Universidad de Valladolid

ESCUELA DE INGENIERÍAS INDUSTRIALES

DEPARTAMENTO DE INGENIERÍA QUÍMICA Y TENCNOLOGÍA DEL MEDIO AMBIENTE

TESIS DOCTORAL:

PRETREATMENT TECHNOLOGIES TO ENHANCE SOLID WASTES ANAEROBIC DIGESTION

Presentada por Raúl Cano Herranz para optar al grado de doctor por la Universidad de Valladolid

Dirigida por:
María Fernández-Polanco Iñiguez de la Torre

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Memoria para optar al grado de Doctor,

presentada por el Ingeniero Químico:

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Valladolid, Febrero de 2014

UNIVERSIDAD DE VALLADOLID

ESCUELA DE INGENIERÍAS INDUSTRIALES

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La presente tesis doctoral queda registrada en el folio número _______ del correspondiente libro de registro número _______________________

Valladolid, a ______ de________________ de 2014

Fdo. El encargado del registro

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Certifica que:

RAÚL CANO HERRANZ ha realizado bajo su dirección el trabajo *"Pretreatment technologies to enhance solid wastes anaerobic digestion"*, en el Departamento de Ingeniería Química y Tecnología del Medio Ambiente de la Escuela de Ingenierías Industriales de la Universidad de Valladolid. Considerando que dicho trabajo reúne los requisitos para ser presentado como Tesis Doctoral expresan su conformidad con dicha presentación.

Valladolid, a ______ de_______________ de 2014

Fdo. María Fernández-Polanco Iñiguez de la Torre

Reunido el tribunal que ha juzgado la Tesis Doctoral titulada *"Pretreatment technologies to enhance solid wastes anaerobic digestion"* presentada por el Ingeniero Químico Raúl Cano Herranz y en cumplimiento con lo establecido por el Real Decreto 99/2011 de 28 de enero de 2011 acuerda conceder por_______________ la calificación de ________________________.

Valladolid, a ______ de_______________ de 2014

PRESIDENTE SECRETARIO

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AGRADECIMIENTOS

En primer lugar agradezco a los dos proyectos que han financiado la investigación que he desarrollado en la Universidad de Valladolid, sin los cuales la Tesis no hubiera salido adelante: Alliance R+i, con todos sus respectivos socios; Topbio y todo el personal de Urbaser que ha participado en el proyecto.

A mi directora de tesis, María Fernández-Polanco Íñiguez de la Torre, por toda su dedicación y confianza en mí que ha tenido durante todos estos años guiándome y ayudándome.

Al grupo de investigación de medioambiente del Departamento de Ingeniería Química y Tecnología del Medioambiente de la Universidad de Valladolid, por haberme dado la oportunidad de trabajar en un ambiente único rodeado de la mejor gente, tanto académica como personalmente. Agradezco especialmente la ayuda de Fernando Fernández-Polanco, Sara Isabel Pérez Elvira y Raúl Muñoz por el apoyo personal y la ayuda profesional que me han brindado para la consecución de la tesis. Gracias también a todo el equipo de técnicos (especialmente de análisis de laboratorio) por toda la dedicación, paciencia y trabajo que han dedicado. Y por supuesto a todos mis compañeros de laboratorio que han pasado por mi lado durante todo este tiempo dándome ganas de trabajar, buenos momentos y de los que he aprendido tanto: Ana, inigualable compañera de trabajo y de tesis, Jose, Chasco, Sergio, Joao, Iris, Cati, Marta, Ieva, Jaime, Roberto, Natalia, Cintia, Lara, Raquel, Sara, Silvia, Araceli, Jose María, Guillermo, Juan Carlos, Ester, Isra, Elisa, Eva, Andrea, Laura, Maru…

También quiero agradecer todo el apoyo recibido durante estos años de mis amigos que no pertenecen al ámbito profesional: amigos de La Huerta, viejos IQs y antiguos compañeros de carrera, compañeros de alemán, a los componentes de *the Rock and Billy Band*, a los de la caña de la montaña… y por supuesto a Vir.

Por último, gracias a toda mi familia, especialmente a mis padres y a mi hermano Alberto.

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LIST OF ABBREVIATIONS AND SYMBOLS

α: co-digestion factor
λ: lag-phase parameter (days) from Gompertz model
φ: Gompertz parameters
τ: shear stress (N/m^2)
γ: shear rate (s^{-1})
A: area
ANOVA: Analyses of variance
B: calculated methane production ($mLCH_4/gVSin$) from Gompertz model
B_{exp}: consumption velocity obtained from measurements
B_m: corresponding velocity calculated by the model
BMP: Biological Methane Potential
COD: Chemical Oxygen Demand
CODs: soluble Chemical Oxygen Demand
CODt: total Chemical Oxygen Demand
CST: Capillary Suction Time
DAF: Dissolved Air Flotation
FC: Filtration Constant
FID: flame ionization detector
FO: First order kinetics
HRT: Hydraulic Retention Time
LCFA: long chain fatty acids
LF: Logistic function
MG: Modified Gompertz equation
MSW: Municipal Solid Waste
N: number of measurements
OFMSW: Organic Fraction Municipal Solid Waste
P: maximum biogas production parameter ($mLCH_4/gVSin$) from Gompertz model
R^2: correlation factor
R_m: methane yield rate parameter ($mLCH_4/gVS/d$) from Gompertz model
SD: Standard deviation
SF: solubilisation factor
TCD: thermal conductivity detector
TF: Transference function
TH: Thermal Hydrolysis
TKN: Total Kjeldahl Nitrogen
TS: Total Solids
V: Volume
VFA: Volatile Fatty Acids
VS: Volatile Solids
WWTP: Waste Water Treatment Plant

SUMMARY

Anaerobic digestion is a process that produces *green* energy and offers an opportunity to integrate biowaste and bioenergy sectors in a simple and conventional unit; then, it has nowadays a wide range of applications and possibilities due to the higher and higher importance of environmental concerns all over the world. This process is therefore a growing sector which must be deeply investigated in order to be optimized in full-scale plants. In order to accelerate the hydrolysis process when digesting solid wastes, pretreatments are applied before anaerobic digestion. These technologies are based on the solubilisation of organic matter by mechanical, chemicals, thermal or biological processes. Therefore, pretreatments will directly influence the kinetics of the process and the methane potential of the substrates leading to lower retention times in digesters and higher biogas productions, at the same time of improving the digestate properties. Pretreatment technologies have been widely tested with sewage sludge and even applied in full-scale continuous processes in several WWTP. Nevertheless, in the area of solid wastes they have been hardly studied and need further research for its implementation in waste treatment plants.

The main objective of the thesis is to enhance solid wastes anaerobic digestion by pretreatment technologies. To that end, biochemical methane potential tests, pretreatment techniques, hydrodynamic tests, modelling tools among others are the main methodologies to study the effect of pretreatments on different solid wastes. Six different solid substrates are studied (some of them together in co-digestion trials): thickened sewage sludge from a municipal WWTP, a pre-selected municipal solid waste (MSW) from a treatment plant, the organic fraction of MSW (synthetic mixture), grease waste from a WWTP, spent grain from brewery industry and cow manure from slaughterhouse. Three disintegration technologies have been tested as pretreatment: thermal hydrolysis, cavitations by ultrasounds and an enzymatic treatment.

Among the studied pretreatment technologies, thermal hydrolysis has presented the best results showing a high potential to be implemented in a full-scale process. First, it has improved significantly methane productions (over 30%) and kinetics (even double) of substrates which have a high fibre content (MSW, spent grain, cow manure) or microbial cellular material (biological sewage sludge). However, it has not shown remarkable effects in substrates rich in lipids (grease waste) or with a high content of easily degradable carbohydrates (synthetic OFMSW). Moreover, it improves the rheology in the digester and digestates dewaterability, reducing associate costs and digestate management costs. As well, thermal hydrolysis presents energy self-sufficiency since it has a high potential to be implemented with full energy integration thanks to the recovery of heat from the biogas engine to generate steam. In fact, thermal hydrolysis can enhance up to 40% the incomes of the digestion plant, even doubling them when digestate management costs are considered. In a full-scale MSW treatment plant of 30000t/year, a thermal hydrolysis plant (which optimum conditions are 15 minutes hydrolysis time at 150ºC) would lead to net benefits of almost 0.5M€/year.

On the other hand, the application of pretreatments to co-digestion processes with sewage sludge has shown interesting perspectives in view of optimizing anaerobic digesters in WWTP. The use of grease waste (also from WWTP) as co-substrate has lead to important advantages concerning management costs and its co-digestion with sludge has been enhanced by thermal hydrolysis when tested in lab-scale semi-continuous reactors.

RESUMEN

La digestión anaerobia es un proceso que produce energía *verde* y ofrece una oportunidad para integrar el sector de los bioresiduos con el de la bioenergía en una unidad simple y convencional; por ello, tiene hoy en día un amplio rango de aplicaciones y posibilidades debido a la creciente importancia de las preocupaciones medioambientales en todo el mundo. Este proceso es por lo tanto un sector en crecimiento que debe ser investigado en profundidad para que sea optimizado en procesos a gran escala. Con el fin de acelerar el proceso de hidrólisis de la digestión de residuos sólidos, se aplican pretratamientos como etapa previa a la digestión anaerobia. Estas tecnologías se basan en la solubilización de la materia orgánica mediante procesos mecánicos, químicos, térmicos o biológicos. Por lo tanto, los pretratamientos influirán directamente en la cinética del proceso y en el potencial metanogénico de los sustratos, obteniéndose menores tiempos de retención en los digestores y mayores producciones de biogás, y mejorando a su vez las propiedades de los digestatos. Las tecnologías de pretratamiento se han estudiado ampliamente con lodos de depuradora y han sido incluso aplicados en procesos continuos a gran escala en numerosas EDAR. Sin embargo, en el sector de los residuos sólidos, no han sido apenas estudiados y necesitan mayor investigación para su implementación en plantas de tratamiento de residuos.

El principal objetivo de esta tesis es mejorar la digestión anaerobia mediante tecnologías de pretratamiento. Para ello, los métodos empleados para estudiar el efecto de los pretratamientos en diferentes residuos sólidos son: ensayos de biodegradabilidad, técnicas de pretratamiento, pruebas hidrodinámicas, herramientas de modelado, entre otros. Se estudian seis residuos sólidos (algunos de ellos juntos en ensayos de co-digestión): lodos de depuradora espesado de una EDAR municipal, un residuo sólido urbano (RSU) preseleccionado de una planta de tratamiento, la fracción orgánica de un RSU (mezcla sintética), residuo de grasa de EDAR, bagazo cervecero de una planta industrial y estiércol vacuno de matadero. Se ensayan tres técnicas de desintegración como pretratamientos: la hidrólisis térmica, las cavitaciones por ultrasonidos y un tratamiento enzimático.

Entre las tecnologías de pretratamiento estudiadas, la hidrólisis térmica ha presentado los mejores resultados, mostrando un gran potencial para ser incorporada en procesos a gran escala. Mejora significativamente las producciones de metano (por encima del 30%) y las cinéticas (incluso dobles) de los sustratos que tienen un gran contenido en fibra (RSU, bagazo, estiércol) o material celular microbiano (lodo secundario de depuradora). Sin embargo, no ha mostrado efectos notables en sustratos ricos en lípidos (grasa) o con un gran contenido en carbohidratos fácilmente biodegradables (FORSU sintética). Además, mejora la rheología del digestor y la deshidratabilidad del digestato, reduciendo costes asociados y de gestión del digestato. También, la hidrólisis térmica presenta autosuficiencia energética ya que tiene un elevado potencial para ser implementado con una integración energética completa gracias a la recuperación de calor en el motor de biogás para generar vapor. De hecho, la hidrólisis térmica puede incrementar hasta un 40% los beneficios de una planta de digestión, incluso duplicándolos si se consideran los costes de gestión del digestato. En una planta real de RSU de 30000t/año, una planta de hidrólisis térmica (cuyas condiciones óptimas de operación son 15 minutos de tiempo de hidrólisis a 150ºC) generaría unos beneficios netos de casi 0.5M€/año.

Por otro lado, la aplicación de pretratamientos a procesos de co-digestión con lodos de depuradora ha mostrado perspectivas prometedoras en vistas a optimizar los digestores anaerobios en las EDAR. La utilización de grasa (también de EDAR) como co-sustrato conlleva a ventajas importantes en cuanto a costes de gestión y su co-digestión con lodos ha sido mejorada mediante el pretratamiento de hidrólisis térmica en reactores semi-continuos a escala laboratorio.

INTRODUCTION

1. Waste problem

The total waste generation in the European Union amounts to 2505 Mt/year (Eurostat, 2010), what supposes a personal production close to 5 t/inhabitant/year. Analyzing the figures from Table 1, where the waste production is referred by sectors, it is remarkable that over 60% of the total waste comes from the mining and construction sector, which is mineral waste. However, excluding this main contribution of mineral waste, the waste production drops down to 927 Mt/year (equivalent to 1.8 t/inhabitant/year), which is still a substantial amount that has to be properly managed.

Economic sector	Production (Mt/year)	Contribution (%)
Agriculture, forestry, fishing	39.4	1.6
Mining	671.8	26.8
Manufacturing	275.6	11.0
Energy	86.0	3.4
Construction	859.7	34.3
Other activities	354.2	14.1
Households	218.6	8.7
TOTAL	2505.4	100

Table 1. Waste production by sectors (Eurostat 2010)

The waste generation, excluding major mineral waste, has been steadily decreasing by 19.8% between 2004 and 2010. By contrast, waste generation from the wastewater management sector saw rapid growth, rising by 44.5% over the same period (in Spain, sewage sludge production surpasses 1.2 Mt/year (Eurostat, 2012). Considering municipal solid wastes (MSW), after a slight increase from 2004 until 2008, the quantity of waste generated by households was unchanged in 2010, just accounting to 8.7% of the total production. In fact, MSW production in the European Union (EU-27) in 2010 amounts to 251 Mt/year, equivalent to 502 kg/inhabitant/year (in Spain this figure is a bit higher: 535 kg/inhabitant/year). MSW are those generated in the activities of urban areas, such as homes, offices, shops or other services. In modern societies, the treatment of MSW generated as a result of a high consumption of products has become a significant problem. This problem is due to factors such as the rapid population growth, the concentration of population in the cities or the use of material goods of rapid aging. This situation presents at the same time an opportunity to develop clean technologies based on energy recovery from these wastes, such as anaerobic digestion.

On the other hand, it is remarkable in Table 1 the scarce contribution of the agricultural sector, with just a 1.6% of the total waste production. The reason is because manure and slurry wastes were excluded in this statistic, which entire EU production available for manure processing is estimated to 1400 Mt/year (Inventory of manure processing activities in Europe, 2011). Manure is usually used for land application as fertilizer by farmers, but sometimes livestock farms do not have the land, equipment or time to recycle all of the manure that is generated; then, manure has to be properly treated and managed. In the European Union, cattle are the main source of manure production with more than 50% in most of the countries, followed by pig slurry (Eurostat, 2011a). These wastes present as well high potentials to be degraded anaerobically in order to recover its bioenergy.

2. Legislation

In the last four decades, the rise of such problems derived from a society based on a high resource and energy consumption (and waste generation) and an increase of an environmental awareness in societies and policies has lead to new legislative frameworks concerning environmental implications.

In 1972, an international conference on the environment took place in Stockholm leading to the first body of 'soft law' in international environmental affairs: Stockholm declaration on the Human Environment and Principles. One year later, in 1973, the first Environmental Action Programme (EAP) from the European Environmental Agency (EEA) defined the future direction of European Union (EU) policy in the environmental field and set specific proposals that the Commission intended to put forward over the next years. The fifth EAP (1993-2000) introduced the concept of "sustainable development". Nowadays, while the sixth EAP (2002-2012) has expired, a proposal for a new EAP (seventh) is being elaborated to be implemented up to 2020.

Concerning waste management, the directive 2008/98/EC (European Parliament 2008) compiles the basic concepts and definitions related to waste management. It describes some management principles, such as the management of the wastes should be done without damaging health or harming the environment and also indicates the implementation of waste management plans for each of the EU Member States. Furthermore, the hierarchy of the waste management is indicated, showing the priorities in legislation and policy as follow: prevention, preparing for re-use, recycling, other recovery, such as energy recovery, and disposal. Moreover, it introduces the concept of 'bio-waste', as biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises, and comparable waste from food processing plants. It does not include forestry or agricultural residues, manure, sewage sludge, or other biodegradable waste such as natural textiles, paper or processed wood. Articles 4 and 13 encourage the separate collection of biowaste with a view towards anaerobic digestion application followed by a composting process. Furthermore, it is stated that anaerobic digestion is especially suitable for treating wet biowaste, including fat, as for example kitchen waste.

