discount rates which can be translated to secure investment on this scenario under most circumstances.

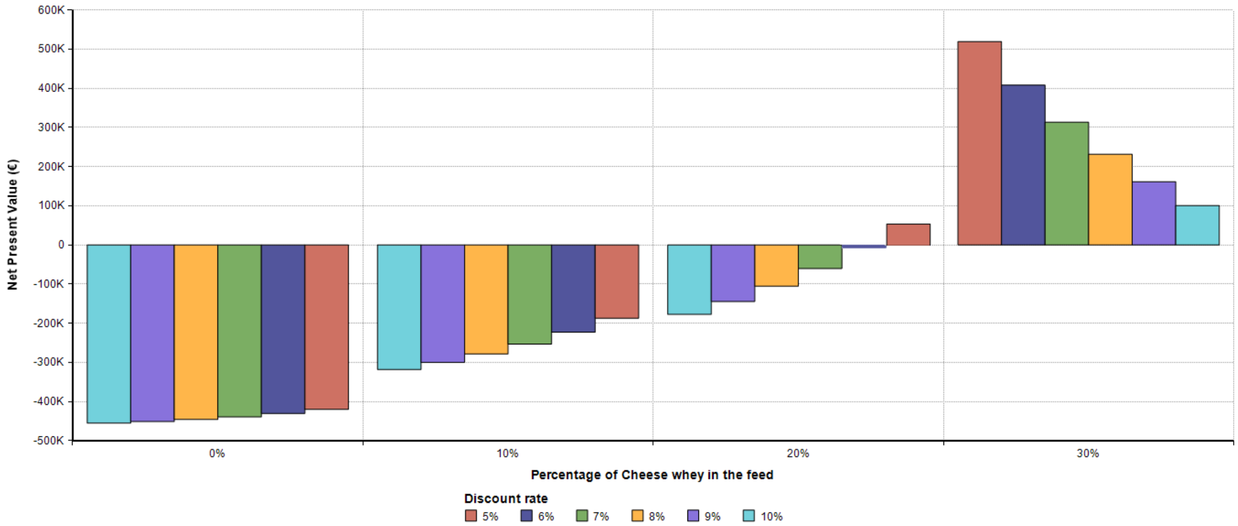


Figure 5. 7 NPV of different scenarios (different cheese whey proportions) at different discount rates

- <u>Farm size and type of animal:</u>

As it was explained in section 5.4.1.2, Anaerobic digestion systems are highly affected from economies of scale making it more difficult to be implemented at small farms. The influence of farm size has been investigated to find the minimum farm size (in adult cattle, Goat and Sheep heads) that makes the whole system profitable.

When considering the minimum farm size needed to make the system profitable, the analysis shows that the minimum number of cow heads (equivalent to the minimum amount of manure needed) in which a positive NPV will be achieved is 126 and 115 with annual revenue of 41,490€ and 30,670€ for the heat & power energy recovery and heat recovery respectively.

An assessment of the minimum farm size of other types of livestock (e.g. goats and sheep) that makes the co-digestion of RM + CW (ratio 70:30) a profitable investment has also been carried out., The economic study shows that the minimum number of goats needed is 1054 goat heads (and an amount of 291.36 m^3 CW/month) and 975 goat heads (and an amount of 269.52 m^3 CW/month) for heat & power recovery and heat recovery systems respectively. In this scenario an annual revenue of 43,070€ and 32,370€ is achieved for both heat & power and heat recovery systems respectively which is equivalent to an IRR of 7% (NPV=0).

Regarding sheep, the minimum number of adult sheep needed to make the co-digestion system profitable is 7512 heads of adult sheep (and an amount of 1,376.4 m^3CW/month). In this scenario annual revenue of 132,100€ is achieved for heat & power recovery system. In case of only heat recovery, the system is not profitable under any conditions. It can be deducted that implementation of AD plant treating sheep manure and sheep cheese whey is only considerable when the farm size is very big and in other circumstances the system will not be profitable.

Biogas production:

In several scientific works higher amounts of biogas are reported when assessing the co-digestion of RM + CW, for example biogas production ranging from 0.24-0.3 $m^3_{biogas}.Kg^{-1}_{COD}$ have been reported. (Rico et al., 2015; Saddoud et al., 2007). These reported values, are close to the theoretical values obtained when using the results obtained in the batch experiments of this work, therefore, another techno-economic assessment of AD system treating cow RM +CW was carried out using data obtained in the batch experiment. Equation 5.5 was used to calculate average of biogas production for each scenario.

$$Y = (M_m \times V_m) + (M_{CW} \times V_{CW}) \quad (5.5)$$

Which Y is the biogas production from anaerobic co-digestion ($m^3_{biogas}.Kg^{-1}{}_{COD}$). M_m is monthly amount of manure in terms of Kg COD that enters the reactor. V_m is volume of manure biogas production ($m^3.Kg^{-1}_{COD}$), M_{cw} is monthly amount of cheese whey enters the reactor (Kg COD) and V_{cw} is biogas produced by cheese whey ($m^3.Kg^{-1}_{COD}$).