Specifically, in the case of Spain, the previous legislation on waste 10/1998 has recently been substituted by the legislation on Waste and Contaminated Soil 22/2011, which indicates the obligation to draw up national plans of waste management (Spanish Government 2011), based in three principles: environmental and human health protection, a waste policy hierarchy (same as directive 2008/98/EC, previously explained) and the "polluter pays principle".

3. Waste treatment

Next, a brief summary with the advantages and disadvantages of the main waste treatment technologies is enclosed taking into account the kind of wastes to deal with:

TREATMENT		ADVANTAGES	DISADVANTAGES	WASTE CATEGORY
Disposal	**Landfill**	-Low cost	-Soil contamination -Lixiviates -Gas emissions -Strongly regulated	Biologically stable Non-compostable Non-recyclables
Thermal	**Incineration** **Gasification** **Pyrolysis** **Plasma**	-Energy recovery (just for high-calorific wastes) -High volume reduction -Complete pathogen destruction	-High costs (capital and operation) -Gaseous emissions -Ash disposal (hazardous waste)	High-calorific wastes
Biological	**Composting**	-Simple operation -High quality biowaste (class A)	-No energy recovery -Large areas required -Odours control	Biodegradables (MSW, sludge, manure, yard waste...)
	Anaerobic digestion	-Energy recovery (biogas) -Biosolids volume reduction -High pathogen removal -No odours	-High capital costs -Large reactors (high HRT) -Operation control for microorganisms growth	

Table 2. Waste treatments

In Europe (EU-27), over 38% of MSW were lanfilled in 2009, 20% were incinerated, 18% composted or digested and 24% recycled (Eurostat, 2011b). These figures reflect the high effort which has been adopted in most of the countries to reduce the landfill disposal, taking into account that in 1995 almost 70% of MSW were landfilled. However, there is still much to be done in order to reach the objective from the European directive 1999/31/CE that sets that just a 35% of the biodegradable waste generated in 1995 can be landfilled in 2016. To that end, it is necessary to strength environmental policies towards recycling of waste materials and energy recovery technologies to treat bio-wastes, such as anaerobic digestion. In Spain, this situation is especially critical since in 2009 the objective was already unaccomplished since more than 50% of the MSW was disposed in landfills.

On the other hand, taking into account the hierarchy of the waste management established by the European directive 2008/98/EC, if a waste cannot be re-used or recycled, a recovery technology has to be implemented prior to disposal; hence, landfill must be anyway avoided. Among the other three treatments concerning recovery, incineration and anaerobic digestion involve an energy recovery, while composting just entails a stabilization process. Therefore, considering the advantages previously exposed in Table 1 and the fact that incineration requires high-calorific wastes, anaerobic digestion is definitively the best technology to treat organic wastes. Next, a brief overview describing the main features of this technology is enclosed.

4. Anaerobic digestion

As it has been previously stated, anaerobic digestion is the most suitable technology to treat organic wastes. Next, an overview of anaerobic digestion is enclosed, with a brief history, its process basis description and different aspects concerning its enhancement: operational conditions considerations, co-digestion or pretreatment and post-treatment techniques.

History

Although anaerobic digestion was already applied for the first time in a wastewater treatment process at the end of the 19th century (Gljzen 2002), it does not arise as a wastewater treatment system till the 1970´s, showing promises as an alternative energy source. In the 1980´s and 1990´s, the extensive diffusion of anaerobic digestion technologies was mainly linked to the wastewater and sewage sludge treatment. Although the first full-scale digester to use MSW as a feedstock started up in 1988 (Valorga reactor in Amiens, France), it is only at the beginning of the new century that anaerobic digestion of biowastes returns with renewed interest. MSW processing facilities have made significant progress towards commercial use in recent years, with several in operation for more than 15 years: Valorga, Kompogas, Dranco, Arrowbio, Waasa, BTA… (Karagiannidis and Perkoulidis 2009)

Process basis

Anaerobic digestion is a natural biological process in which the organic matter is transformed into biogas by the action of specific bacteria in the absence of oxygen. The obtained biogas contains 50-70% methane and is susceptible for energy recovery through combustion. On the other hand, a waste that has not been degraded (digestate) is produced, which, after an appropriate treatment, can have agricultural applications as fertilizer (Hilkiah Igoni et al. 2008).

The anaerobic digestion process consists in several consecutive steps of biological processes. Thus, the degradation rate of the overall process is limited by the slowest step, in this case the hydrolysis (especially when dealing with solid wastes). Hydrolysis is the first stage in which complex organic matter (proteins, lipids, carbohydrates...) becomes simple soluble matter (amino acids, sugars, fatty acids...) more easily assimilated by bacteria in further steps. Therefore, this stage is crucial for the whole process success and for a fast and profitable biogas generation.

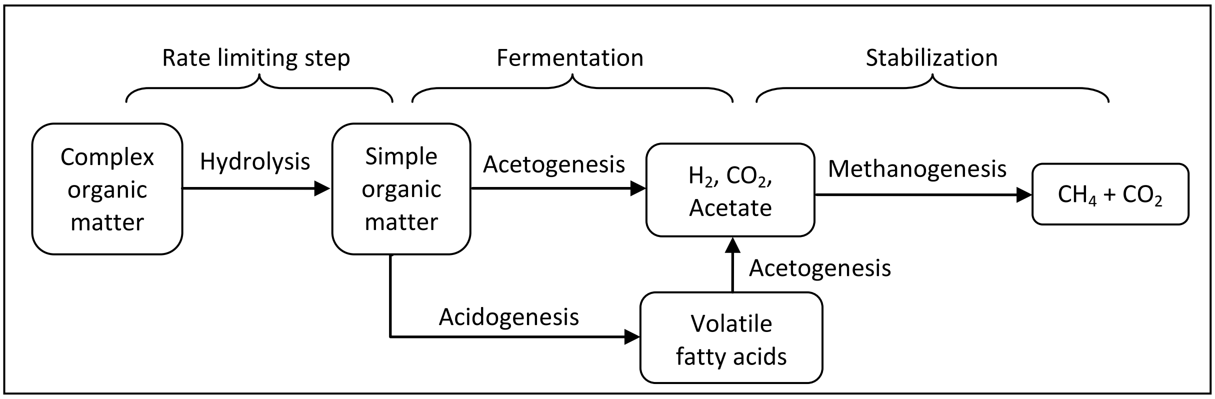

Figure 1. Stages of anaerobic digestion

Enhancing anaerobic digestion

In this section, different actions are described which can contribute to enhance the anaerobic digestion process. First, the operational conditions of the process are briefly reviewed, which should be carefully optimized; next, the main advantages related to a co-digestion process are enclosed; and finally, pretreatments and post-treatments considerations are described.

- **Optimization of operational conditions**

Selecting the most appropriate conditions to carry out the anaerobic digestion of a substrate is the first step to develop a correct design of the digester. Lots of studies have already been performed in this area and the operational conditions are strongly optimized:

- <u>Inoculum</u>: different sources of inoculum exist. Inoculum has to provide a correct biological activity to the system. It usually comes from an operating digester (typically from a WWTP or a pilot plant).
- <u>Substrate</u>: a wide range of wastes are susceptible to be anaerobically degraded. Organic compounds have to be available for bacteria to let a correct degradation; for this, different pretreatments techniques can be used.
- <u>Temperature</u>: mesophilic condition (35ºC) is the most common; thermophilic condition (55ºC) can lead to higher biogas productions, but its higher energy consumption is usually not balanced.
- <u>Organic load</u>: the amount of substrate which is fed into the system (per time unit in the case of continuous processes or per inoculum unit in the case of batch processes) is a key parameter and has to be carefully determined to optimize the process without reaching overloading.
- <u>Hydraulic retention time</u>: directly related with the substrate feeding rate or with the digester volume, it should enable a sufficient time to carry out the complete digestion.
- <u>Mixing</u>: enough mixing is as well important to assure a correct biological activity. Different mixing conditions can be considered depending on the reactor configuration and the nature of the substrate (wet or dry route).
- <u>Media</u>: specific conditions in the liquid media should be present to assure a correct biological activity: average pH (7-8), enough alkalinity, nutrients...
- <u>Toxicity and inhibition</u>: different compounds (ammonium, Maillard compounds...) are responsible of causing a lack of degradation by the inactivation of certain bacterial communities. Methanogenic bacteria are strongly affected by changes in pH, causing accumulation of volatile fatty acids. This is often caused by an overloading of organic matter (too high organic load).

- **Co-digestion**

A co-digestion process offers several benefits over conventional digestion such as increasing cost efficiency and improving the degradation of the substrates due to possible synergistic effects (Luostarinen et al. 2009). The co-digestion of biowastes with sludge offers economic and environmental benefits due to cost-sharing by processing multiple waste streams with complementary characteristics in a single facility in order to improve the methane production and prevent inhibition problems. Several studies have reported the economic and environmental benefits of co-digestion of multiple substrates (Mata-Alvarez et al. 2000).

- **Pretreatments**

In order to accelerate and improve the hydrolysis process when digesting solid wastes, pretreatments are applied before anaerobic digestion. These technologies are based on the solubilisation of organic matter by mechanical, chemicals, thermal or biological processes. Therefore, pretreatments will directly influence the kinetics of the process and the methane potential of the substrates by increasing its availability and its degradable fraction, leading to lower HRT in digesters and higher biogas production. They can also deal with some other problems that take place in anaerobic digesters such as ammonia inhibition, volatile fatty acids accumulation, mixing problems, digestate minimization and stabilization... Pretreatment technologies have been widely tested with sewage sludge and even applied in full-scale continuous processes in several WWTP. Nevertheless, in the area of solid wastes they have been hardly studied and need further research for its implementation in waste treatment plants. This is where the main topic of the thesis lies in.

- **Post-treatments**

Besides the produced biogas, anaerobic digestion also generates a solid residue (digestate) representing about 60/70% of the initial solids content. To manage correctly this waste, a dewatering process takes usually place to reduce its volume prior to disposal (landfill or agricultural use), mainly to reduce transport costs. Several techniques can be implemented: centrifugation, filtration, thermal drying, incineration... The application of a pretreatment before digestion can deeply influence the hydrodynamic characteristics of the digestate, then the improvements by post-treatments are often linked to pretreatment techniques.

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THESIS OUTLINE

The **main objective of the thesis is to enhance solid wastes anaerobic digestion by pretreatment technologies**. To that end, biochemical methane potential tests, pretreatment techniques, hydrodynamic tests, modelling tools among others are the main methodologies to study the effect of pretreatments on different solid wastes. Six different solid substrates are studied (some of them together in co-digestion trials): thickened sewage sludge from a municipal WWTP, a pre-selected municipal solid waste (MSW) from a treatment plant, the organic fraction of MSW (synthetic mixture), grease waste from a WWTP, spent grain from brewery industry and cow manure from slaughterhouse. Three disintegration technologies have been tested as pretreatment: thermal hydrolysis, cavitations by ultrasounds and an enzymatic treatment.

This is next developed in four different sections (overview, initial trials, optimization and final assessment), where the eight chapters which define the thesis lie in, as the next Table shows:

Chapters:

Pretreatments to solid wastes overview:

1. Review of current pretreatment technologies
2. Energy feasibility study of pretreatments

Initial trials:

3. Thermal hydrolysis to different solid wastes and modelling tools

Optimization of pretreatment technologies to solid wastes:

- Co-digestion enhancement of sewage sludge with:
  4. Cow manure
  5. Grease waste

- Municipal solid waste anaerobic digestion enhancement. Optimisation of pretreatments conditions:
  6. Ultrasounds and thermal hydrolysis to the organic fraction municipal solid waste
  7. Thermal hydrolysis to preselected municipal solid waste

Thermal hydrolysis energy integration and economic assessment

8. Thermal hydrolysis energy integration and economic assessment

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Table 1. Thesis outline diagram

As departure point, an overview of different pretreatments to different solid wastes has been done. First, **Chapter 1** compiles a **review of the current pretreatment technologies**, paying special attention to those applied to MSW, either at lab-scale or full-scale. Pretreatments to sewage sludge have been quickly reviewed just to show the broad extent of these technologies for sludge treatment. Among all the technologies which are reviewed for MSW, it is difficult to conclude that there is one which could satisfy all the desired necessities required for an optimal MSW anaerobic digestion process. Substrate properties can widely vary depending on the kind of waste to treat or even on its origin of production. Therefore, a complete characterization of the matter must be firstly achieved in order to select the appropriate treatment. Mechanical processes are usually required for high particle sized wastes or for high fibre content substrates. Chemical treatments are used to go with another one such as thermals, whose joint action often leads to synergistic effects. Thermal ones alone have as well a strong impact, with the additional advantage that no external reactants are added. However, high temperature processes are often the cause of refractory compounds formation which causes the inactivation of bacterial processes. On the other hand, biological processes can also be very effective since the enzymatic activity is fast and selective. Commercial enzymes can be purchased and are have selective effect on certain components, but natural enzymes (autoenzymatic process) have shown interesting results with additional advantages such as its cost efficiency. The combination of some of these processes has usually interesting perspectives due to the addition of several effects: thermal hydrolysis combines the thermal power of the steam with a quick depressurization (steam explosion) or a mechanical process such as microwaves can be enhanced by a chemical oxidation process. While there is a broad experience in full-scale pretreatments for sewage sludge in WWTP (thermal hydrolysis and ultrasounds mainly), there are very few plants with pretreatment to MSW (just three Norwegian plants with THP from Cambi) and few patented technologies for other solid wastes. This situation gives a big opportunity to the development of new research studies in order to assess the impact of pretreatments in solid wastes, so that new industrial plants could implement these technologies in full-scale with the highest environmental, energetic and economical benefits.

In this moment, in order to select the most appropriate pretreatments to be further studied, an **energy feasibility assessment of the current technologies** is developed in **Chapter 2**, based on previous reports and studies from literature and focusing in sewage sludge since it is the most reported substrate in this area. Then, an energy feasibility study of different pretreatments is performed for sludge. It is concluded that not all the pretreatment technologies have an energy self-sufficiency to be implemented in a WWTP. Generally, pretreatments consuming electricity do not satisfy its energy demands from the biogas production in the same process, except ultrasounds applied in full-scale plants (Sonix, Biosonator). In the case of thermal pretreatments, the potential to be implemented with full energy integration in WWTP is much higher, since they can recover heat from the biogas engine. This way, full energy integration can be achieved in thermal hydrolysis plants (Cambi, Exelys) and theoretical approaches set a minimum sludge concentration of 5%TS, as the main key factor to assure energy self-sufficiency. Therefore, the selected pretreatments which will be considered for further research are ultrasounds and thermal hydrolysis. Ultrasounds consist in the application of sonication waves to produce cavitations in the sludge causing cell break up and disintegration of organic matter. Thermal hydrolysis process uses steam to reach high temperature and pressure in a reactor before pressure releases suddenly into an atmospheric flash tank. In addition, a third pretreatment, the enzymatic one, has been considered in some tests: it consists in the addition of commercial enzymes which act specifically for certain components. Enzymes have not been considered in the review because their different pretreatment nature: they do not consume electric or thermal energy, but an external agent is added. All pretreatments are deeper described in the next section *Materials and Methods*.

Next, experimental work is performed, starting with some initial trials to check different aspects of the study considering one pretreatment (thermal hydrolysis) applied to raw substrates. Here in **Chapter 3**, **thermal hydrolysis to different solid wastes** is studied and **modelling tools** are evaluated. Then, the methodology adopted to study the pretreatment is established: whether all substrates are feasible to be pretreated; experimental procedures are set to carry out the pretreatment, BMP tests and analytical techniques; and modelling tools to determine parameters and measure properly the effect of pretreatments are assessed. Modelling the biodegradation of solid substrates by simple equations has resulted to be a reliable method to determine kinetic parameters and methane potentials from experimental data with a high degree of accuracy. The Modified Gompertz equation has the best results of fine-tuning (average R^2 over 0.98), even with the most complex kinetics. Thermal hydrolysis pretreatment has improved significantly methane productions (over 30%) and kinetics (double), especially in substrates which have a high fibre content (cow manure, spent grain or MSW) or microbial cellular material (biological sludge). However, thermal hydrolysis has not shown remarkable effects in substrates with a high content of easily degradable carbohydrates (synthetic organic fraction of MSW) or rich in lipids (grease waste from WWTP), although the latest presented a considerable methane potential in view of a co-digestion process.

Then, considering all these previous works, either bibliographic or experimental, the main body of the thesis lies in the **optimization of pretreatment technologies to different solid wastes**, focusing on two different areas which are based in two different research private projects that financed the research:

- Co-digestion of sewage sludge (*Alliance* project): focused on the co-digestion with other solid co-substrates. The main co-partners of this project are Cetaqua and Suez Environment, which were looking for the optimisation of WWTP anaerobic digestion processes. Then, the effect of the pretreatments was always addressed considering sewage sludge and pretreatment technologies always pointing to its application in WWTP. Different co-substrates were selected according to internal decisions in the project; among them, cow manure and grease waste were deeply investigated in a lab-extent and the results are here enclosed in Chapters 4 and 5.

- Municipal solid waste anaerobic digestion *(Topbio* project): belongs to Urbaser, which is a MSW management company, and then the central area of research is the study of the anaerobic digestion of the organic fraction of MSW in view of a full-scale implementation. First, Chapter 6 compiles lab-scale tests where ultrasounds and thermal hydrolysis pretreatments are applied to a synthetic mixture of the organic fraction of MSW. Then, in Chapter 7, thermal hydrolysis pretreatment is optimised using a preselected MSW from a real full-scale MSW treatment plant in order to simulate more real conditions.

As it has been previously explained, **Chapters 4 and 5** focus on the **enhancement of sewage sludge co-digestion**. Since operational conditions of pretreatments to biological sludge have been deeply optimised (as it can be observed from all reported studies in Chapter 2), this study has paid attention in the configuration of how the pretreatments are implemented in a co-digestion process of a WWTP, considering the optimised operational conditions for sewage sludge.

First, **Chapter 4** considers cow manure as co-substrate and the **optimization of cow manure and sewage sludge co-digestion using several disintegration technologies** is carried out by lab-scale tests comparing thermal hydrolysis, ultrasounds and enzymatic pretreatments. Cow manure is a common waste which is produced worldwide in the cattle farm sector and has a high methane potential, but its high fibre and protein content could cause certain limitations in the anaerobic digestion process. By the application of thermal hydrolysis and ultrasounds pretreatments, raw cow manure methane potential is increased by 28%. The co-digestion of cow manure and mixed sewage sludge does not lead to synergistic effects. However, when pretreatments are applied to cow manure and biological sludge, a considerable improvement of methane production takes place, providing a faster hydrolysis process (4 times faster) and over 60% more biogas yield. Thermal hydrolysis optimization resulted in the highest biogas production so long as biological sludge was pretreated. The assessment of hydrodynamic tests indicates dewaterability and rheology were also improved by the pretreatment.

Then, **Chapter 5** deals with the **optimization of grease waste and sewage sludge co-digestion**, focusing on thermal hydrolysis pretreatment. It is divided in two sections (corresponding to two published articles in Water Science and Technology): a first study, which was partially developed in the University of Valladolid, where co-digestion mixtures were optimised and different pretreatments were tested; and a second part where thermal hydrolysis was optimized and tested in a semi-continuous reactor (fully developed in University of Valladolid). Grease waste from WWTP is a very interesting co-substrate to be co-digested with sewage sludge since it presents a very high methane potential (489 $NmLCH_4$/gVSin) and both are produced in the same facility. Moreover, the limitations that grease waste presents for anaerobic digestion (slow degradation by its high fat content) can be overcome by the co-digestion with sludge. Thermal hydrolysis has lead to 43% higher kinetic rate of grease waste, although its lag-phase remained still high after the pretreatment (16 days). Moreover, no synergistic effect of grease and mixed sludge co-digestion was found at the studied mixture ratio (52%VS grease), but the lag-phase was reduced to 4 days. The best configuration to implement the thermal hydrolysis to the co-digestion process is pretreating the biological sludge alone, providing a 7.5% higher methane production, 20% faster kinetics and no lag-phase. The implementation of this assay in semi-continuous reactors resulted in a considerable methane production (363 $NmLCH_4$/gVSin) and thermal hydrolysis improved the rheology and dewaterability properties of the digestate. This leads to important economical savings when combining with co-digestion, reducing final wastes management costs and showing interesting perspectives for full-scale application.

On the other hand, **Chapters 6 and 7** focus on the **enhancement of the municipal solid waste anaerobic digestion** and the optimization of the pretreatments operational conditions. To that end, different sets of experiments have been performed in BMP lab-scale tests in order to cover a wide range of experimental conditions for different pretreatments and substrates.

Chapter 6 deals with **ultrasounds and thermal hydrolysis pretreatments to enhance anaerobic digestion of a synthetic mixture of the organic fraction of municipal solid waste (OFMSW)**. This synthetic mixture is composed of a mixture of basic foods in a certain proportion as their presence in household waste, according to real composition data provided by Urbaser. The fact of using a synthetic waste assures a constant composition of the substrate for all the experiments, avoiding external variations and it has already been used with similar purposes in other studies to simulate a real waste. Ultrasounds have not generated improvements in either the methanogenic potentials or the kinetic rates of the OFMSW biodegradation. However, thermal hydrolysis has played an essential role in improving kinetics. Among the studied parameters, the hydrolysis time has not presented a great influence but the hydrolysis temperature is critical: while intermediate temperatures (120°C) can improve kinetics (more than double) reducing biodegradation time to 20 days, higher temperatures (170°C) lead to slow biodegradations probably caused by the formation of recalcitrant compounds. Moreover, digestate properties (viscosity, dewaterability) are improved for all thermally hydrolysed samples. However, it is believed that the high content of easily degradable compounds from the synthetic OFMSW has influenced negatively and overshadowed the effects of pretreatments since the raw mixture already presented an acceptable methane potential and quite favourable kinetics.

Then, a further study was developed to check the effect of pretreatments in a more real waste (just thermal hydrolysis here considered because its higher efficiency from previous tests). Thus, a real MSW from a municipal plant was sampled and, after a pre-selection and cleaning of the organic fraction, it was subjected to a set of experiments where thermal hydrolysis was studied in lab-scale. The pre-selection and cleaning process was necessary because the bulky materials and inorganics contained in the raw waste could cause important disturbances to carry out the pretreatment and its characterization. This way, **Chapter 7** compiles the trials where **thermal hydrolysis optimization of a pre-selected municipal solid waste** takes place. Thermal hydrolysis as a pretreatment to enhance pre-selected MSW anaerobic digestion has resulted a useful and efficient technology not only to increase methane production in the digester (by 30%) and kinetics (by 70%), but also to improve rheological properties and dewaterability, reducing associate costs of the process such as pumping and mixing requirements or digestate management costs. These results show that the effect of thermal hydrolysis in a real MSW is much stronger as for the synthetic OFMSW, as it was suspected. The main responsible mechanism of this fact is thought to be the higher fibre content and lower easily degradable sugars contained in the real pre-selected MSW, what reduces the availability of organic compounds when no pretreatment is applied. The optimum conditions to carry out the pretreatment were set at 15 minutes hydrolysis time at 150ºC, which are below the typical values reported for sewage sludge.

Finally, with the aim of concluding the study, an **energy integration and economic assessment of thermal hydrolysis pretreatment** has been performed in **Chapter 8** from a more theoretical approach to study its energetic and economic feasibility. Special attention has been paid to MSW in order to set the basis for the scale-up of the pretreatment in a MSW treatment plant. The study has determined that a proper energy integration design could lead to important economic savings (5€/t) and thermal hydrolysis can enhance up to 40% the incomes of the digestion plant, even doubling them when digestate management costs are considered. In a real MSW treatment plant (30000 t/year), thermal hydrolysis would lead to net benefits of almost 0.5M€/year, with a full refund period of the initial investment of two years. With this, the bases to develop a thermal hydrolysis pretreatment for a MSW treatment plant are set. It is considered that a further pilot scale-up of the process would be helpful to understand and optimize the pretreatment, but this could not be performed in lab-scale as this work has been performed. This way, a more precise economic evaluation could be performed.

Remark: it should be mentioned that most of the chapters follow the typical structure from papers, although not all of them have been considered for publication. This idea was initially set to provide higher homogeneity in the manuscript and in view of letting an open opportunity for its publication without substantial changes. Therefore, it can occur that some repetitions among different sections happen, especially in Materials and Methods subsection (to that end, a common Materials and Methods synopsis is next enclosed).

OBJECTIVES

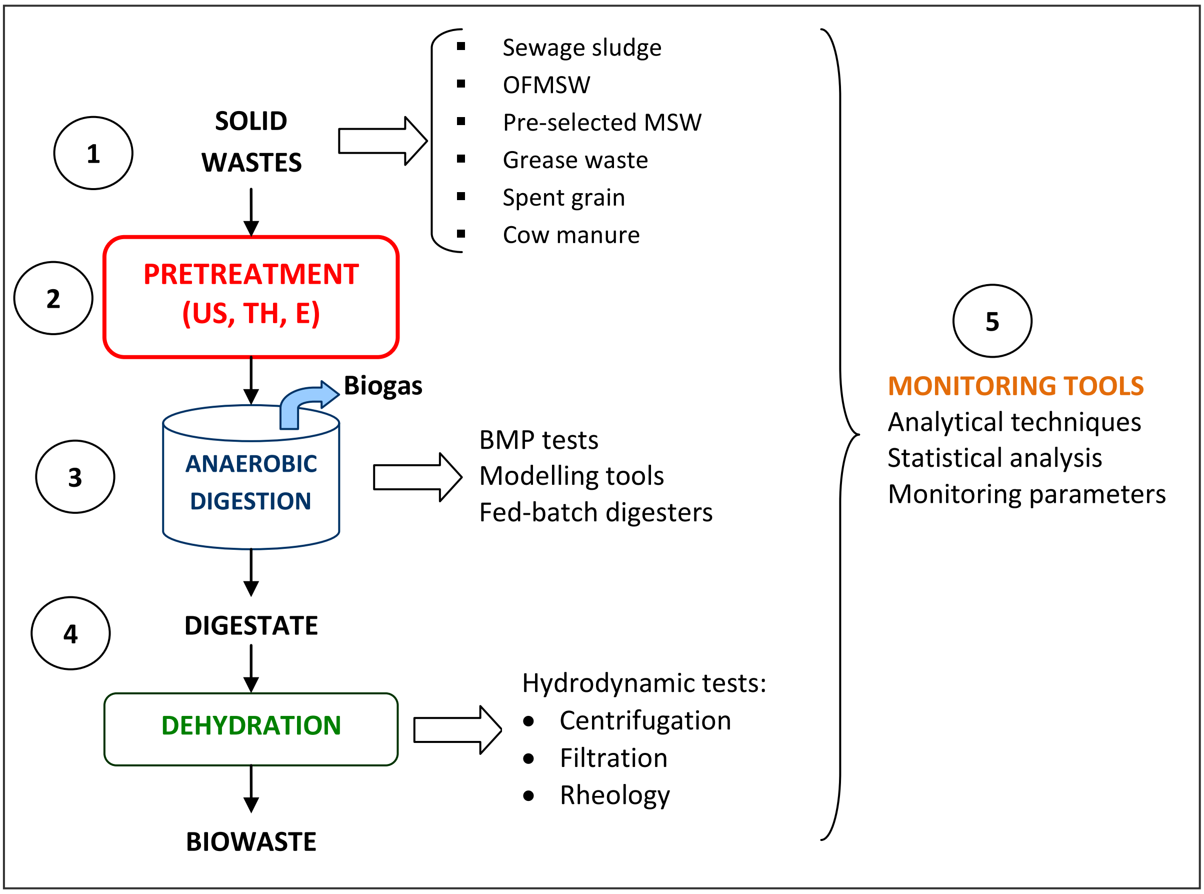
The main objective of the study is to **enhance solid wastes anaerobic digestion by pretreatment technologies**.

For this, some specific objectives are next enclosed, linked to their corresponding chapter(s) where they are studied:

	CHAPTER
SUBSTRATE	
• Test different solid wastes	3
• Combine different co-substrates (Co-digestion)	4,5
• Check the technical feasibility to perform pretreatments to all of them	3
PRETREATMENT	
• Compare different pretreatment technologies	1,2
• Optimize the operational conditions for the most favourable pretreatments	6,7
• Evaluate different monitoring tools to check the impact of pretreatments (BMP tests, modelling tools, hydrodynamic tests, analytical techniques…)	3,4,5,6,7
• Understand the main mechanisms that take place	3,4,5,6,7
• Perform an energy and economical assessment to the most promising pretreatment to study its real feasibility	8
• Set the basis for a process scale-up	8
DIGESTATE	
• Compare different minimisation techniques	4,5,6,7
• Study the effect of pretreatments on digestate's properties	4,5,6,7,8
• Estimate its impact on the overall process	8
• Evaluate biowaste management considerations	8

MATERIALS AND METHODS

The study of the pretreatment is the central point of study in this work. Next, a graphical representation of all its interactions with the other parameters that are described in this section is enclosed:



1. Solid wastes

Six different solid substrates are selected considering: their importance in real scale plants in order to optimise their anaerobic digestion; their availability; and their diversity of composition, origin, production and biodegradability according to the substrate classification of Carlsson et al. (2012). These substrates are:

- Biological sludge (thickened to 7% total solids) from a municipal WWTP in Valladolid.
- Primary sludge (thickened to 17% total solids) from a municipal WWTP in Valladolid.
- The organic fraction of municipal solid waste (OFMSW), which is a synthetic mixture of basic foods in an appropriate proportion as their presence in household waste.
- Pre-selected Municipal solid waste (MSW) from a MSW treatment plant.
- Grease waste from a dissolved air flotation tank (DAF) of a WWTP.
- Spent grain from brewery industry.
- Cow manure from slaughterhouse.

Parameter	Units	**Biological sludge**	**Primary sludge**	**OFMSW**	**MSW**	**Grease waste**	**Spent grain**	**Cow manure**
TS	g/kg	71.2	167.5	109.9	351.4	505.2	243.6	221.6
VS	g/kg	54.9	115.6	105.1	246.0	468.2	233.4	208.5
CODt	g/kg	83.9	188.2	150	332.5	648.3	303.4	258.8
CODs	g/kg	6.3	10.3	91.8	-	-	70	81
TKN	N-g/ kg	5.75	4.69	3.79	5.35	3.27	8.73	27.46
NH_4^+	N-g/ kg	0.24	0.29	0.82	1.05	0.24	1.22	0.75
Grease	g/kg	1.16	15.49	2.68	5.80	128.0	6.66	4.65
Carbohydrates	%	0.10	0.1	6.28	0.19	-	-	-
Fibre	%	0.21	2.67	0.82	7.23	-	-	-
Proteins	%	3.83	2.28	2.43	3.67	2.04	4.69	16.7

Substrates characterization (TS, VS: total and volatile solids; CODt/s: total/soluble chemical oxygen demand; TKN: total Kjeldahl nitrogen; NH_4^+: ammonium)

Substrates (from left to right): Organic fraction municipal solid waste, spent grain, cow manure, grease waste and pre-selected municipal solid waste.

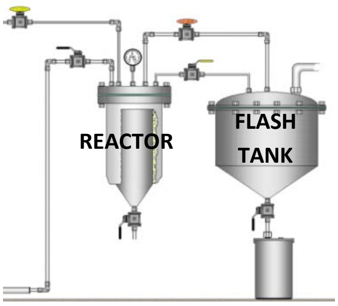
2. Pretreatments

Three disintegration technologies are studied. A brief description of the equipments is enclosed:

- *Thermal hydrolysis*: The hydrolysis plant (home-built) is made up with a 2L reactor connected to a flash tank by a decompression valve. The reactor, which is fed with a substrate in a batch mode, is heated with steam and supports high pressures (up to 10 bar). The flash tank is an open-air 5L vessel where the steam explosion takes place after the hydrolysis reaction time has elapsed. Temperature and pressure are manually controlled by the steam injection.

- *Ultrasounds:* two ultrasounds homogenizers have been used: a *Hielscher UP400S* with 200W nominal power and a *Hielscher UIP 1000 hd (20 kHz)* with 1kW nominal power. The ultrasound homogenizer converts electrical energy in mechanical vibrations (ultrasounds), which are transmitted to the sample by a sonotrode. Both equipments work in batch mode: the sample is introduced in a 250 mL stainless steel cell where the sonotrode is completely immersed. It has a water jacket as refrigeration system to control the temperature inside the cell. The power input can be set and the reaction time has to be controlled manually.
- *Enzymatic treatment:* The substrate, the enzymatic solution (commercial protease from *Aspergillus oryzae,* 500 U/g activity) and a buffer solution are introduced in 300 mL closed bottles and stirred for 12 hours under controlled conditions (37ºC and pH 5.3).