The average amount of biogas obtained under this conditions is 0.34 $m^3{}_{biogas}$ $kg^{-1}{}_{COD}$, 0.28 $m^3{}_{biogas}$ $kg^{-1}{}_{COD}$ and 0.21 $m^3{}_{biogas}$ $kg^{-1}{}_{COD}$ respectively for mixing ratios RM:CW of 70:30, 80:20 and 90:10 (v:v). The monthly biogas production increased 80%, 180% and 308% respectively compared with the sole digestion of RM and as expected, with higher biogas productions, the economic ratios have improved greatly and positive NPV (with a discount rate of 7%) are obtained for both heat and heat & power energy recovery systems at all tested RM:CW mixing ratios indicating that the AD system will be profitable and that the projected earnings generated by the system - in present euros - exceeds its anticipated costs. Table 5.6 shows the revenues and the studied economic indices for this sensitivity scenario.

Table 5. 6 Economic performance of system with different proportion of CW at sensitivity scenarios

	RM + 30% CW		RM + 20% CW		RM + 10% CW		RM	
	Heat & power recovery	Heat recovery	Heat & power recovery	Heat recovery	Heat & power recovery	Heat recovery	Heat & power recovery	Heat recovery
Biogas production								
Biogas production ($m^3.Kg^{-1}$ COD)	0.34	0.34	0.28	0.28	0.21	0.21	0.14	0.14
Total biogas production (m^3/month)	40,120	40,120	27,500	27,500	17,680	17,680	9,828	9,828
Energy production								
Biogas calorific value ($MJ \cdot m^{-3}_{biogas}$)	22	22	22	22	22	22	22	22
Gross generated energy (MJ)	882,600	882,600	604,900	604,900	389,000	389,000	216,200	216,200
Net electricity production (kwh/month)	63,740	0	43,690	0	28,090	0	15,620	0
Net heat production (MJ/month)	351,100	615,900	223,600	405,000	124,400	241,000	44,990	109,900
Revenues								
Electricity sell price (€/KWh)	0.14	-	0.14	-	0.14	-	0.14	-
Heat avoided costs (€/MJ)	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025
Electricity revenues (€/year)	107,088	0	73,392	0	47,196	0	26,232	0
Heat avoided costs (€/year)	105,336	134,520	67,176	121,560	37,308	72,312	13,500	32,952
Total revenues (€/year)	212,040	134,160	140,040	121,080	84,108	71,916	39,336	32,556
Net revenue (€/year)*	203,200	125,600	131,400	112,700	75,570	63,600	30,890	24,330
Economic Indices								
NPV	1,629,000	828,600	857,000	742,600	256,200	220,700	NG**	NG**
IRR (%)	34.56	22.5	22.08	22.46	11.89	12.05	1.85	1.46
IPP (years)	4	6	6	6	9	9	21	22

* Net revenue = Total revenue - OPEX cost (from table 5.2)
**NG=Negative

Chapter 6:
Conclusion

In this document, two different experiments have been carried out to treat livestock waste in medium and small size farms. The studied work aimed to promote energy recovery from livestock wastes and agro-industrial by-products at small to medium farms.

- In the first case study of this document, biogas production and biodegradability of raw and briquetted straw as co-substrate with cattle manure was investigated at pilot scale using semi-continuous anaerobic reactors. No difference was observed in biogas production from briquetted and raw straw co-digestion with cattle manure. On the contrary, several operational improvements such as preventing the VS accumulation inside the reactors were achieved in the AD of briquetted straw compared to the AD of raw straw. The specific biogas production per cubic meter of reactor increased from 0.12 $L_{biogas}/L_{reactor}$·d in cattle manure digestion to more than 1.11 $L_{biogas}/L_{reactor}$ during the co-digestion of cattle manure with both briquetted or raw straw. This increase in biogas production can clearly contribute to improve the economic performance of AD reactors at livestock farms.

  Different pre-treatments for anaerobic digestion of wheat straw were investigated in this study as an alternative solution to increase biodegradability of straw. The batch test with alkali-pretreatment showed to be the most effective with 156% increase in the biogas production.

- In the second case study of this document, biogas production and biodegradability of different livestock manure (Cow, Goat and Sheep) as well as their corresponding cheese whey (Cow cheese whey, Goat cheese whey and Sheep cheese whey) was investigated. Anaerobic co-digestion of each livestock manure and cheese whey was also studied in semi-continuous reactors. The highest specific biogas production at proportion of 70% of manure solution and 30% of cheese whey, belonged to anaerobic co-digestion of Cow manure and Cow CW with 1.20 $L_{biogas}/L_{reactor}$

(0.178 L. Kg^{-1}COD), Goat manure and Goat CW with 1.15 $L_{biogas}/L_{reactor}$ (0.211 L.Kg^{-1}COD) and Sheep manure and Sheep CW with 0.78 $L_{biogas}/L_{reactor}$ (0.154 L. Kg^{-1}COD) respectively.

Economic evaluation of installation of AD plant for different scenarios was investigated.

- In both case studies, the result show that Mono digestion of cattle manure is not economically viable at small to medium size farms. However, co-digestion can significantly improve the economic performance of the process.
- The best Positive returns for the first case study of experiments (straw as co-substrate) have been obtained for OLR of 2 kg VS·$m^{-3}_{reactor}$ and better results were obtained when considering heat & power recovery instead of only heat recovery. The sensitivity analysis reveals that systems are highly sensitive to changes on the straw production cost and electricity sell price.

  Sensitivity analysis for chemical pretreatment were also investigated. The results show that the system will be profitable if the price of pretreated straw is at least less than 198 €/ton for alkali pretreatment and 173€/ton for Micro-alkali pretreatment respectively.
- In the second case study of this study (Cheese whey as co-substrate), Economic evaluation of implementation of AD plant was investigated. The best positive returns have been obtained for 30% of cheese whey in the feedstock and when the system is designed to recover heat & power instead of only heat recovery.