Ultrasounds homogenizers and thermal hydrolysis plant

3. Anaerobic digestion

Biochemical methane potential tests

Biochemical methane potential (BMP) tests allow determining kinetics and methane potentials of the substrates. The BMP tests follow an internal protocol based on standardized assays for research purposes (Angelidaki et al., 2009):

- The assays are always performed by triplicates.
- Two reactors types have been used: 300mL and 2L glass bottles.
- A substrate-inoculum ratio of 1:1 in terms of VS is applied.
- The inoculum is WWTP mesophilic digested sludge and was pre-incubated for 2 days at 35ºC.
- A buffer solution (5 g$NaHCO_3$/L) and micro and macro-nutrients (1mL/L) are added to assure inoculum activity. Also some Na_2S assures oxygen depletion.
- Inoculum alone is also tested by triplicates to determine its methane production so that it can be subtracted in the other reactors and calculate the net methane productions.
- An extra reactor with cellulose as substrate is always prepared as a control test.
- The gas chamber is washed with helium to displace air before closing the reactors with a septum.
- The incubation temperature is for all the tests 35ºC (mesophilic conditions).
- Reactors are stirred in a horizontal shaker (300 mL) or in a rotary shaker (2L).

- Periodical monitoring analyses (every 2-3 days) of biogas production by pressure meter (*IFM Electronics*, PI-1696) and biogas composition by gas chromatography (*Varian 3800*, sample uptake with a 100µL *Hamilton* syringe) are performed during the tests.
- Methane potentials are always expressed as average values of the net volume of methane per gram of initial substrate VS content.

Gas chromatograph, pressure meter, BMP reactor and rotary shaker

Modelling BMP tests

The Modified Gompertz equation (Lay et al. 1997), next presented in equation 1, has been considered in order to fine-tune the experimental data from BMP tests to a theoretical equation:

$$B = P \times exp\left\{-exp\left[\frac{R_m \cdot e}{P}(\lambda - t) + 1\right]\right\} \tag{1}$$

The model has three parameters: the methane yield rate (R_m) which indicates the initial slope of the curve ($mLCH_4/gVS/d$), the maximum biogas production (P) expressed as $mLCH_4/gVSin$ and the lag-phase (λ) in days. B is the calculated methane production ($mLCH_4/gVSin$) for time t. The model fine-tuning to the experimental data was achieved by least squares methodology, by minimising the next objective function (2):

$$OF(\varphi) = min \sum_{t=1}^{N} \left(B_{exp}(t) - B_m(t, \varphi)\right)^2 \tag{2}$$

where B_{exp} is the consumption velocity obtained from measurements (plotted in BMP results graphs as points). B_m is the corresponding velocity calculated by the model (plotted with continuous curves), N is the number of measurements, t is time and φ represents the Gompertz parameters. The correlation factor (R^2) was then calculated to assess the accuracy of each model with respect to the experimental data.

Fed-batch digesters

The fed-batch experiments are carried out in two cylindrical reactors of 20L of useful capacity and 10L of gas chamber. Both reactors are operated at mesophilic temperature range (35ºC±1ºC) with an automatic controller. The biogas production is continuously measured by a pulse electric system and analyzed by gas chromatography (*Varian CP-3800*). Biogas internal recycle assures a correct mixing. Feeding is carried out once per day. The stability of the operation is controlled carrying out periodical analysis of alkalinity, pH, total and volatile solids (TS, VS), total and soluble chemical oxygen demand (CODt/s), volatile fatty acids (VFA), total nitrogen (TKN) and ammonium (NH_4^+).

Fed-batch reactors, pulse electric meter, pumping feed system

4. Digestate

Hydrodynamic and dewaterability tests

To assess the dewaterability and hydrodynamic properties of pretreated, raw substrates and digestates, filterability, centrifugability and rheology tests are performed following an internal method established from the experiments in sludge characterization in the *Department of Chemical Engineering and Environmental Technology,* at the *University of Valladolid*. These tests are very relevant in terms of assessing the impact on mixing requirements, digestate dewaterability and handling properties.

- *Filterability*, defined as the viability of sludge to flow through a filter, is measured by forcing the sludge to pass through a filter under a 1 barg pressure. The filtration constant (*FC*) is calculated as a ratio of the slope from plotting filtrate volume (V^2) versus filtration time and the area of the filtering paper.
- *Capillary suction time* (CST) is measured to evaluate digestate dewatering behaviour: a long CST means a high cake specific resistance. The CST is determined using a Triton Electronics Ltd. (Type 319) and Whatman No. 17 filter paper.
- *Centrifugability* assesses the liquid and solid phase separation after 5 minutes centrifugation at 5000 rpm in a *Kubota 5100* centrifuge. After measuring the separation performance and determining the suspended solids concentration in the liquid phase, the next parameters are calculated: % separated liquid, % solid recovery in cake and solid concentration in cake (%TS).
- *Rheology* is evaluated by viscosity curves, as the slope from plotting the shear stress (τ, N/m^2) versus the shear rate (γ, s^{-1}) obtained with a *Brookfield Digital Viscometer DV*-I. Since sludge is not a Newtonian fluid, there is not a constant value of the viscosity, so the curves have to be evaluated.

Viscometer, filtration column, CST meter, centrifuge

5. **Monitoring tools**

Analytical methods

Substrates characterization was partially performed in the University of Valladolid, following an internal protocol based on Standard methods (Apha, 2005) to determine the next parameters: total and volatile solids, soluble and total chemical oxygen demand, total Kjeldahl nitrogen, ammonium and volatile fatty acids. Other parameters were determined in an external laboratory: grease (EPA Method 1664), carbohydrates (CE Regulation 152/2009), fibre content (Weende, CE Regulation 152/2009), proteins (IT-MA-014, AOAC Official Method) and elemental content (IT-MA-014, AOAC official method).

Next, a brief methodology of the main parameters determination is described:

- **Total and volatile solids** (TS, VS): both are determined by gravimetric methods and are expressed as g/kg. Total solids are determined from the weight loss that 25-50g of sample suffers after a drying process at 105ºC for 24 hours. The previous sample is then subjected to a calcination process at 550ºC until dry weight becomes constant (about 2 hours) to determine volatile solids.
- **Chemical oxygen demand** (COD): the organic matter of the sample is oxidised with $K_2Cr_2O_7$ (oxidiser) in an acidic medium (H_2SO_4) with the addition of Ag_2SO_4 (catalyser) and $HgSO_4$ (complexer agent of chlorides) at 150ºC for 2 hours. After the digestion, the excess of oxidiser is quantified with Mohr salt ($Fe((NH_4)_2SO_4)_2{\cdot}_6H2O)$) by titration with ferroin as indicator. If the sample is previously filtered (filters AP40), soluble COD is determined. COD is expressed as mgO_2/kg.
- **Total Kjeldahl nitrogen** (TKN): the sample is firstly digested in an acidic medium (H_2SO_4) with a catalyser at 370ºC for 1 hour. Then, a distillation process recovers ammonia by NaOH addition. Finally, titration with H_2SO_4 using boric acid as indicator lets the determination of all organic and ammoniacal nitrogen (TKN).
- **Ammonium** (NH_4^+): the sample is previously filtered (filter AP40) to obtain the soluble phase. A selective electrode Orion 9512HPWBNWP is used to determine ammonium in the range 1-100 ppmN.
- **pH**: selective electrode CRISON pH 20+ with temperature probe for liquid samples and a CRISON pH 25 for solid samples.

- **Alkalinity**: it is measured by volumetric analysis, adding a solution of H_2SO_4 (0.1N) to 50 mL of the soluble phase (AP40 filters) of the sample; the pH drops down to 5.75 (V_1, partial alkalinity) and 4.30 (V_2, total alkalinity). Alkalinity is then expressed in $mgCaCO_3$/L and the alkalinity ratio can be calculated as $(V_2-V_1)/V_2$.
- **Biogas composition**: is determined by gas chromatography (Varian 3800) with a thermal conductivity detector (TCD) and two columns (using He as carrier gas at 13.7 mL/min) to determine O_2, N_2 and CH_4 in the first one, and CO_2 and H_2S in the second one. The sample is injected with a 100µL *Hamilton* syringe.
- **Volatile fatty acids** (VFA): an Agilent 7820A chromatograph with a flame ionization detector (FID) is used where the filtered (0.22 µm filter) supernatant soluble phase (previous acidification) is injected using N_2 as carrier gas.

Statistical analysis

All BMP tests are carried out by triplicates. The experimental methane productions are always referred to average values and standard deviations are calculated and represented in BMP graphs with vertical lines. For the hydrodynamic tests, duplicates are measured and the results are averaged. Analyses of variance (ANOVA) have been also performed to study the significance degree of the interrelation between different parameters from experimental data, with a significance degree of 95%.

Monitoring parameters

- **Co-digestion factor (α)**

It is calculated to assess the synergic effect that co-digestion mixtures have respect to the single substrates degradation. It indicates the ratio between the experimental methane potential of the co-digested mixture (P_{exp}) and the theoretical value (P_{theo}) calculated according to the mixture ratio from the individual co-substrates (i) methane potentials according to the next equation:

$$\alpha = \frac{P_{exp}}{P_{theo}} = \frac{P_{exp}}{\sum_i ratio_i\ (VS\ basis) \cdot P_i\ (\mathrm{mLCH_4/gVS})}$$

- **Solubilisation factors**

Solubilisation factors (SF) are determined after pretreatments to quantify the increase of soluble matter which takes place for each treatment condition.
Solubilisation factors (SF) is calculated as the % increase of solubleCOD/totalCOD:

$$SF\ (\%) = \frac{COD_s/COD_t - COD_{so}/COD_{to}}{COD_{so}/COD_{to}} \cdot 100$$

where COD_s and COD_t are the soluble concentrations after pretreatment and COD_{so} and COD_{to} the soluble and total concentrations in the raw sample.

- **Pretreatments effect on BMP tests**

The quantification of methane production increase and methane yield rate improvement by the effect of pretreatments is determined as the relative percentage increase of the Gompertz parameters (γ) with the next equation:

$$\%\,Increase = \frac{\gamma - \gamma_0}{\gamma_0} \cdot 100$$

The lag-phase reduction is calculated as:

$$\lambda_0 - \lambda$$

- **Dewaterability and rheologic parameters**

From hydrodynamic and dewaterability tests, the next parameters are quantified:

- The filtration constant (*FC*) is calculated as a ratio of the slope from plotting filtrate volume (V^2) versus filtration time and the area of the filtering paper (A). It represents the ease of the sample to be filtrated, it is proportional to its velocity and is measured in m^2/s.
- *Capillary suction time* (CST) represents the time (usually expressed in seconds) that takes to the sample to move by capillarity, then a long CST means a high cake specific resistance. It is therefore inversely proportional to the FC.
- *Centrifugability* parameters are: % separated liquid (enables the quantification of the biowaste respect to the digestate), % solid recovery in cake (indicates the efficiency of the centrifugation) and the solid concentration in cake (% total solids of the biowaste).
- *Rheology*: viscosity curves have to be evaluated.

Target	**Parameter**	**Symbol/Equation**	**Method**
Substrate	Initial characterization	TS, VS, CODt/s, TKN, NH4+, VFA, pH, carbohydrates, proteins, fats, fibre	Analytical methods
	Methane production	P	BMP test / Modelling
	Methane yield rate	R_m	
	Lag-phase	λ	
Pretreatment	Solubilisation factor	$SF\,(\%) = \frac{COD_s/COD_t - COD_{so}/COD_{to}}{COD_{so}/COD_{to}} \cdot 100$	COD analyses
	Model parameters increase	$\%\,Increase = \frac{\gamma - \gamma_0}{\gamma_0} \cdot 100$ $\lambda_0 - \lambda$	BMP test / Modelling
Co-digestion synergy	Co-digestion factor	$\alpha = \frac{P_{exp}}{P_{theo}} = \frac{P_{exp}}{\sum_i ratio_i\,(VS\ basis) \cdot P_i\ (\mathrm{mLCH_4/gVS})}$	BMP test
Hydrodynamic properties of digestate	Filtration constant	FC = V^2/A	Filtration in column
	Capillary suction time	CST	CST test
	Centrifugability	% separate liquid; % solid recovery in cake; % total solids in cake	Centrifugation test
	Viscosity	Viscosity curves	Viscosimeter

Summary of the main monitoring parameters

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PRETREATMENTS TO SOLID WASTES OVERVIEW

CHAPTER 1. REVIEW OF CURRENT PRETREATMENT TECHNOLOGIES

As departure point, an overview of different pretreatments to different solid wastes has been done. **Chapter 1** compiles a **Review of the current pretreatment technologies**, paying special attention to those applied to municipal solid wastes (MSW), either at lab-scale or full-scale. Pretreatments to sewage sludge have been quickly reviewed just to show the broad extent of these technologies for sludge treatment. Among all the technologies which are reviewed for MSW, it is difficult to conclude that there is one which could satisfy all the desired necessities required for an optimal MSW anaerobic digestion process. Substrate properties can widely vary depending on the kind of waste to treat or even on its origin of production. Therefore, a complete characterization of the matter must be firstly achieved in order to select the appropriate treatment. Mechanical processes are usually required for high particle sized wastes or for high fibre content substrates. Chemical treatments are used to go with another one such as thermals, whose joint action often leads to synergistic effects. Thermal ones alone have as well a strong impact, with the additional advantage that no external reactants are added. However, high temperature processes are often the cause of refractory compounds formation which causes the inactivation of bacterial processes. On the other hand, biological processes can also be very effective since the enzymatic activity is fast and selective. Commercial enzymes can be purchased and are have selective effect on certain components, but natural enzymes (autoenzymatic process) have shown interesting results with additional advantages such as its cost efficiency. The combination of some of these processes has usually interesting perspectives due to the addition of several effects: thermal hydrolysis combines the thermal power of the steam with a quick depressurization (steam explosion) or a mechanical process such as microwaves can be enhanced by a chemical oxidation process. While there is a broad experience in full-scale pretreatments for sewage sludge in WWTP (thermal hydrolysis and ultrasounds mainly), there are very few plants with pretreatment to MSW (just three Norwegian plants with THP from Cambi) and few patented technologies for other solid wastes. This situation gives a big opportunity to the development of new research studies in order to assess the impact of pretreatments in solid wastes, so that new industrial plants could implement these technologies in full-scale with the highest environmental, energetic and economical benefits.

Keywords: pretreatment, review, sewage sludge, solid waste

PRETREATMENTS TO SLUDGE

Initially, sludge minimization technologies were applied in water treatment processes to improve WWTP efficiency. Nowadays, its extent is spread to many processes concerning wastes treatment. Perez-Elvira et al. (2006a) reviewed all the existing technologies for sewage sludge with a detailed classification based on where the pretreatment is applied and its nature. To give an idea of the amount and variety of possible technologies that could be implemented in a treatment plant and a brief description of each one, a summary with the main features of each technology regarding sludge and some references is next enclosed, without the aim of a full review.

1. **Processes in the sludge line:** Treatments that reduce the final stream of sludge to be disposed of, which can be classified in two categories: Pretreatments to the reactor and modification of the anaerobic reactor.

   a. **Physical pretreatment**: The disintegration of solid particles present in the sludge releases cell compounds and creates new surface where biodegradation takes place.

      i. *High pressure homogenizers*: These units consist of a multistep high-pressure pump and a homogenizing valve. The pump compresses the suspension to pressures up to several hundred bars. When passing through the homogenizing valve, the pressure drops below the vapour pressure of the fluid, and the velocity increase. The cavitation bubbles formed implode, inducing into the fluid temperatures of several hundred degrees Celsius, which disrupt the cell membranes. However, energy balance could lead to negative values due to the high pressure pump consumption. (Nah et al. 2000; Engelhart et al. 2000)

      ii. *Ultrasonic homogenizers*: These devices consist of three components: a generator supplies a high frequent voltage of 20 to 40 kHz, a piezo-electrical material transforms electrical into mechanical impulses which are transmitted by a sonotrode into the fluid. Cavitation bubbles are created by alternating overpressure and underpressure. When imploding, they generate a great amount of energy that causes cell disruption. Ultrasound pretreatment has been widely tested in sewage sludge at lab-scale (Bougrier et al. 2006; Climent et al. 2007; Donoso-Bravo et al. 2010) showing positive effects for biological sludge degradation but usually a negative energy balance. There are also many commercial sonicators that have been applied in full-scale plants (Pilli et al. 2011) leading to 50% increase of biogas productions with a positive energy balance.

      iii. *Impact grinding*: Two rotors revolve in opposite direction in a grinding chamber, generating pressure differences which diminishes the particle size. The flocs are disrupted, but the cells are not disintegrated

      iv. *Stirred ball mills*: This device consist of a cylindrical grinding chamber (up to 1 m^3 volume) almost completely filled with grinding beads. An agitator forces the beads into a rotational movement. The microorganisms are disintegrated in between the beads by shear- and pressure- forces.

v. *High performance pulse technique*: This device is an electro-hydraulic method. The sludge is treated by a high voltage of up to 10 kV, in pulse periods of only 10 ms. The shockwaves created in the sludge induce sudden disruption and the release of organic substances takes place. A pulse power technique was tried by Choi et al. (2006).

vi. *Lysat centrifugal technique*: The centrifugal forces created in this thickening centrifuge are deliberately applied to cell destruction. This disruption takes place using a special beater (ring) which is integrated into the centrifugal thickener and which dissipates the kinetic energy provided by the centrifuge.

vii. *Gamma irradiation*: The technology of irradiation liberates the soluble carbohydrates existing in the sludge. It has been shown quickly, efficiently and reliably to deal with potential health hazard materials in sewage sludge. Irradiation of sludge can be carried out with cobalt-60 source, which emits gamma rays. These rays penetrate and pass through the sludge, inactivating microorganisms and decomposing various organic compounds without leaving in any residual radioactivity or making the sludge radioactive.

viii. *Microwave pretreatment* has been tested by Climent et al. (2007).

b. Chemical pretreatment

i. *Acid/Alkaline Hydrolysis*: We refer here to the use of alkaline as it is more widely used. During the alkaline pre-treatment, the pH of the sludge is increased up to 12, maintaining this value for a period of time (normally 24h). This process may be used to hydrolyse and decompose lipids, hydrocarbons and proteins into smaller soluble substances such as aliphatic acids, polysaccharides and amino acids. Chemical addition can be used together with thermal pre-treatment.

ii. *Ozone*: The aim of ozone pre-treatment is partial oxidation and hydrolysis of the organic matter. A complete oxidation is avoided and larger molecules are cracked into smaller ones instead. Barely degradable compounds are transferred into more easily degradable ones. This process has a special advantage because no chemicals are needed and no increase in salt concentration occurs. Recently, Kianmehr et al. (2010) has obtained higher biogas production for long SRT sludge, but Bougrier et al. (2006) has found inhibition while pretreating with ozone.

c. Biological pretreatment: The biochemical sludge disintegration is based on enzyme activity that are either produced within the system (autolysis) or externally. The enzymatic break up cracks the compounds of the cell wall by an enzyme catalysed reaction. This process is of interest in combination with mechanical disintegration as well, because enzymes are also located in the intracellular liquid. Carvajal et al. (2013) has applied an autohydrolysis treatment to biological sludge (55ºC for 12h under microaerobic conditions prior digestion).

d. Thermal pretreatment

i. *Thermal*: Thermal pretreatment destroys the cell walls and makes the inside of the cell accessible for biological degradation. The optimum temperature for this process is between 160 and 180ºC. Above 180 ºC the formation of recalcitrant non-biodegradable compounds takes place. Many studies have focused on applying thermal energy to sludge since long time ago (Haug et al. 1978; Stuckey and McCarty 1984), claiming that 175ºC is the optimum temperature. More recent studies (Bougrier et al. 2008) still confirm those results, but others (Climent et al. 2007; Borges and Chernicharo 2009) state that at lower temperatures, such as 70ºC for several hours, similar biogas productions are reached.

ii. *Freezing and thawing*: By freezing and thawing activated sludge, the floc structure will be irreversibly changed into a more compact form, the bound water content will be reduced, and therefore the sludge dewatering characteristics can be improved. Montusiewicz et al. (2010) tested freezing pretreatment at -25ºC for 24h with mixed sludge.

e. Combined

i. *Thermo-chemical*: The sludge can be acidified by addition of an acid (e.g. sulphuric) to a pH between 1 and 2 and then hydrolyzed thermally in a pressure vessel (140ºC, 3.5 bars, 30–40 min), such is the Kepro-process (developed by the Kemira Kemwater AB); or an alkali (e.g. sodium hydroxide) can be added till pH 12 before the thermal treatment (Stuckey and McCarty 1984; Valo et al. 2004).

ii. *Wet oxidation*: The sludge is oxidized at high pressure and temperature in an enriched oxygen atmosphere. Strong et al. (2011) has tried this technique at 20bar and 220ºC.

iii. *Thermal hydrolysis (Thermal – Explosive decompression – Shear forces)*: The sludge is pressurized and pumped to a pre-treatment reactor, where it is mixed with steam to heat and soften the sludge. The pressure is suddenly reduced and explosive decompression forces are imparted which partially disrupt the cellular integrity of the sludge. Shear forces are then applied to the sludge to further discharge the cellular integrity of it. This process was patented in 1998 by Rivard & Nagle (1998) and since then, it has been further tested in lab-scale (Schieder et al. 2000; Perez-Elvira 2006b; Donoso-Bravo et al. 2011), in pilot scale plants (Perez-Elvira et al. 2010), in continuous processes (Fdz-Polanco et al. 2008) and even in full-scale plants (Panter 2005; Perez-Elvira et al. 2008; Kopp et al. 2010).

f. Modified anaerobic processes

i. *Two stage anaerobic digestion*: This process requires two reactors that separate the primary anaerobic respiration processes into a first acid stage and a second gas stage. The acid stage contains the hydrolysis reactions, acidification and acetification in the first small reactor. Some methanogenic activity may produce gas, but the production is primarily carried out in the second larger reactor.

ii. *Temperature phased anaerobic digestion*: This technique applies thermophilic digestion to the first stage and mesophilic to the second one.

iii. *Anoxic gas flotation (AGF)*: It is an improved anaerobic digestion process that uses anoxic gas (without oxygen) to float, concentrate and return bacteria, organic acids, protein, enzymes, and undigested substrate to the anaerobic digester for the rapid and complete conversion of waste slurries to gas and soluble constituents.

2. **Processes in the final waste line:** Sludge produced is treated to get a final stable, dewatered and pathogen free residue.

   a. **Incineration**: Incineration of sludge involves burning it in the presence of oxygen at high temperature in a combustion device. Incineration reduces biosolids to a residue primarily consisting of ash, which is approximately 20% of the original volume. Air production control devices are required to protect air quality. Moreover, incineration is an expensive disposal option for sludge, and leaves the problem of what to do with the residues.

   b. **Gasification – Pyrolysis**: Gasification and pyrolysis of wastewater sludge are rather new methods of sludge processing. Gasification is a thermal conversion of hydrocarbons to gas by partial combustion of the sludge in the presence of oxygen or air. In the absence of air, the process is known as pyrolysis.

   c. **Wet air oxidation (WAO)**: The organic content of the sludge (approximately 5% DS) is oxidised in specific reactors at temperatures of between 200 and 300ºC and at pressure levels between 30 and 150 bar.

   d. **Supercritical water oxidation (SCWO)**: It takes place at very elevated temperatures and pressures (typically 25 MPa and 600ºC), and is the total solution for the destruction of sewage sludge. Although the cost is high, it is claimed that the value from the process in the form of sludge volume reduction with more than 90% recovery of energy will compensate the cost of running the process.

PRETREATMENTS TO SOLID WASTES

All these pretreatment technologies have been widely tested with sewage sludge and even applied in full-scale continuous processes in several waste water treatment plants (WWTP). Nevertheless, in the area of solid wastes they have hardly been studied and need further research for its implementation in solid waste treatment plants. Therefore, it is considered that a review of the latest studies in this area is interesting in order to summarize the most researched areas and compare the main results. Moreover, a classification of these technologies can help to organize future works and look for different perspectives in next studies.

Solid wastes include several kinds of wastes; in fact, according to Carlsson et al. (2012) classification, there are municipal solid wastes, organic wastes from food industry, energy crops and agricultural residues, manure and WWTP residues (sewage sludge here included). However, in this review we will especially focus in municipal solid wastes (MSW) on one hand, and in other substrates (covering manures, agricultural wastes, energy crops and other solid wastes, but not anymore sewage sludge) on the other hand. First, the reason for which sewage sludge is excluded is that its digestion enhancement by pretreatments has been deeply studied and reviewed by many authors (Carrère et al. 2010; Pilli et al. 2011; Perez-Elvira et al. 2006) and an overview was previously shown. Moreover, it was pretended to go deeper in municipal solid waste pretreatments because its high potential to be implemented in full-scale plants, the considerable impact that this waste produces in our society (rising production in cities, problems of waste management, possibility to produce energy on-site, existence of full-scale plants to be enhanced...) and the importance of this waste in the present thesis work.

The review is divided in four different sections: physical pre-separation of non-degradable fractions for conditioning a waste stream free of undesirable materials (specially focused on MSW); pretreatments or disintegration technologies to enhance the hydrolysis step by organic matter solubilisation (to MSW on one hand and to other substrates on the other hand); and a review of full-scale treatment plants where pretreatments have been applied to solid wastes (excluding sewage sludge).

1. Pre-separation

Physical separation without chemical transformation for removal of inorganic materials: metals, plastics, glass, sand... is an important step to obtain a solid waste product free of non-digestable material. This is the basis for a correct operation in the digester, consisting in an effective mixing and absence of settleable and floating material inside the reactor. Moreover, avoiding the entrance of these materials, the reactor volume is optimised because the biodegradable fraction gets higher, so the volume is not missed.

Among those techniques, we find equipments of separation by size, such as rotating drums (called also Tromel) which is the most common because its versatility and simplicity, and vibrating or disk sieves; magnetic separators which collect selectively iron materials by a magnet; electrostatic separator (Eddy Current Separator), based on the application of Foucault currents to separate non-ferrous metals like aluminium; density separators, where a fluid is used to drag some materials: pneumatic classifiers remove light materials (paper, plastic bags) by an air stream, or water can be used to float light materials (plastics, paper, cardboard, wood) and settle heavy materials (sand, metals, glass).

The same way as a correct separation of undesirable materials has to be carried out previous digestion, an efficient post-separation enables a digestate with the best conditions to be reused. This separation employs the same basis and operations as the previous ones and it also shares purposes, looking for a stabilized digestate free of inorganic material, such as metals, plastics... This inorganic fraction can represent 28% of the initial digestate (total solids basis) and contains the main part of the heavy metals (Cu, Pb, Zn). This way a Class A digested waste can be obtained. Moreover, a post-separation can entail a dewaterability process which minimizes the digestate volume by dehydration. This operation can be carried out by different techniques: centrifugation, thermal drying with air, filtration...

2. Pretreatments to MSW for organic matter disintegration

The classification has been done depending on the nature of each treatment: mechanical, chemical, biological, thermal or combinations; and is focused in MSW.

a. Physical

i. Mechanical size reduction

This process is not really a hydrolysis pretreatment, but it can be considered a physical treatment necessary to achieve an adequate particle size of the waste previous to the applied pretreatment or digestion. Bernstad et al. (2013) highlight the role that an efficient physical pretreatment process of source-separated solid organic household waste has on its anaerobic digestion (increase of both the methane yield and nutrient recovery) by the study of different Swedish full-scale plants. Thus, the targeted particle size will avoid operational problems such as blocking or obstructions and will increase the substrate surface area, leading to an enhancement of its degradation degree on one hand, and its degradation rate on the other for substrates with high fibre content (Palmowski and Muller 2000). Two associate effects have been also reported: the cell rupture and sample structure alterations implying lignin-cellulose arrangements when comminuting fibre substrates. In fact, in another study, Palmowski and Muller (2003) modelled successfully the degradation of lignocellulosic substrates as a function of the surface area with different particle sizes, concluding that this parameter is a key factor related with the accessibility for the microbial enzymes.

Grinding or milling is an adequate pretreatment for high fibre content substrates, making hydrolysis step faster. However, an economical analysis can result in a negative energy balance. An optimal particle size of 0.6 mm for MSW was found by Izumi et al. (2010) with a bed mill. Lower sizes can produce acidification of the media and volatile fatty acids accumulation.

On the other hand, maceration is a method that presents low operational cost for a full degradation of particulate organic matter. Results indicate that the biodegradability of the fibres is rather enhanced by shearing, which is not necessarily reflected by a change in size distribution. Macerating fibres from manure showed an increase in biogas production

(Hartmann et al. 2000; Angelidaki and Ahring 2000). Therefore, municipal solid wastes with high fibre content could be an interesting candidate for a macerator pretreatment.

Anyway, Hansen et al. (2007) and Davidsson et al. (2007) have analysed the OFMSW from different mechanical treatments in real plants (screw press, disc screen, and shredder) and both agree that the OFMSW methane yield suffers no variation because the kind of pretreatment and the sorting system. Therefore, the decision of choosing one or another mechanical pretreatment does not seem crucial for the digestion process.

ii. Microwaves

Microwave pretreatment was tested by Shahriari et al. (2012) with an artificial OFMSW at 115, 145 and 175ºC. At 175ºC, inhibition was observed, at the same time that a brown colour could be identified. These facts were attributed to the formation of inhibitory compounds to biodegradation, such as melanoidins or humic acids. The formation of these compounds by high temperatures will be later discussed in thermal treatments section. In contrast, Marin et al. (2010) obtained a slight increase in biogas production when applying microwaves at 175ºC to kitchen waste.

iii. Ultrasounds

Cesaro et al. (2012) applied sonolysis to a mixture of sludge and OFMSW to obtain a pretreated mixture to be co-digested. While partially sonicated samples provided an increase of biogas, total sonication resulted in inhibition. In this case, the excess of pretreatment could cause a disinfection effect, but could also be due to some refractory compound formation by the high temperatures reached during the sonolysis. Therefore, Cesaro et al. (2012) designed two possible configurations for a continuous operation: sonication just to a feed fraction, or internal recycle with sonication.

iv. Electroporation

Electroporation supplies short and intense electric pulses at high voltage (Carlsson et al. 2008). The treatment causes the formation of pores in cell membranes of organisms. Depending on the intensity of the pulses, transient or permanent pores are formed. The disintegration of cell material is likely to promote the performance of anaerobic digestion, i.e. it enhances the degradation kinetics and increases the mass specific methane yield. In fact, Carlsson et al. (2008) found considerable increases of biogas productions in continuous laboratory scale trials and stated that the ratio of input energy to increased yield is 2-8%.

v. Pressurisation

The application of high pressures to organic matter as a pretreatment is commonly combined with high temperatures, so it is later included in this review. Just one study (Ma et al. 2011) has been found in which mixed kitchen waste (diluted with sewage sludge) was pressurized to 10 bar with CO_2 as pressurizing gas. After few minutes of contact time, the depressurization of the reactor to atmospheric pressure was performed by quick release of the CO_2 gas. After performing batch and continuous tests, higher biogas production and hydrolysis rate were obtained after the pressure treatment. Nevertheless, a negative economical balance makes the process unprofitable. (Ma et al. 2011)

vi. Rotating tubes

It consists in a horizontally mounted, rotating steel cylinder which automatically shreds, mixes and sorts the refuse into components for either recycling, biological processing or combustion with energy recovery and landfilling. In a continuous operation, the rotation of the drum leads to a breakdown of the softer components by particle collision and attrition, what creates a material with a very large surface area which is of great benefit in any biological degradation process and also makes it easy to screen and separate the organic fraction from the higher calorific waste components and the inert fractions.

There are studies (Zhu et al. 2009; Zhu et al. 2010) where a 38m length and 3m diameter rotary drum reactor (RDR) treats MSW obtaining optimal conditions at 3 days retention time. Other studies (Jiang et al. 2005; Chen et al. 2007) have worked with soybean meal waste, using a rotational drum fermentor (RDF) to improve the hydrolysis and acidogenesis stages prior the methanogenic reactor. In fact, this configuration corresponds to a two-phase anaerobic digestion process, which has been long time ago developed (Ghosh 1990) and patented by Zhang (2002) as the anaerobic phased system (APS) solid digester. Cho et al. (1995) tested a two-phase anaerobic digestion with Korean food waste, avoiding VFA accumulation and inhibition that took place in a conventional digestion.