  The sensitivity analysis reveals that system is highly sensitive to the farm size and type of livestock manure and cheese whey and discount rate.

Chapter 7:
Bibliography

Akhtar, N., Goyal, D., Goyal, A., 2017. Characterization of microwave-alkali-acid pre-treated rice straw for optimization of ethanol production via simultaneous saccharification and fermentation (SSF). Energy Convers. Manag. 141, 133–144. https://doi.org/10.1016/j.enconman.2016.06.081

Almeida, C.M.R., Santos, F., Ferreira, A.C.F., Lourinha, I., Basto, M.C.P., Mucha, A.P., 2017. Can veterinary antibiotics affect constructed wetlands performance during treatment of livestock wastewater ? Ecol. Eng. 102, 583–588. https://doi.org/10.1016/j.ecoleng.2017.02.035

American public health association, 2017. Standard methods for the examination of water and waste water, 23rd ed. Washington, DC.

Amery, F., 2014. Agricultural phosphorus legislation in Europe.

Anthony Bennett, Frederic Lhoste, Jay Crook, J.P., 2005. The future of small scale dairying. Retrieved from Food and Agriculture Organization of the United Nations: [WWW Document]. URL http://www.fao.org/

Astals, S., Nolla-Ardèvol, V., Mata-Alvarez, J., 2012. Anaerobic co-digestion of pig manure and crude glycerol at mesophilic conditions: Biogas and digestate. Bioresour. Technol. 110, 63–70. https://doi.org/10.1016/j.biortech.2012.01.080

Athanasoulia, E., Melidis, P., Aivasidis, A., 2014. Co-digestion of sewage sludge and crude glycerol from biodiesel production. Renew. Energy 62, 73–78. https://doi.org/10.1016/j.renene.2013.06.040

Bah, H., Zhang, W., Wu, S., Qi, D., Kizito, S., Dong, R., 2014. Evaluation of batch anaerobic co-digestion of palm pressed fiber and cattle manure under mesophilic conditions. Waste Manag. 34, 1984–1991. https://doi.org/10.1016/j.wasman.2014.07.015

Baldasso, C., Barros, T.C., Tessaro, I.C., 2011. Concentration and purification of whey proteins by ultrafiltration. Desalination 278, 381–386. https://doi.org/10.1016/j.desal.2011.05.055

Baldini, C., Bava, L., Zucali, M., Guarino, M., 2018. Milk production Life Cycle Assessment : A comparison between estimated and measured emission inventory for manure handling. Sci. Total Environ. 625, 209–219. https://doi.org/10.1016/j.scitotenv.2017.12.261

Blumenstein, B., Siegmeier, T., Möller, D., 2016. Economics of anaerobic digestion in organic agriculture: Between system constraints and policy regulations. Biomass and Bioenergy 86, 105–119. https://doi.org/10.1016/j.biombioe.2016.01.015

Bowen, E.J., Dol, J., Davenport, R.J., Read, F.L., Curtis, T.P., Curtis, T.P., 2014. Low-temperature limitation of bioreactor sludge in anaerobic treatment of domestic wastewater 1004–1013. https://doi.org/10.2166/wst.2013.821

Carvalheiro, F., Esteves, M.P., Parajó, J.C., Pereira, H., Gírio, F.M., 2004. Production of oligosaccharides by autohydrolysis of brewery's spent grain. Bioresour. Technol. 91, 93–100. https://doi.org/10.1016/S0960-8524(03)00148-2

Carvalheiro, F., Garrote, G., Parajó, J.C., Pereira, H., Gírio, F.M., 2005. Kinetic Modeling of Brewer's Spent Grain Autohydrolysis. Biotechnol. Prog. 21, 233–243. https://doi.org/10.1021/bp049764z

Chau, J., Sowlati, T., Sokhansanj, S., Preto, F., Melin, S., Bi, X., 2009. Techno-economic analysis of wood biomass boilers for the greenhouse industry. Appl. Energy 86, 364–371.

https://doi.org/10.1016/j.apenergy.2008.05.010

Cheng, X.Y., Zhong, C., 2014. Effects of feed to inoculum ratio, co-digestion, and pretreatment on biogas production from anaerobic digestion of cotton stalk. Energy and Fuels 28, 3157–3166. https://doi.org/10.1021/ef402562z

Comino, E., Riggio, V.A., Rosso, M., 2012. Biogas production by anaerobic co-digestion of cattle slurry and cheese whey. Bioresour. Technol. 114, 46–53. https://doi.org/10.1016/j.biortech.2012.02.090

Dareioti, M.A., Kornaros, M., 2015. Anaerobic mesophilic co-digestion of ensiled sorghum, cheese whey and liquid cow manure in a two-stage CSTR system: Effect of hydraulic retention time. Bioresour. Technol. 175, 553–562. https://doi.org/10.1016/j.biortech.2014.10.102

de Wit, J.N., 2001. Lecturer's Handbook on whey and whey products, European Whey Products Asociation.

Delivand, M.K., Barz, M., Gheewala, S.H., Sajjakulnukit, B., 2011. Economic feasibility assessment of rice straw utilization for electricity generating through combustion in Thailand. Appl. Energy 88, 3651–3658. https://doi.org/10.1016/j.apenergy.2011.04.001

Demirbas, A., 2009. Political, economic and environmental impacts of biofuels: A review. Appl. Energy 86, S108–S117. https://doi.org/10.1016/j.apenergy.2009.04.036

Dereli, R.K., van der Zee, F.P., Ozturk, I., van Lier, J.B., 2019. Treatment of cheese whey by a cross-flow anaerobic membrane bioreactor: Biological and filtration performance. Environ. Res. 168, 109–117. https://doi.org/10.1016/j.envres.2018.09.021

EC, 1991. Council directive 96/61/EC concerning integrated pollution prevention and control.

Ekama, G.A., Wentzel, M.C., 2008. Organic Material Removal. Biol. Wastewater Treat. Princ. Model. Des. 53–86.

Ergu, T.H., Tezel, U., Gu, E., Demirer, G.N., 2001. Anaerobic Biotransformation and Methane Generation Potential of 21, 643–650.

Escalante-Hernández, Jaimes-Estévez, J., Humberto, Besson, V., Castro-Molano, L.D.P., 2017. Feasibility of the anaerobic digestion of cheese whey in a Plug Flow Reactor (PFR) under local conditions. Ing. Investig. y Tecnol. 18, 264–277. https://doi.org/10.22201/fi.25940732e.2017.18n3.024

Escalante, H., Castro, L., Amaya, M.P., Jaimes, L., Jaimes-Estévez, J., 2018. Anaerobic digestion of cheese whey: Energetic and nutritional potential for the dairy sector in developing countries. Waste Manag. 71, 711–718. https://doi.org/10.1016/j.wasman.2017.09.026

European Biogas Association, 2017. EBA Statistical Report [WWW Document]. URL http://european-biogas.eu/2017/12/14/eba-statistical-report-2017-published-soon/

European comission, 2014a. Environment Action Programme to 2020 [WWW Document]. URL http://ec.europa.eu/environment/action-programme/

European comission, 2014b. Framework for EU climate and energy policies in the 2020-2030 period [WWW Document]. URL http://data.consilium.europa.eu/doc/document/ST-169-2014-INIT/en/pdf

European comission, 2010. 2020 climate & energy package [WWW Document]. URL https://ec.europa.eu/clima/policies/strategies/2020_en

European Commission - Press release Database, 2018. Statement Europe leads the global clean energy transition: Commission welcomes ambitious agreement on further renewable energy development in the EU [WWW Document]. URL http://europa.eu/rapid/press-release_STATEMENT-18-4155_en.htm

European Commission - Press release Database, 2012. Waste – a short cut to job creation and lower costs [WWW Document]. URL http://europa.eu/rapid/press-release_IP-12-18_en.htm

European CommissionCOM(2005) 666, 2005. Thematic Strategy on the Prevention and Recycling of Waste, Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions. Taking sustainable use of resources forward.

European Environmental Agency (EEA), 2017. Air quality in Europe. Report No 13/2017.

European Parliament, 2017. Circular economy: MEPs back plans to boost recycling and cut landfilling [WWW Document]. URL http://www.europarl.europa.eu/RegData/etudes/BRIE/2017/599288/EPRS_BRI%282017%29599288_EN.pdf

European Parliament, 2016. Waste management in the EU: infographic with facts and figures [WWW Document]. URL http://www.europarl.europa.eu/news/en/headlines/society/20180328STO00751/eu-waste-management-infographic-with-facts-and-figures

European Parliament, 2013. General Union Environment Action Programme to 2020 ‘Living well, within the limits of our planet' [WWW Document]. URL https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32013D1386&from=EN

Eurostat, 2017. Agri-environmental indicator - ammonia emissions [WWW Document]. URL https://ec.europa.eu/eurostat/statistics-explained/index.php/Agri-environmental_indicator_-_ammonia_emissions

Fang, C., Boe, K., Angelidaki, I., 2011. Anaerobic co-digestion of by-products from sugar production with cow manure. Water Res. 45, 3473–3480. https://doi.org/10.1016/j.watres.2011.04.008

FAO, 2017. The state of food and agriculture. Leveraging Food Systems for Inclusive Rural Transition. Rome, Italy.

FAOSTAT, 2017. FAOSTAT Live animals database.

Ferreira, L., Duarte, E., Figueiredo, D., 2012. Utilization of wasted sardine oil as co-substrate with pig slurry for biogas production - A pilot experience of decentralized industrial organic waste management in a Portuguese pig farm. Bioresour. Technol. 116, 285–289. https://doi.org/10.1016/j.biortech.2012.03.063

Ferreira, L.C., Donoso-bravo, A., Nilsen, P.J., Fdz-polanco, F., Pérez-elvira, S.I., 2013. Bioresource Technology Influence of thermal pretreatment on the biochemical methane potential of wheat straw. Bioresour. Technol. 143, 251–257. https://doi.org/10.1016/j.biortech.2013.05.065

Gelegenis, J., Georgakakis, D., Angelidaki, I., Mavris, V., 2007. Optimization of biogas production by co-digesting whey with diluted poultry manure. Renew. Energy 32, 2147–

2160. https://doi.org/10.1016/j.renene.2006.11.015

Ghaly, A.E., 1996. A COMPARATIVE STUDY OF ANAEROBIC DIGESTION OF ACID CHEESE WHEY AND DAIRY MANURE IN A TWO- STAGE REACTOR. Bioresour. Technol. 58, 61–72. https://doi.org/Doi 10.1166/Jnn.2008.037

Girard, M., Nikiema, J., Brzezinski, R., Buelna, G., Heitz, M., 2014. A review of the environmental pollution originating from the piggery industry and of the available mitigation technologies: towards the simultaneous biofiltration of swine slurry and methane. J. Environ. Eng. Sci. 9, 80–92.