On the other hand, rotating tubes are also considered mechanical-biological treatments (MBT), which is nowadays a spread technology that is applied in many waste treatment plants. Between 1990 and 2010, it is estimated that 180 new MBT plants have been built in Europe (Montejo et al. 2013). However, it has to be said that not all MBT plants entail a rotating tube. Nowadays, this device is commercialised as *Keppel Seghers Dano Drum* (Keppel Seghers technology).

b. <u>Chemical</u>

The addition of a chemical agent as a unique treatment for biodegradation of solid wastes has hardly been studied. It is usually combined with other treatments such as thermal ones.

i. Alkali hydrolysis

Alkaline pretreatment to OFMSW was studied by López Torres and Espinosa Lloréns (2008) adding $Ca(OH)_2$ (from 40 to 100 mEq/L). While 62 mEq/L (2.3 g $Ca(OH)_2$/L) reached a biogas increase of 173%, higher doses, lead to the formation of complex non-soluble compounds (non-degradables). Hamzawi et al. (1998) also found positive results when pretreating with an alkali a mixture of OFMSW and sewage sludge.

ii. Acid hydrolysis

A similar mixture was subjected to an acid treatment by the addition of HCl with no remarkable results (Ma et al. 2011).

c. <u>Biological</u>

Two main biological pretreatments before digestion are differenced: auto-enzymatic process, where enzyme activity is due to the activation of the proper enzymes contained in the waste (this is the case of pre-composting and ATAD processes); and external enzymes processes, where commercial enzymes are externally added.

i. Auto-enzymatic

- Pre-composting

Enzymes secretion takes place during a first aerobic phase before the anaerobic process. The liberated enzymes will lead to a natural hydrolytic process where a solubilisation of the organic matter occurs, leading to a faster methane production in the anaerobic reactor. Charles et al. have studied the enzymatic treatment of the OFMSW by a pre-aeration phase during two days under thermophilic conditions. Thus, anaerobic phase increased its methane production in just 7 days HRT and no acidification took place. Moreover, during the aerobic step, a self-heating in thermophilic range was achieved due to the enzyme activity (Charles et al. 2009).

- ATAD (Autothermal Thermophilic Aerobic Digestion)

This process is analogue to the previous one. It has just been tested for wastewater sludge with remarkable results: a pre-aeration step during 10 minutes is followed by a self-heated thermophilic digestion for 7 days (Riley and Forster 2002).

Although autoenzymatic processes appear to be very adequate pretreatments for sludge, very few trials with solid wastes have been done, so further research in this area could prove the acceptance of this method for MSW organic fraction.

ii. External enzymes

Fdez.-Güelfo et al. (2011a) compared the addition of external enzymes from different sources to the OFMSW: *Fungus Aspergillus* (Commercial enzymes), activated sludge from WWTP and mature compost (anaerobic digested sludge) from WWTP. The higher solubilisation was obtained with the last one, resulting in a cheap alternative. Then, the latest study was complemented with a second phase of study (Fdez.-Güelfo et al. 2011b), in which semi-continuous tests were performed under the next conditions: 24 hours of incubation with mature compost followed by a dry thermophilic digestion. Higher substrate removals were obtained and methane production also rose. Continuous trials have shown promising results for a low cost pretreatment that does need neither much investment nor considerable operating costs.

A mixture of different commercial enzymes was also tested by Kim et al. (2006): Viscozyme (carbohydrase), Flavourzyme (protease) and Palatase (lipase) (mixed in 1:2:1 ratio respectively). Enzyme dose was optimized considering COD solubilisation and VFA production but no anaerobic tests were carried out.

Moreover, it has to be remarked that buying or growing external enzymes is usually costly and not always assures a correct activity with the substrate, as well as require an accurate control of the operating conditions and an adequate preparation of the media (buffer solutions, pH, temperature control...).

d. <u>Thermal</u>

Thermal pretreatments consist either on decreasing radically the temperature (freezing) or increasing it; the latter is usually combined with other processes such as pressurization or chemical treatments, reviewed later on. In both cases, organic matter solubilisation is pursued in order to increase methane potential by heat addition or removal, what entails the advantage of no external reactants addition, but sometimes requires high energy inputs.

i. Heating

A thermal treatment to municipal biowaste at 175ºC increased the biogas yield and produced a digestate with better settlability properties (Wang et al. 2010). The municipal biowaste was composed by three fractions: food waste, fruit and vegetables, and sewage sludge that acts as diluter and improves heat transfer.

Another thermal treatment at 175ºC (Liu et al. 2012) was studied to three different solid substrates: kitchen waste, vegetable and fruit residue, and waste activated sludge. Liu et al. set some advantages of this process, such as sterilization or decrease of the viscosity, but also some drawbacks of the high temperatures application, such as the inactivation of methanogenic bacteria (studied by Hu and Chen 2007) to produce H_2 by anaerobic pathway inhibiting methanogenic activity and generating refractory compounds). The present study evaluated also some properties of the digestate: viscosity decreases after pretreatment, dewaterability tests reached a 60% recovery of organic matter in the supernatant liquid phase, an opportunity to increase the organic loading rate in an UASB reactor. Particle size analysis showed an increase of high molecular weight fractions (>300 kDa), although in lower molecular weight fractions (<10 kDa) refractory compounds (melanoidins) were detected for both kitchen waste and vegetable-fruit residue, causing a decrease in their methane potentials. Therefore, Liu et al. suggested as an optimal process the co-digestion of thermally treated activated sludge with raw kitchen waste and vegetable-fruit residue.

In a similar study, Qiao et al. (2011) tested hydrothermal pretreatment at 170ºC to different wastes. Higher methane yields were obtained for most of the wastes, except for food waste, where a decrease was achieved after pretreatment. This behaviour could not be explained, but Qiao et al. (2011) related it to the high lipid and protein content of this kind of waste. However, this inhibitory response could be also due to the effect that high temperatures have in this kind of substrates, as in the previous work (Liu et al. 2012).

Inhibitory behaviours in anaerobic digestion caused by high temperatures have been widely studied and attributed to different refractory compounds formed during Maillard reactions, which are activated by high temperatures (Benzing-Purdie et al. 1985). Among these compounds, melanoidins have been found to be the main responsible. Melanoidins are nitrogenous polymers formed in complex non-enzymatic reactions of carbonyl groups (glucose, glycine) and amino groups (amino acids, peptides) which, by the action of temperature, get a discoloration (browning) and fragmentation. They can be found in several common foods such as coffee, cacao in the form of different compositions (phenolic generally). The reason of its inhibition stems on his antimicrobial properties (especially against gram-positive bacteria, because the absence of outer membrane). (Wang et al. 2011)

ii. Freeze-Thaw

Ma et al. again tried to improve kitchen waste and sewage sludge mixture biodegradation, this time by freezing and thawing treatment (Ma et al. 2011). Raw mixed kitchen waste was frozen at -80 ºC and then thawed at 55 ºC. Higher biogas production and hydrolysis rate were reached and the economical balance was favourable. Furthermore, freezing presents other advantages: odour control, no chemical addition or hygienisation.

e. Combinations

Finally, an overview of some combined treatments is enclosed. These techniques show many times the best results since they overcome most of the individual drawbacks of previous processes and combine the advantages of each one.

i. Thermo-chemical

The addition of a chemical agent (acid or alkaline) combined with the heat effect can produce extraordinary high solubilisation results in the organic matter, as subsequent studies have demonstrated. However, the addition of an external reactant supposes always an economical disadvantage and sometimes produces undesirable inhibitory effects. Ma et al. (2011) acidified a mixture of kitchen waste and sewage sludge with HCl till pH 2 and then they autoclaved it at 120 ºC. A high solubilisation was reached but the formation of some inhibitory compounds did not lead to an increase in the methane potential, as it was also observed by Hamzawi et al. (1998) when pretreating a mixture of OFMSW and sewage sludge for co-digestion. In another case, an analogue alkaline treatment was carried out using NaOH instead of HCl. Wang et al. (2009b) optimised the temperature and the NaOH dose for a waste composed by municipal solid waste, kitchen waste and leaves. Optimum values were found at the highest temperature and dose tested (170ºC, 4 gNaOH/100g). Another similar work with MSW from an industrial plant (Fdez.-Güelfo et al. 2011a) obtained as optimum values 180ºC, 3gNaOH/L and 3 bar pressure. Under these conditions, a very high solubilisation of the organic matter took place, but a cost limitation was identified.

ii. Wet oxidation

This technique consists in an oxidation at high pressure and temperature in an enriched oxygen atmosphere. Lissens et al. (2004) have applied this pretreatment at temperatures between 185 and 220ºC and pressures up to 12bar to different biowastes: food waste, yard waste and digested biowaste. They found a higher biogas increase in substrates with high lignin content (yard waste), obtaining a double biogas production at lab-scale and observing that the higher the pressure, the higher the lignin degradation.

iii. Mechanic-chemical (microwave + oxidation)

In the already mentioned study of microwave pretreatment (Shahriari et al. 2012), the addition of hydrogen peroxide (H_2O_2) in combination with microwave treatment was also tested to the same artificial OFMSW. An oxidation process with H_2O_2 was followed by a microwave treatment at 85ºC. The COD solubilisation increase was still higher than for the microwaves alone but anaerobic tests showed again inhibitory behaviours (slow degradation rates). The causes were attributed to VFA accumulation or ammonia formation by rapid protein digestion, although ammonia levels did not surpassed inhibitory limits (over 1000 $mgNH_4^+/L$), set by Kayhanian (1994).

iv. Thermal Hydrolysis

This technology has been one of the most effective methods used as a disintegration technology, widely studied for sewage sludge as it is described in sludge pretreatments. It mainly consists on the application of high pressure and temperature by the addition of steam. Finally, the decompression takes place suddenly in a flash tank (steam explosion), providing a high solubilisation of the organic matter. It is sometimes believed that the consumption of steam makes the process uneconomical, but with an adequate energy integration design, heat can be reused allowing a complete energy recovery. Schieder et al. (2000), working with food scraps and canteen waste in a pilot plant (1800 tons per year), claimed that the thermal hydrolysis process gives complete energy recovery, what means more energy is produced than is needed for running the plant. This fact is also supported by Perez-Elvira et al. (2008), designing an energy integration system to recover heat and produce steam from biogas in a co-generation system as a full-scale assessment study for sewage sludge.

Cuetos et al. (2010) studied the co-digestion of MSW and slaughterhouse waste, applying thermal sterilization to avoid biodegradation problems due to ammonia inhibition and high long chain fatty acids (LCFA) accumulation. The treatment consisted in grinding the waste to a particle size of 3 mm followed by a thermal hydrolysis process at 133ºC and 3bar for 20 minutes, but no steam explosion was carried out. Biogas production rose but volatile fatty acids inhibition and refractory compounds formation took place. There were toxic compounds and complex polymers with slow biodegradability, which formation could be due to Maillard reactions by high temperatures, as it has already been explained in thermal treatments.

In the design of the Super Blue Box Recycling (SUBBOR) plant, Vogt et al. (2002) incorporate also thermal hydrolysis as an inter-stage treatment of the organic fraction of MSW digestion. After milling the waste till a particle size of 5 mm, the OFMSW is digested in two thermophilic reactors; between them thermal hydrolysis at 230ºC is applied. The results showed a positive energy balance for thermal hydrolysis process, an increase on biogas production and a lower residence time in the second digester (15 days versus 35 days in the first stage) since a four times higher kinetics took place after pretreatment. This process shows the advantages of thermal hydrolysis treatment and the variability to implement it in the process.

In a recent study, Zhou et al. (2013) tested the effect of thermal hydrolysis in a co-digestion process of sewage sludge and organic food waste in a continuous pilot plant. No difference in terms of biogas production was found, but significant improvements of kinetics and reactor stability were obtained: kinetics almost doubled and lag-phase was reduced, which means shorter hydraulic retention times could be operated; lower VFA accumulation lead to a more stable process; and lower viscosity and better dewaterability were other advantages that make thermal hydrolysis a pretreatment with a positive cost balance.

3. Pretreatments to other solid wastes

Many studies have focused in improving the anaerobic digestion from other wastes by similar pretreatments as the previously explained. Without the aim of providing a full review, some works are next presented.

a. Manure

Dairy, cow and swine manures are the main ones produced in an extensive way. First, mechanical maceration of fibres from manure has shown an increase in biogas production (Hartmann et al. 2000; Angelidaki and Ahring 2000) by the same mechanisms explained for MSW. Also, Palmowski et al. (2006) improved the anaerobic digestibility of dairy manure by sonolysis. Working as well with dairy manure, Jin et al. (2009) applied different thermochemical pretreatments with microwaves to improve its digestion and enhance struvite precipitation for phosphate recovery. Best results were obtained at 147ºC with NaOH or HCl addition since microwaves produced an explosion effect by temperature inhomogeneity. Cow manure degradation was enhanced by thermal treatment at 170ºC (optimal temperature) by Yoneyama et al. (2006). Swine manure has been extensively studied and some studies can be highlighted: ultrasounds pretreatment provided a full energy recovery by the methane production increase (Elbeshbishy et al. 2011); thermal over 135ºC and thermochemical (pH 10) treatments enhanced methane production (optimal temperature at 190ºC) since a reduction of the hemicellulosic fraction took place (Carrère et al. 2009); however, Rafique et al. (2010) found methane increases at 100ºC thermal pretreatment and even at 70ºC when calcium hydroxide was added (thermochemical pretreatment); on the other hand, González-Fernández et al. (2008) set the optimal temperature for thermal pretreatment at 170ºC, obtaining also good results with alkali pretreatment with NaOH. Hence, it has to be said that the optimal operating conditions for each pretreatment are very dependent on the kind of manure and on its origin.

b. Lignocellulosic materials

This kind of materials involves a large number of substrates with diverse origin but a common vegetable character: energy crops, agricultural residues... Two main pretreatments to these substrates have been found: ultrasounds and thermo-chemical (or wet oxidation).

Chen et al. (2008) have tried ultrasonic hydrolysis of fermentation broth, with the objective of carrying out the acidogenic fermentation, so VFA desorption during the pretreatment was pursued. Ultrasounds were applied following two different configurations: direct ultrasonic irradiation (DUSI) and modified ultrasonic treatment (MUST) with water dilution. The former (DUSI) obtained an increase in VS degradation, but no VFA desorption was achieved, and MUST presented better results for the fermentation process: VFA desorption took place, dilution improved rheology, and a reduction of particle size lead to a higher solubilisation, then, higher TS and VS degradation.

Wet oxidation treatments (also including thermo-chemical here) involve an oxidative process with a chemical agent at high temperature and pressure. Varga et al. (2003), working with corn stover to enhance its fermentation for ethanol production, reached a high solubilisation of hemicelluslose and lignin fractions at 195ºC, 12bar and Na_2CO addition. Uellendahl et al. (2008) obtained a positive energy balance to produce biogas from perennial energy crops. Fernandes et al. (2009) applied a thermo-chemical treatment to three different lignocellulosic biomasses: hay, straw and bracken. The results showed that not all the chemical additives worked for all the substrates: hay degradation could not be improved anyway, straw was enhanced only by ammonium and bracken was remarkably affected by all of them, due to its high lignin content. Another case of inefficiency of wet explosion took place when Wang et al. (2009a) treated wheat straw at 180ºC and 10bar, adding H_2O_2 to be co-digested with swine manure: soluble sugars augmented but methane potential decreased, due to inhibition by high temperatures.
Moreover, there are many studies describing biological pretreatments to enhance the enzymatic hydrolysis of lignocellulosic materials (Cacchio et al. 2001; Zheng et al. 2002), but not with an aim of being implemented in anaerobic process.

Further studies with different pretreatments to lignocellulosic biomasses can be found in a full review by Hendriks and Zeeman (2009), where the effects of pretreatments on lignin, hemicellulose and cellulose fractions are analysed. They conclude that steam, lime, hot water and ammonia are the most effective treatments for this substrate and the main mechanisms that take place are: dissolving hemicelluloses, altering lignin structure and improving the accessibility for hydrolytic enzymes. They also state that the effect of the pretreatments is strongly influenced by the biomass composition and the operating conditions, what justifies the diversity of results previously explained. (Hendriks and Zeeman 2009)

c. Food industry waste

Luste et al. (2009) have studied the anaerobic digestion enhancement of four by-products from meat-processing industry (pig and cow slaughterhouse). Five different pretreatments were applied: thermal (70ºC), ultrasounds, acid (HCl), alkali (NaOH) and bacterial (external enzymes addition). Ultrasounds and bacterial pretreatments lead to high solubilisations, but the thermal treatment increased the most methane yields and lead to a sterilized digestate according to regulations for category II animal wastes. (Luste et al. 2009)

4. Pretreatments in full-scale plants

In the area of sewage sludge, some of the previous pretreatment technologies, which have been deeply studied in lab-scale experiments, have been also applied in full-scale plants with a complete implementation and full operation. Thermal hydrolysis technology is the most spread technology to enhance waste activated sludge anaerobic digestion in WWTP. Since 1995, when the first Cambi thermal hydrolysis (THP) plant started up in Hamar (Norway) (Kepp et al. 2000), many other plants (up to 20) have adopted this technology. Other authors have studied the feasibility to implement thermal hydrolysis in pilot scale plants (Graja et al. 2005; Zhou et al. 2013), in full-scale plants by modelling tools (Phothilangka et al. 2008), or even with a complete energy integration in the WWTP (Perez-Elvira et al. 2008), leading to an energetically self-sufficient process. Other companies have recently commercialized their own continuous thermal hydrolysis process for biosolids pretreatment, such as Turbotec (Sustec) in 2011 with one pilot plant, Exelys (Kruger-Veolia) in 2010 with one full-scale plant or CTH (Aqualogy) in one full-scale WWTP. Ultrasounds technology has also been worldwide applied in full-scale WWTP (UK, US, Australia…), mainly with Sonix technology (Pilli et al. 2011), or even in Singapore (Xie et al. 2007) for mixed sludge in 5000m^3 digesters. A full energy recovery has also been reached with ultrasounds in industrial plants in Germany (Barber 2005) and commercial processes have been also patented, such as Biosonator (Ultrawaves). Other pretreatments technologies to sewage sludge that have also been implemented in full-scale plants are ozonization (Chu et al. 2009) and focused-pulse technology (Rittmann et al. 2008; Zhang et al. 2009).