Goberna, M., Schoen, M.A., Sperl, D., Wett, B., Insam, H., 2010. Mesophilic and thermophilic co-fermentation of cattle excreta and olive mill wastes in pilot anaerobic digesters. Biomass and Bioenergy 34, 340–346. https://doi.org/10.1016/j.biombioe.2009.11.005

Grinsven, H.J.M. Van, Berge, H.F.M., Dalgaard, T., Fraters, B., Durand, P., Hart, A., Hofman, G., 2012. Management , regulation and environmental impacts of nitrogen fertilization in northwestern Europe under the Nitrates Directive ; a benchmark study 5143–5160. https://doi.org/10.5194/bg-9-5143-2012

Grosser, A., Neczaj, E., Singh, B.R., Almås, R., Brattebø, H., Kacprzak, M., 2017. Anaerobic digestion of sewage sludge with grease trap sludge and municipal solid waste as co-substrates. Environ. Res. 155, 249–260. https://doi.org/10.1016/j.envres.2017.02.007

Hartmann, H., Ahring, B.K., 2005. Anaerobic digestion of the organic fraction of municipal solid waste: Influence of co-digestion with manure. Water Res. 39, 1543–1552. https://doi.org/10.1016/j.watres.2005.02.001

Hassan, M., Ding, W., Umar, M., Rasool, G., 2017. Batch and semi-continuous anaerobic co-digestion of goose manure with alkali solubilized wheat straw: A case of carbon to nitrogen ratio and organic loading rate regression optimization. Bioresour. Technol. 230, 24–32. https://doi.org/10.1016/j.biortech.2017.01.025

He, L., Huang, H., Lei, Z., Liu, C., Zhang, Z., 2014. Enhanced hydrogen production from anaerobic fermentation of rice straw pretreated by hydrothermal technology. Bioresour. Technol. 171, 145–151. https://doi.org/10.1016/j.biortech.2014.08.049

Herrero, M., Henderson, B., Havlík, P., Thornton, P.K., Conant, R.T., Smith, P., Wirsenius, S., Hristov, A.N., Gerber, P., Gill, M., 2016. livestock sector. Nat. Publ. Gr. 6, 452–461. https://doi.org/10.1038/nclimate2925

Hooda, P.S., Edwards, A.C., Anderson, H.A., Miller, A., 2000. A review of water quality concerns in livestock farming areas.

Hou, Y., Bai, Z., Peter, J., Staritsky, I.G., Sikirica, N., Ma, L., Velthof, G.L., Oenema, O., 2016. Feed use and nitrogen excretion of livestock in EU-27. "Agriculture, Ecosyst. Environ. 218, 232–244. https://doi.org/10.1016/j.agee.2015.11.025

J. A. Ogejo, S. Wildeus, P. Knight, R. B. Wilke, 2010. Estimating Goat and Sheep Manure Production and their Nutrient Contribution in the Chesapeake Bay Watershed. Appl. Eng. Agric. 26, 1061–1065. https://doi.org/10.13031/2013.35912

Janczukowicz, W., Zieliński, M., Debowski, M., 2008. Biodegradability evaluation of dairy effluents originated in selected sections of dairy production. Bioresour. Technol. 99, 4199–4205. https://doi.org/10.1016/j.biortech.2007.08.077

Jasko, J., Skripsts, E., Dubrovskis, V., Zabarovskis, E., Kotelenecs, V., 2011. Biogas Production From Cheese Whey in Two Phase. Eng. Rural Dev. 5, 373–376.

Kavacik, B., Topaloglu, B., 2010. Biogas production from co-digestion of a mixture of cheese whey and dairy manure. Biomass and Bioenergy 34, 1321–1329. https://doi.org/10.1016/j.biombioe.2010.04.006

Kim, S., Dale, B.E., 2004. Global potential bioethanol production from wasted crops and crop residues. Biomass and Bioenergy 26, 361–375. https://doi.org/10.1016/j.biombioe.2003.08.002

KIM, T.-H., KIM, J., LEE, M., PARK, C., KIM, S., LEE, J., KIM, S.-W., 2003. Effects of Various Pretreatments for Enhanced Anaerobic Digestion with Waste Activated Sludge. J. Biosci. Bioeng. 95, 271–275. https://doi.org/10.1263/jbb.95.271

Kothari, R., Pandey, A.K., Kumar, S., Tyagi, V. V, Tyagi, S.K., 2014. Different aspects of dry anaerobic digestion for bio-energy : An overview. Renew. Sustain. Energy Rev. 39, 174–195. https://doi.org/10.1016/j.rser.2014.07.011

Kougias, P.G., Boe, K., Angelidaki, I., 2013. Effect of organic loading rate and feedstock composition on foaming in manure-based biogas reactors. Bioresour. Technol. 144, 1–7. https://doi.org/10.1016/j.biortech.2013.06.028

Kusari, S., Zu, S., Ã, M.S., Sukul, P., Lamsho, M., 2009. Metabolism and excretion kinetics of 14 C-labeled and non-labeled difloxacin in pigs after oral administration , and antimicrobial activity of manure containing difloxacin and its metabolites $, $$ 109, 225–231. https://doi.org/10.1016/j.envres.2008.12.007

Lee, D.H., Behera, S.K., Kim, J.W., Park, H.S., 2009. Methane production potential of leachate generated from Korean food waste recycling facilities: A lab-scale study. Waste Manag. 29, 876–882. https://doi.org/10.1016/j.wasman.2008.06.033

Leip, A., Billen, G., Garnier, J., Grizzetti, B., Lassaletta, L., Reis, S., Simpson, D., Sutton, M.A., Vries, W. de, Weiss, F., Westhoek, H., 2015. Impacts of European livestock production : nitrogen , sulphur , phosphorus and greenhouse gas emissions , land-use , water eutrophication and biodiversity Impacts of European livestock production : nitrogen , sulphur , phosphorus and greenhouse gas emissi.

Li, F., Cheng, S., Yu, H., Yang, D., 2016. Waste from livestock and poultry breeding and its potential assessment of biogas energy in rural China. J. Clean. Prod. 126, 451–460. https://doi.org/10.1016/j.jclepro.2016.02.104

Li, R.P., Chen, S.L., Li, X.J., Lar, J.S., He, Y.F., Zhu, B.N., 2009. Anaerobic Codigestion of Kitchen Waste with Cattle Manure for Biogas Production. Energy & Fuels 23, 2225–2228. https://doi.org/10.1021/ef8008772

Li, X., Li, L., Zheng, M., Fu, G., Lar, J.S., 2009. Anaerobic co-digestion of cattle manure with corn stover pretreated by sodium hydroxide for efficient biogas production. Energy and Fuels 23, 4635–4639. https://doi.org/10.1021/ef900384p

Li, Y., Chen, Y., Wu, J., 2019. Enhancement of methane production in anaerobic digestion process: A review. Appl. Energy 240, 120–137. https://doi.org/10.1016/j.apenergy.2019.01.243

Lin, L., Xu, F., Ge, X., Li, Y., 2018. Improving the sustainability of organic waste management practices in the food-energy-water nexus: A comparative review of anaerobic digestion and composting. Renew. Sustain. Energy Rev. 89, 151–167. https://doi.org/10.1016/j.rser.2018.03.025

Mallin, M.A., Mciver, M.R., Robuck, A.R., Dickens, A.K., 2015. Industrial Swine and Poultry Production Causes Chronic Nutrient and Fecal Microbial Stream Pollution. https://doi.org/10.1007/s11270-015-2669-y

Mancini, G., Papirio, S., Lens, P.N.L., Esposito, G., 2018. Increased biogas production from wheat straw by chemical pretreatments. Renew. Energy 119, 608–614. https://doi.org/10.1016/j.renene.2017.12.045

Mao, C., Feng, Y., Wang, X., Ren, G., 2015. Review on research achievements of biogas from anaerobic digestion. Renew. Sustain. Energy Rev. 45, 540–555. https://doi.org/10.1016/j.rser.2015.02.032

Maragkaki, A.E., Fountoulakis, M., Gypakis, A., Kyriakou, A., Lasaridi, K., Manios, T., 2017. Pilot-scale anaerobic co-digestion of sewage sludge with agro-industrial by-products for increased biogas production of existing digesters at wastewater treatment plants. Waste Manag. 59, 362–370. https://doi.org/10.1016/j.wasman.2016.10.043

Martinez, J., Dabert, P., Barrington, S., Burton, C., 2009. Bioresource Technology Livestock waste treatment systems for environmental quality , food safety , and sustainability. Bioresour. Technol. 100, 5527–5536. https://doi.org/10.1016/j.biortech.2009.02.038

Martinez, J.L., 2009. Environmental pollution by antibiotics and by antibiotic resistance determinants. Environ. Pollut. 157, 2893–2902. https://doi.org/10.1016/j.envpol.2009.05.051

Matheri, A.N., Belaid, M., Seodigeng, T., Ngila, C.J., 2016. Modelling the kinetic of biogas production from co-digestion of pig waste and grass clippings. Lect. Notes Eng. Comput. Sci. 2224.

McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass. Bioresour. Technol 83, 37–46. https://doi.org/10.1016/S0960-8524(01)00118-3

Molaey, R., Bayrakdar, A., Sürmeli, R.Ö., Çalli, B., 2018. Anaerobic digestion of chicken manure: Mitigating process inhibition at high ammonia concentrations by selenium supplementation. Biomass and Bioenergy 108, 439–446. https://doi.org/10.1016/j.biombioe.2017.10.050

Neshat, S.A., Mohammadi, M., Najafpour, G.D., Lahijani, P., 2017. Anaerobic co-digestion of animal manures and lignocellulosic residues as a potent approach for sustainable biogas production. Renew. Sustain. Energy Rev. 79, 308–322. https://doi.org/10.1016/j.rser.2017.05.137

Nolan, A., Mc Donnell, K., Devlin, G.J., Carroll, J.P., Finnan, J., 2010. Economic Analysis of Manufacturing Costs of Pellet Production in the Republic of Ireland Using Non-Woody Biomass~!2009-07-23~!2009-12-22~!2010-03-02~! Open Renew. Energy J. 3, 1–11. https://doi.org/10.2174/1876387101003010001

Pajpai, P., 2017. Process Parameters Affecting Anaerobic Digestion, in: Anaerobic Technology in Pulp and Paper Industry. SpringerBriefs in Applied Sciences and Technology, pp. 978–981. https://doi.org/10.1007/978-981-10-4130-3

Pellera, F., Gidarakos, E., 2017. Anaerobic digestion of solid agroindustrial waste in semi-continuous mode : Evaluation of mono-digestion and co-digestion systems. Waste Manag.

68, 103–119. https://doi.org/10.1016/j.wasman.2017.06.026

Poggi-Varaldo, H., Medina, E., Fernandez-Villagomez, G., Caffarel-Mendez, S., 1997. Inhibition of mesophilic solid substrate anaerobic digestion (DASS) by ammonia-rich wastes. Proc. 52nd Purdue Ind. Waste Conf. West Lafayette,.