On the other hand, concerning municipal solid wastes, very few plants have implemented pretreatments to anaerobic processes; just Cambi thermal hydrolysis technology is applied in some full-scale biowaste treatment plants in Norway: *Glør, Lillehammer (2001, 14000 t/year), Ecopro, Verdal (2008, 30000 t/year) and Oslo (2012, 50000 t/year)* (Román et al, 2007). For example, Glør plant (Lillehammer) treats household source-separated wastes and produces 100 Nm^3 biogas per ton of biowaste (70/82% food waste) and 150 kg biosolids. The Ecopro plant treats a multiwaste (municipal organic waste, sewage sludge and slaughterhouse waste), producing 40-50 million kWh per year. A pathogen-free biosolid with more than 30% dried matter is produced after digestion and can be used as fertilizer in agriculture or as an organic soil improver. *In fact, b*oth Glør and Ecopro plants have received permits to use the bio-fertilizer in the agricultural sector and also for land remediation purposes (Sargalski, 2008). A bigger plant in Oslo with two THP systems has been recently built with the aim of treating 50000 t/year food wastes and producing 27000 t/year of nutritious biofertilizer.

Regarding other kind of wastes, thermal hydrolysis pretreatment has been patented by different companies with different technologies and objectives: TPH (thermal-pressure-hydrolysis) by ATZ development center can treat any kind of waste previously grinded (food and kitchen waste, animal by-products, sludge...); TPP (thermo-pressure preparation) by NWT enhances ethanol/biogas production from lignocellulosic biomass; Turbotec II (Sustec) has developed a batch process to pretreat green waste and straw; Biorefinex (Biosphere Technology) applies thermal hydrolysis to animal by-products and carcass material with sanitization purposes and is starting up a full-scale demonstration in 2013 (Lacombe Biorefinery). However, all these technologies are still under development and no full-scale results can be found. (Perez-Elvira et al. 2013)

CONCLUSIONS

Among all the technologies which have been described, it is difficult to conclude that there is one which could satisfy all the desired necessities required for an optimal MSW anaerobic digestion process. Substrate properties can widely vary depending on the kind of waste to treat or even on its origin of production. Therefore, a complete characterization of the matter must be firstly achieved in order to select the appropriate treatment.

Mechanical processes are usually required for high particle sized wastes or for high fibre content substrates. Chemical treatments are used to go with another one such as thermals, whose joint action leads often to synergistic effects. Thermal ones alone have as well a strong impact, with the additional advantage that no external reactants are added. However, high temperature processes are often the cause of refractory compounds formation which causes the inactivation of bacterial processes. In the other hand, biological processes can also be very effective since the enzymatic activity is fast and selective. Commercial enzymes can be purchased, but natural enzymes (autoenzymatic process) have shown interesting results with additional advantages. The combination of some of these processes has usually interesting perspectives due to the addition of several effects: thermal hydrolysis combines the thermal power of the steam with a quick depressurization (steam explosion) or a mechanical process such as microwaves can be enhanced by a chemical oxidation process.

While there is a broad experience in full-scale pretreatments for sewage sludge in WWTP (thermal hydrolysis and ultrasounds mainly), there are very few plants with pretreatment to municipal solid wastes (just three Norwegian plants with THP from Cambi) and few patented technologies for other solid wastes. This situation gives a big opportunity to the development of new research studies in order to assess the impact of pretreatments in solid wastes, so that new industrial plants could implement these technologies in full-scale with the highest environmental, energetic and economical benefits.

PRETREATMENTS		FUNDAMENTALS	ADVANTAGES	DRAWBACKS	MAIN RESULTS	SUBSTRATE*	REFERENCES
MECHANICAL	Size reduction	Grinding, macerating, shredding Particle size reduction Surface/area increase	Avoids blocking Higher biogas production Rapid digestion of fibres Faster hydrolysis	Acidification if excessive treatment Negative energy balance	Opt. particle size: 0.6mm +40%COD solubilisation +25%biogas No influence of the technique in BMP	MSW LM CM	Bernstad (2013); Palmowski and Muller (2000); Izumi (2010); Hartmann (2000); Angelidaki (2000); Hansen (2007); Davidsson (2007)
	Microwaves	Microwave irradiation (high T, 175ºC)	High solubilisation	Inhibition of anaerobic digestion by high T	+50%COD solubilisation Slight biogas increase (+9%)	s-OFMSW KW	Shahriari (2002); Marin (2010)
	Ultrasounds	Cavitations	High solubilisation Full energy recovery	Inhibition by excess of sonication No VFA desorption for adidogenesis	+72%COD solubilisation +24%BMP (SS + OFMSW) +28%BMP (SM) Manure digestibility increase +188%COD solubilisation (SW)	SS + OFMSW DM SM SW LM	Cesaro (2012); Palmowski (2006); Elbeshbishy (2011); Luste (2009); Chen (2008)
	Electroporation	Intense electric pulses	Disintegration of cell material	No further research	Improve kinetics and BMP (+20/40%)	MSW	Carlsson (2008)
	Pressurization	Application of high pressures (10 bar)	No chemical addition	Negative economical balance	Higher biogas production	KW + SS	Ma (2011)
	Rotating tubes	Rotating steel cylinder	Automatic sorting Continuous operation Screening and breakdown	Non developed technology	Opt. HRT: 3 days	MSW LM	Zhu (2009); Zhu (2010); Chen (2007); Jiang (2005)
CHEMICAL	Acid/Alkali hydrolysis	Chemical agent addition	Aggressive treatment	External agent addition Complex non-soluble compounds formation	+11.5% solubilisation +172% BMP (+$Ca(OH)_2$) No results (+HCl pH 2) +13%biogas (SM)	OFMSW (+SS) KW SM SW	López-Torres (2008); Ma (2011); Hamzawi (1998); González-Fernández (2008); Luste (2009)
BIOLOGICAL	Auto-enzymatic	Natural enzyme secretion at low T	Natural hydrolysis Self-heating Low cost	Difficult aeration with solid wastes Untested activity	More biogas in 7 days HRT (pre-aeration at 55ºC for 2 days)	SS OFMSW	Charles(2009); Riley (2002)
	External enzymes	External source of enzymes: natural (sludge) or commercial	Tested activity High COD solubilisation	Costly (commercial enzymes) Accurate pH and T control	VFA production x3 +51% solubilisation +74% methane	OFMSW SW	Fdez Güelfo (2011); Kim (2006); Luste (2009)

THERMAL	Heating	Application of heat (different T tested)	No chemical addition Sterilization Decrease of viscosity Reduction of the hemicellulosic fraction Better settlability	Inactivation of methanogenic bacteria by high T Refractory compounds formation (melanoidins)	+60%solubilisation +14%biogas (KW + SS) Inhibition at 175ºC (FW) +30%biogas (CM) at 170ºC +25%biogas (SM): 100ºC +35%biogas (SM): 170ºC High CH_4 yield at 70ºC for SW	KW + SS FW WAS CM SM SW	Ma (2011); Wang (2010); Liu (2012); Qiao (2011); Yoneyama (2006); Carrère (2009); Rafique (2010); González-Fernández (2008); Luste (2009)
	Freezing Thawing	Application of low T (-80ºC)	No chemical addition Odour control Hygienisation Positive energy balance	No further research	Higher biogas production	KW	Ma (2011)
COMBINATIONS	Thermo-chemical	Addition of a chemical agent combined with heat effect	High solubilisation Sterilization Reduction of the hemicellulosic fraction Strong effect for lignin	Inhibitory compounds Chemical addition Costly	+32% solubilisation No biogas increase (HCl, 120ºC) +246%solubilisation (NaOH,180ºC) Higher BMP (SM): pH 10, 150ºC +60%biogas (SM) 70ºC+$Ca(OH)_2$	KW + SS OFMSW + SS MSW SM LM	Ma (2011); Hamzawi (1998); Wang (2009); Fdez Güelfo (2011); Carrère (2009); Rafique (2010); Fernandes (2009)
	Wet oxidation	Oxidation at high P (12bar) and T (220ºC) in O_2 atmosphere	Biogas production increase Lignin degradation Positive energy balance	Extreme conditions	+98% biogas (yard W) +35/40% biogas in full-scale +60%LM solubilisation (+Na_2CO) Inhibition when adding H_2O_2	FW yard W LM	Lissens (2004); Varga (2003); Uellendahl (2008); (Wang et al. 2009a)
	Mechanic-chemical	Microwave (85ºC) + oxidation H_2O_2 Microwave (147ºC) + chemical (NaOH, HCl)	High solubilisation Enhance struvite precipitation	Anaerobic digestion inhibition by VFA/ NH_4^+	COD solubilisation Inhibition	s-OFMSW DM	Shahriari (2012); Jin (2009)
	Thermal Hydrolysis	Injection of steam (high T and P) and sudden decompression (steam explosion)	High disintegration Sterilization Complete energy recovery	Inhibitory compounds by high T	Inhibition (133ºC, 3bar) Interstage TH (230ºC): +40% biogas hydrolysis rate x4 Better dewaterability Lower viscosity	MSW + SW FW WAS OFMSW FW + SS	Schieder (1999); Cuetos (2010); Vogt (2002); Perez-Elvira (2008); Zhou (2013)

Substrates legend: MSW (municipal solid waste), OFMSW (organic fraction municipal solid waste), s-OFMSW (synthetic organic fraction municipal solid waste), KW (kitchen waste), FW (food waste), W (waste), SS (sewage sludge), WAS (waste activated sludge), LM (lignocellulosic material), CM (cow manure), DM (dairy manure), SM (swine manure), SW (slaughterhouse waste)

Table 2. Summary table of different pretreatments to solid wastes

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CHAPTER 2. ENERGY FEASIBILITY STUDY OF PRETREATMENTS

In order to select the most appropriate pretreatments to be further studied, an energy feasibility assessment of the current technologies is developed in this chapter, based on previous reports and studies from literature and focusing in sewage sludge since it is the most reported substrate in this area. Most of the pretreatments in lab-scale studies show high potentials to be implemented in an anaerobic digester since they produce an increase in the biogas production. However, no energetic assessments are usually considered in scientific reports. By making a simple evaluation of energy consumption by pretreatments, it can be stated that unfortunately not all the pretreatment technologies have an energy self-sufficiency to be implemented in a WWTP, requiring many times a continuous energy investment. Generally, pretreatments consuming electricity do not satisfy its energy demands from the biogas production in the same process, although high solubilisation or biogas production increases are reached. Just ultrasounds applied in full-scale plants, with commercial technologies such as Sonix or Biosonator, provide an energetically self-sufficient pretreatment. In the case of thermal pretreatments, the potential to be implemented with full energy integration is much higher, since they can recover heat from the biogas engine as well as electrical energy in the same extent as for electric pretreatments. This way, full energy integration can be achieved in thermal hydrolysis plants; such is the case of commercial technologies such as Cambi, Exelys (Veolia) or CTH (Aqualogy). Several theoretical approaches and simulations also state that thermal hydrolysis presents a high potential to be fully integrated in WWTP with a complete energy recovery and self-sufficiency.

Keywords: energy integration, self-sufficiency, pretreatment, sewage sludge, thermal hydrolysis

Energy feasibility study of sludge pretreatments: a review

1. Introduction

As a simplified model, wastewater is a diluted mixture of water and organic matter. From a thermodynamic point of view, the organic matter of wastewater can be considered as an energy source. All the organic compounds included in the wastewater contain energy stored within their chemical bonds. To perform energy balances, it is necessary to calculate the 'energy content' (EC) of the wastewater. According to Garrido et al (2013), COD is a conservative parameter, easy to measure and follow during wastewater treatment. The paper of Shizas & Bagley (2004) seems to be the first experimental approach to determine the energy stored in domestic wastewater. They estimate that the experimental average value of the energy stored in the different streams of a waste water treatment plant (WWTP) is 12.4 kJ/g COD. In a more recent paper, Heidrich et al. (2013) present experimental results for two samples of wastewater from different facilities; the EC values in this study were 22.5 and 17.7 kJ/g COD. COD may be converted to methane in anaerobic digesters. Considering stoichiometry 1kg CH_4 is equivalent to 4kg COD. Applying Hess's law, the heat of combustion of COD is 13.88 kJ/gCOD, in agreement with the experimental values proposed by Shizas & Bagley (2004). This way, the EC of each stream in the flow diagram of the WWTP can be calculated as a function of the COD mass flux (FCOD) and the COD heat of combustion (equation 1).

$$EC\ (kJ/d) = FCOD\ (kg\ COD/d) \times \Delta U_C\ (kJ/kg\ COD) \qquad (1)$$

In a conventional WWTP more than 60% of the initially diluted COD is concentrated as sludge. Then, 60% of the initial energy content of the wastewater is now concentrated in the sludge and can be recovered as biogas produced in anaerobic digesters.

Anaerobic digestion of sludge shows certain limitations in the first hydrolytic step, leading to slow degradation of the organic matter and too high retention times. In order to improve the kinetics of anaerobic biodegradation of sludge, many pretreatment technologies have been tested with the aim of accelerating the hydrolysis limiting step and enhancing biogas productivity as well as the characteristics of the digested sludge. Pérez-Elvira et al (2006a), Carrère et al (2010) and Carlsson et al (2012) have compiled most of these pretreatment techniques in very complete reviews. Some of these technologies tested at laboratory or pilot scale have been extrapolated to industrial scale and are operative in different WWTP. Thermal hydrolysis technology is the most spread technology to enhance sludge anaerobic digestion in WWTP. Since 1995, when the first Cambi thermal hydrolysis (THP) plant started up in Hamar (Norway)(Kepp et al. 2000), many other plants (up to 20) have adopted this technology. Other companies have recently commercialized their own thermal hydrolysis process for biosolids pretreatment, such as Biothelys (Veolia) in 2006 with ten full-scale operative plants, Exelys (Kruger-Veolia) in 2010 with one full-scale plant, Turbotec (Sustec) in 2011 with one pilot plant or CTH -continuous thermal hydrolysis- (Aqualogy) in 2012 with an industrial prototype. Other patented thermal hydrolysis technologies are under development to treat a wide variety of wastes: TPH (thermal-pressure-hydrolysis) by ATZ development center, TPP (thermo-pressure preparation) by NWT, Lysotherm (Stulz H+E) and Biorefinex (Biosphere Technology). Ultrasounds technology has also been worldwide applied in full-scale WWTP (Pilli et al. 2011). Sonix (Sonico, UK), Biosonator (Ultrawaves, Germany), smart DMS (Weber Ultrasonics) and Sonolyzer (Ovivo) are some of the patented technologies. Other pretreatments technologies to sewage sludge that have also been implemented in full-scale plants are high pressure homogenizers (MicroSludge - Pradigm Environmental Technology, Crown – Biogest, Cellruptor - Eosolids), OpenCEL focused-pulse technology (Rittmann et al. 2008; Zhang et al. 2009) and ozonization (Chu et al. 2009).

Table 1 shows the main technologies used at laboratory scale while Table 2 shows the main processes applied at industrial scale. It should be noted that commercial information is sometimes difficult to locate and standardize.

PRETREATMENTS		REFERENCES
Physical	High pressure homogenizer Impact grinding Electroporation/Pulse electric fields Ultrasounds Microwaves	Nah et al. 2000; Engelhart et al. 2000; Bougrier et al. 2006; Climent et al. 2007; Donoso-Bravo et al. 2010; Pilli et al. 2011; Choi et al. 2006; Muller et al. 2004; Appels et al. 2013; Solyom et al. 2011; Perez-Elvira et al. 2009
Chemical	Acid Alkali Ozone	Kianmehr et al. 2010; Bougrier et al. 2006; Chu et al. 2009; Bohler and Siegrist 2004; Salsabil et al. 2010
Biological	Autoenzymatic External enzymes	Carvajal et al. 2013; Barjenbruch and Kopplow 2003; Davidsson et al. 2007; Hasegawa 2000
Thermal	Heating Freezing / Thawing	Stuckey and McCarty 1984; Bougrier et al. 2008; Climent et al. 2007; Borges and Chernicharo 2009; Montusiewicz et al. 2010
Combined	Thermo-chemical Wet oxidation Thermal hydrolysis	Valo et al. 2004; Strong et al. 2011; Schieder et al. 2000; Donoso-Bravo et al. 2011; Perez-Elvira et al. 2010 Wang et al. 2009b; Xu et al. 2010

Table 1. Pretreatment technologies tested at lab-scale.