Ponsá, S., 2010. Different Indices to Express Biodegradability in Organic Solid Wastes. Universitat Autònoma de Barcelona, Spain.

Ponsá, S., Ferrer, I., Vázquez, F., Font, X., 2008a. Optimization of the hydrolytic-acidogenic anaerobic digestion stage (55 °C) of sewage sludge: Influence of pH and solid content. Water Res. 42, 3972–3980. https://doi.org/10.1016/j.watres.2008.07.002

Ponsá, S., Gea, T., Alerm, L., Cerezo, J., Sánchez, A., 2008b. Comparison of aerobic and anaerobic stability indices through a MSW biological treatment process. Waste Manag. 28, 2735–2742. https://doi.org/10.1016/j.wasman.2007.12.002

Ponsá, S., Gea, T., Sánchez, A., 2010. Different Indices to Express Biodegradability in Organic Solid Wastes. PhD thesis. https://doi.org/10.2134/jeq2009.0294

Ponsá, S., Puyuelo, B., Gea, T., Sánchez, A., 2011. Modelling the aerobic degradation of organic wastes based on slowly and rapidly degradable fractions. Waste Manag. 31, 1472–1479. https://doi.org/10.1016/j.wasman.2011.02.013

Prazeres, A.R., Carvalho, F., Rivas, J., 2012. Cheese whey management: A review. J. Environ. Manage. 110, 48–68. https://doi.org/10.1016/j.jenvman.2012.05.018

Puñal, A., Trevisan, M., Rozzi, A., Lema, J.M., 2000. Influence of C:N ratio on the start-up of up-flow anaerobic filter reactors. Water Res. 34, 2614–2619. https://doi.org/10.1016/S0043-

1354(00)00161-5

Rico, C., Muñoz, N., Rico, J.L., 2015. Anaerobic co-digestion of cheese whey and the screened liquid fraction of dairy manure in a single continuously stirred tank reactor process: Limits in co-substrate ratios and organic loading rate. Bioresour. Technol. 189, 327–333. https://doi.org/10.1016/j.biortech.2015.04.032

Riggio, V.A., Comino, E., Rosso, M., 2015. Above ground part of common reed to enhance anaerobic co-digestion of farm biomasses: Potential, monitoring and efficiency. Ecol. Eng. 79, 35–41. https://doi.org/10.1016/j.ecoleng.2015.01.015

Rijal, B., Igathinathane, C., Karki, B., Yu, M., Pryor, S.W., 2012. Combined effect of pelleting and pretreatment on enzymatic hydrolysis of switchgrass. Bioresour. Technol. 116, 36–41. https://doi.org/10.1016/j.biortech.2012.04.054

Risberg, K., Sun, L., Levén, L., Jarle, S., Schnürer, A., 2013. Bioresource Technology Biogas production from wheat straw and manure – Impact of pretreatment and process operating parameters. Bioresour. Technol. 149, 232–237. https://doi.org/10.1016/j.biortech.2013.09.054

Robra, S., Serpa da Cruz, R., de Oliveira, A.M., Neto, J.A.A., Santos, J. V., 2010. Generation of biogas using crude glycerin from biodiesel production as a supplement to cattle slurry. Biomass and Bioenergy 34, 1330–1335. https://doi.org/10.1016/j.biombioe.2010.04.021

Saddoud, A., Hassaïri, I., Sayadi, S., 2007. Anaerobic membrane reactor with phase separation for the treatment of cheese whey. Bioresour. Technol. 98, 2102–2108. https://doi.org/10.1016/j.biortech.2006.08.013

Shen, F., Li, H., Wu, X., Wang, Y., Zhang, Q., 2018. Effect of organic loading rate on anaerobic co-digestion of rice straw and pig manure with or without biological pretreatment. Bioresour. Technol. 250, 155–162. https://doi.org/10.1016/j.biortech.2017.11.037

Silvestre, G., Illa, J., Fernández, B., Bonmatí, A., 2014. Thermophilic anaerobic co-digestion of sewage sludge with grease waste: Effect of long chain fatty acids in the methane yield and its dewatering properties. Appl. Energy 117, 87–94. https://doi.org/10.1016/j.apenergy.2013.11.075

Singh, J., Panesar, B.S., Sharma, S.K., 2010. A mathematical model for transporting the biomass to biomass based power plant. Biomass and Bioenergy 34, 483–488. https://doi.org/10.1016/j.biombioe.2009.12.012

Smithers, G.W., 2008. Whey and whey proteins-From “gutter-to-gold.” Int. Dairy J. 18, 695–704. https://doi.org/10.1016/j.idairyj.2008.03.008

Song, Y., Kwon, S., Woo, J., 2004. Mesophilic and thermophilic temperature co-phase anaerobic digestion compared with single-stage mesophilic- and thermophilic digestion of sewage sludge 38, 1653–1662. https://doi.org/10.1016/j.watres.2003.12.019

Sun, C., Cao, W., Banks, C.J., Heaven, S., Liu, R., 2016. Bioresource Technology Biogas production from undiluted chicken manure and maize silage : A study of ammonia inhibition in high solids anaerobic digestion. Bioresour. Technol. 218, 1215–1223. https://doi.org/10.1016/j.biortech.2016.07.082

Tullo, E., Finzi, A., Guarino, M., 2019. Review : Environmental impact of livestock farming and Precision Livestock Farming as a mitigation strategy. Sci. Total Environ. 650, 2751–2760. https://doi.org/10.1016/j.scitotenv.2018.10.018

Vivekanand, V., Mulat, D.G., Eijsink, V.G.H., Horn, S.J., 2018. Synergistic effects of anaerobic co-digestion of whey, manure and fish ensilage. Bioresour. Technol. 249, 35–41. https://doi.org/10.1016/j.biortech.2017.09.169

Wang, D., Huang, H., Shen, F., Yang, G., Zhang, Y., Deng, S., Zhang, J., Zeng, Y., Hu, Y., 2016. Effects of biomass densification on anaerobic digestion for biogas production. RSC Adv. 6, 91748–91755. https://doi.org/10.1039/C6RA17298A

Wang, X., Li, Z., Bai, X., Zhou, X., Cheng, S., Gao, R., Sun, J., 2018. Study on improving anaerobic co-digestion of cow manure and corn straw by fruit and vegetable waste: Methane production and microbial community in CSTR process. Bioresour. Technol. 249, 290–297. https://doi.org/10.1016/j.biortech.2017.10.038

Webb, J., Menzi, H., Pain, B.F., Misselbrook, T.H., Da, U., 2005. Managing ammonia emissions from livestock production in Europe 135, 399–406. https://doi.org/10.1016/j.envpol.2004.11.013

Westerholm, M., Hansson, M., Schnürer, A., 2012. Improved biogas production from whole stillage by co-digestion with cattle manure. Bioresour. Technol. 114, 314–319. https://doi.org/10.1016/j.biortech.2012.03.005

Wu, X., Yao, W., Zhu, J., Miller, C., 2010. Biogas and CH4productivity by co-digesting swine manure with three crop residues as an external carbon source. Bioresour. Technol. 101, 4042–4047. https://doi.org/10.1016/j.biortech.2010.01.052

Xavier, C.A.N., Moset, V., Wahid, R., Møller, H.B., 2015. The efficiency of shredded and briquetted wheat straw in anaerobic co-digestion with dairy cattle manure. Biosyst. Eng. 139, 16–24. https://doi.org/10.1016/j.biosystemseng.2015.07.008

Yadvika, Santosh, Sreekrishnan, T.R., Kohli, S., Rana, V., 2004. Enhancement of biogas production from solid substrates using different techniques — a review 95, 1–10. https://doi.org/10.1016/j.biortech.2004.02.010

Yang, J., Wang, D., Luo, Z., Zeng, W., 2019. Anaerobic mono-digestion of pig manure in a leach bed coupled with a methanogenic reactor: Effects of the filter media. J. Clean. Prod. 234, 1094–1101. https://doi.org/10.1016/j.jclepro.2019.06.054

Yang, L., Xu, F., Ge, X., Li, Y., 2015. Challenges and strategies for solid-state anaerobic digestion of lignocellulosic biomass. Renew. Sustain. Energy Rev. 44, 824–834. https://doi.org/10.1016/j.rser.2015.01.002

Yen, H.W., Brune, D.E., 2007. Anaerobic co-digestion of algal sludge and waste paper to produce methane. Bioresour. Technol. 98, 130–134. https://doi.org/10.1016/j.biortech.2005.11.010

Yue, Y., Lin, Q., Xu, Y., Li, G., Zhao, X., 2017. Slow pyrolysis as a measure for rapidly treating cow manure and the biochar characteristics. J. Anal. Appl. Pyrolysis 124, 355–361. https://doi.org/10.1016/j.jaap.2017.01.008

Zhang, L., Lee, Y., Jahng, D., 2011. Bioresource Technology Anaerobic co-digestion of food waste and piggery wastewater : Focusing on the role of trace elements. Bioresour. Technol. 102, 5048–5059. https://doi.org/10.1016/j.biortech.2011.01.082

Zhang, P., Chen, Y., Zhou, Q., 2009. Waste activated sludge hydrolysis and short-chain fatty acids accumulation under mesophilic and thermophilic conditions: Effect of pH. Water Res. 43, 3735–3742. https://doi.org/10.1016/j.watres.2009.05.036

Zhang, T., Song, Z., Ren, G., Han, X., Liu, L., Yang, G., Feng, Y., 2013. Biogas Production by Co-Digestion of Goat Manure with Three Crop Residues. PLoS One 8, e66845. https://doi.org/10.1371/journal.pone.0066845

Zhang, Y., Sun, W., Wang, H., Geng, A., 2013. Polyhydroxybutyrate production from oil palm empty fruit bunch using bacillus megaterium R11. Bioresour. Technol. 147, 307–314. https://doi.org/10.1016/j.biortech.2013.08.029

Zheng, Y., Zhao, J., Xu, F., Li, Y., 2014. Pretreatment of lignocellulosic biomass for enhanced biogas production. Prog. Energy Combust. Sci. 42, 35–53. https://doi.org/10.1016/j.pecs.2014.01.001

Zhou, X., Hua, X., Huang, L., Xu, Y., 2019. Bio-utilization of cheese manufacturing wastes (cheese whey powder) for bioethanol and specific product (galactonic acid) production via a two-step bioprocess. Bioresour. Technol. 272, 70–76. https://doi.org/10.1016/j.biortech.2018.10.001

Zhou, Y., Li, C., Nges, I.A., Liu, J., 2017. The effects of pre-aeration and inoculation on solid-state anaerobic digestion of rice straw. Bioresour. Technol. 224, 78–86. https://doi.org/10.1016/j.biortech.2016.11.104