Thermal Hydrolysis	Ultrasounds	High pressure homogenizer	Pulse Electric Fields
Cambi (1995): 20 plants	Biosonator	MicroSludge	OpenCEL
Biothelys (2006): 10 plants	Sonix	Crown	PowerMod
Exelys (2010): 1 plant	Iwe.Tec	Cellruptor	
Turbotec (2011): 1 pilot	Smart DMS		
CTH (2012): 1 plant	Sonolyzer		
Lysotherm (2012): 1 plant	Hielscher		
Biorefinex (2013): 1 plant			

Table 2. Pretreatment technologies applied at industrial scale.

Given the high number of existing pretreatments, the aim of this work is to present the main guidelines to integrate pretreatment technologies in WWTP.

2. Interaction between pretreatment and WWTP

The main effects that pretreatments have on different substrates, as reported in literature (Carlsson et al. 2012), are: i) particle size reduction, ii) solubilization, iii) biodegradability enhancement, iv) formation of refractory compounds, v) loss of organic material. As a matter of fact only the first three parameters are studied in most of the papers, while the last two parameters are referenced only circumstantially. Pilli et all (2011) present a complete review of ultrasonic pretreatment of sludge evaluating sonication effect paying attention to particle size, dewaterability, settleabilty, solubilization, protein assessment and OUR. Considering now the crucial aspect of energy consumption, the data presented in the section devoted to sludge biodegradability and methane production do not allow realistic energy balances to quantify energy consumption (kJ/kg sludge). In addition, these parameters refer only to the pretreatment itself and do not take into account the interaction between pretreatment and the WWTP plant.

Figure 1 summarizes the physical links between the pretreatment and the rest of the elements of the WWTP. The circled numbers represent the WWTP streams or equipments which are affected by the presence of the pretreatment system. The main parameters affected in each location are shown in Table 1.

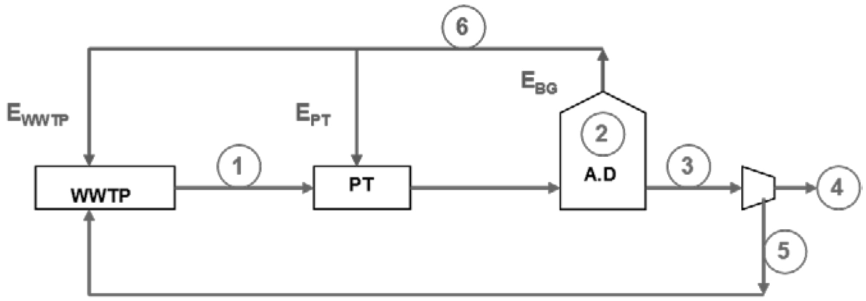

Figure 1. Interaction between pretreatment (PT) and WWTP

1. Sludge feed	Type of sludge (1ary, 2ary, mixed) Concentration
2. Anaerobic digester	COD and VS removal Rehology (viscosity) Mixing energy Foam formation
3. Digestate	Dewaterability Filterability Centrifugability
4. Biowaste	Sanitation PPCP's removal
5. Supernatant liquor	COD + nutrients Recycle to WWTP Recovery
6. Biogas	Energy to PT (electrical or thermal) and to WWTP (electrical)

Table 3. Key parameters on pretreatment integration.

Comparing the parameters usually reported in scientific literature Carrère et al. (2010), Pilli et all (2011), Carlsson et al (2012) and the parameters controlling technical and economical viability of the pretreatment process (Table 3), it is easy to verify that the objectives of scientific papers clearly differ from the technical requirements of the industrial scale. Among them, the key factors in the energy balance are the recovery of heat from hot streams (6) and the concentration of sludge (1) (Perez-Elvira et al. 2008). First, it is immediately noticeable that the extra biogas produced in the digestion will directly influence the pretreatment feasibility, but the amount of recovered energy in terms of heat or electricity to the pretreatment is what would lead to an energy integrated process. On the other hand, the sludge concentration in the feed stream is one of the key parameters to assess the energy and economic feasibility of the pretreatment since it is directly related to the energy requirements per sludge volume (kWh/m^3 sludge). Most of the literature focuses on the biogas production increase with the pretreatment, without paying attention to the energy integration in the system and the influence of the sludge concentration. Hence, in this study, these two premises will be considered as starting points to perform an energy feasibility study of different pretreatment technologies: from theoretical energy considerations to the energetic assessment of different lab-scale studies and industrial processes.

3. Pretreatments energy feasibility

Energy balances

The energy production (E) in an anaerobic process can be expressed in a simplified model as a function of the process efficiency (η_{AD}) and the sludge concentration (c) fed into the system. Next, in a sequence of three equations, a simple mathematical correlation representing this statement is obtained (some typical values for sewage sludge have been substituted):

$$\text{Organic load} = (OL) = (SV/ST)\ \text{Kg SV/KgST} \cdot (c)\ \text{KgST/m}^3 \cdot (r_{COD})\ \text{Kg COD/KgSV}$$
$$= (0.7)\ (c)\ (1.4) = (0.98\ c)\ \text{Kg COD/m}^3 \quad (2)$$

$$\text{Biogas produced} = (B) = (OL)\ \text{Kg COD/m}^3 \cdot (\eta_{AD})\ \text{Kg COD}_{REM}\text{/Kg COD} \cdot (r_{CH4})\ \text{Nm}^3\text{CH}_4\text{/Kg COD}_{REM}$$
$$= (0.98\ c)\ (\eta_{AD})\ (0.35) = (0.34\ c\ \eta_{AD})\ \text{Nm}^3\text{CH}_4\text{/m}^3_{sludge} \quad (3)$$

$$\text{Total energy} = (E) = (B)\ \text{Nm}^3\text{CH}_4\text{/m}^3\ .\ (\Delta H_C)_{CH4}\ \text{kWh/Nm}^3\ \text{CH}_4 =$$
$$= (0.34\ c\ \eta_{AD})\ (11) = (3.77\ c\ \eta_{AD})\ \text{kWh/m}^3_{sludge}$$

$$\boxed{E = (3.77\ c\ \eta_{AD})\ \text{kWh/m}^3_{sludge}} \quad (4)$$

Anaerobic digestion efficiency (η_{AD}) can be considered as the biodegradability extent in the digestion and acquires typical values around 45% in full-scale digesters, considering a conservative value. However, when pretreatments are applied prior digestion, the biogas production and the biodegradation extent can surpass a 40% enhancement, leading to efficiencies over 60%. This way, substituting these figures in the equation (4) we obtain:

Fresh sludge (η_{AD}= 0.45): $E_F = (1.70\ c)\ \text{kWh/m}^3_{sludge}$ (5)

Pretreated (η_{AD}= 0.63): $E_{PT} = (2.38\ c)\ \text{kWh/m}^3_{sludge}$ (6)

The energy contained in the biogas has to be recovered and transformed in order to store it for selling or reuse it in the WWTP. A combined heat and power system (CHP) is an efficient way to produce electricity (E.E) and recover heat in a gaseous stream at 400ºC (exhaust gases, E.G) and in a liquid stream at low temperature (hot water, HW). Typically, 15% of the biogas energy is lost and, from the rest, 35% is converted into electric energy and 65% into thermal energy (30% in EG and 35% in HW). Unfortunately, most of the times, just the electric energy is useful and generates profit, which only represents a 30% of the total energy contained in the biogas.

(E) = (EE) + (EG) + (HW) + (0.15 EB)
EE = 0.35 (0.85 EB)
EG = 0.30 (0.85 EB)
HW = 0.35 (0.85 EB)

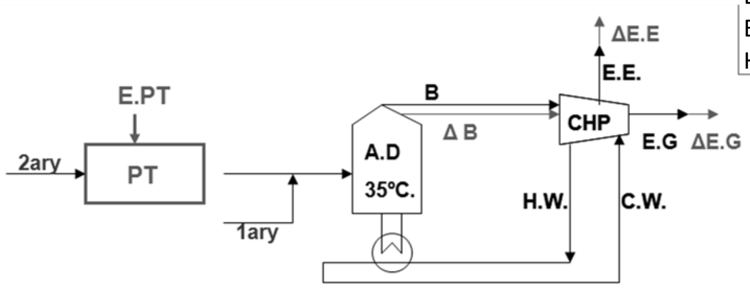

Figure 2. Energy recovery from biogas with a CHP system

Therefore, when a pretreatment is implemented in an anaerobic digester, its energy requirements (E.PT) should be lower than the increase of electric energy that produces (ΔE.E) in order to assure an energetically self-sufficient process. However, when talking about thermal pretreatments, the recovery of the waste heat that is produced in the CHP (exhaust gases mainly, E.G+ΔE.G) for the pretreatment step would lead to an efficient energy integration and the amount of energy which could be recovered for the pretreatment would be greater [(E.G + ΔE.G) + ΔE.E]. This can be expressed as:

Pretreatments consuming:

- Electricity $E.PT \leq \Delta E.E$ (7)
- Heat $E.PT \leq (E.G + \Delta E.G) + \Delta E.E$ (8)

From now on, the energy feasibility assessment will be considered separately for both pretreatment types. These inequalities could be arranged and expressed as a function of c, combining them with equations (5) and (6) and considering: $\Delta E = E_{PT} - E_F$

Pretreatments consuming:

- Electricity $E.PT \leq \Delta E.E = 0.35\ (0.85\ \Delta E) = (0.20\ c)\ kWh/m^3_{sludge}$ (9)
- Heat $E.PT \leq (E.G + \Delta E.G) + \Delta E.E = 0.30\ (0.85\ E_{PT}) + 0.35\ (0.85\ \Delta E)$
$= (0.81\ c)\ kWh/m^3_{sludge}$ (10)

Pretreatments consuming electricity

Most of the pretreatments (ultrasounds, microwaves, ozonization, pulse electric fields, high pressure homogenizers...) usually use electricity as energy source, which could be produced from the biogas in the same system. This would lead to a lower footprint, but in the other hand it would reduce the net profits of the digestion since the green electricity sold is lower.

According to equation (9), the energy consumption during these pretreatments should be lower than:

$$\mathbf{E.PT \leq (0.20\ c)\ kWh/m^3_{sludge}} \qquad (11)$$

The maximum energy consumed is a linear function of the sludge concentration, what means that the energy invested in the pretreatment increases proportionally as the solids content in the sludge rises (0.2 kWh for each kg TS). This simple equation (11) enables a quick evaluation of different pretreatment techniques, either applied at lab-scale or industrial scale, to check if the energy balances are satisfied and the process is energetically self-sufficient. Plotting the previous equation (11) in a graph representing the energy input versus the sludge concentration (Figure 3, red line), the different pretreatments can be placed according to energy consumptions obtained in literature and shown in Table 4: lab-scale studies on one hand, and full-scale results on the other (Figure 3).

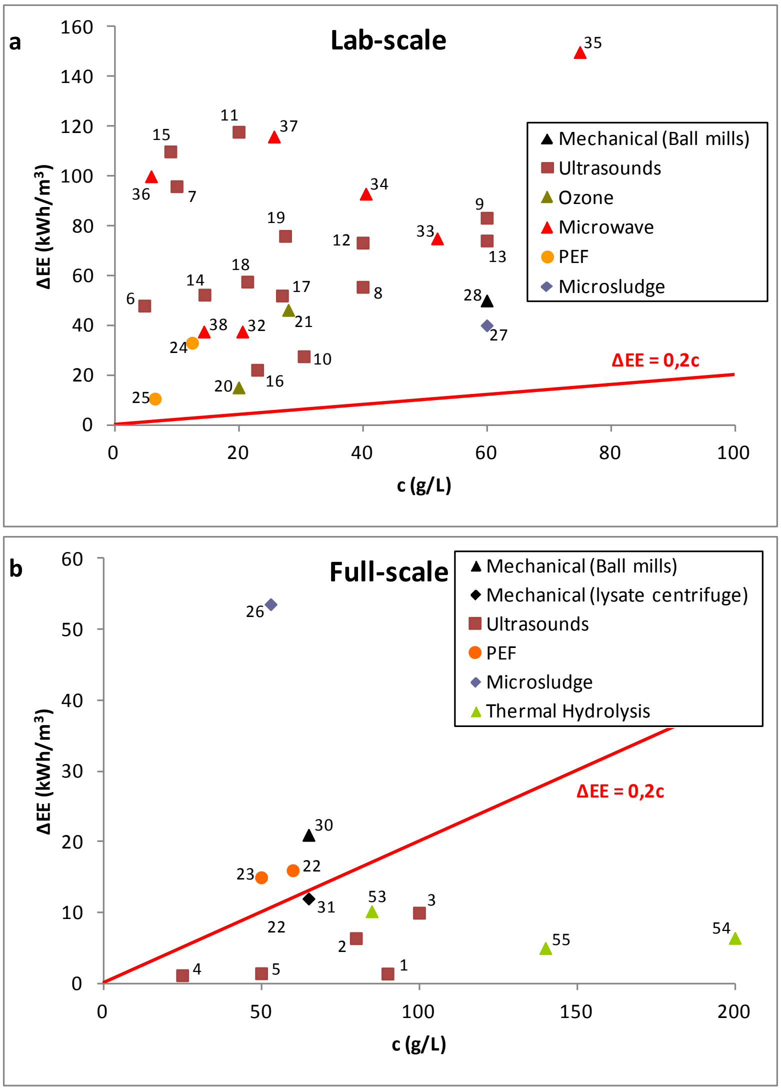

Figure 3. Pretreatments consuming electricity: a) lab-scale b) full-scale

At a glance, the fact of representing separately lab-scale and full-scale results shows immediately the main conclusion: all lab-scale experiments lead to energetically inefficient pretreatments (points above the line) and full-scale ones reduce considerably their energy consumptions, leading in some cases to energetically self-sufficient pretreatments (points under the line) but not in all of them. Ultrasounds pretreatment shows the most interesting behaviour: while lab-scale works have shown spread energy consumptions in a wild range (27-118 kWh/m^3_{sludge}) for different sludge concentrations (5-60 g/L) leading to quite heterogenic results but all of them far away from energy efficiency, talking about commercial sonicators (full-scale), ultrasounds enable treating concentrated sludge (till 10%TS) with low energy consumption (below 10 kWh/m^3_{sludge}), explaining the wide extent of this pretreatment in WWTP worldwide. Among the other technologies, mechanical grinding and pulse electric fields (PEF) are placed just in the limit of energy inefficiency, so they would not lead to any profit in the digestion process since all the extra energy obtained in the digester is back invested in the pretreatment. Finally, high pressure homogenizer (Microsludge) shows a strong negative energy balance and in no case could be considered as energetically efficient. Figure 3b also shows some points from thermal hydrolysis pretreatment implemented in full-scale (although it is not an electricity consumer, but a thermal pretreatment, which will be later presented and discussed) just to show their potential in relation with pretreatments consuming electricity.

	Nº	EC (kWh/m^3)	c (g/L)	Lab-scale	Full-scale	Reference
Ultrasounds	1	1,4	90		x	Sonix (Perez-Elvira et al. 2009)
	2	6,4	80		x	Biosonator (Perez-Elvira et al. 2009)
	3	10	100		x	IWE TEc (Perez-Elvira et al. 2009)
	4	1,16	25		x	Xie et al. (2007)
	5	1,44	50		x	Barber (2005)
	6	47,9	4,8	x		Wu et al. (2000)
	7	96	10	x		Wang et al. (2005)
	8	55,5	40	x		Zhang et al. (2007)
	9	83,3	60	x		Zhang et al. (2007)
	10	27,6	30,5	x		Hart (1986)
	11	117,9	20	x		Visscher and Langehove (1998)
	12	73,3	40	x		Visscher and Langehove (1998)
	13	74,15	60	x		Visscher and Langehove (1998)
	14	52,4	14,5	x		Feng et al. (2009)
	15	110	9	x		Chu et al. (2002)
	16	22.1	23	x		Pham et al. (2009)
	17	52	27	x		Bougrier et al. (2005)
	18	57,6	21,4	x		Eren and Filibeli (2009)
	19	76	27,5	x		Zhang et al. (2007)
Ozone	20	15	20	x		Chu et al. (2009)
	21	46.2	28	x		Bernal-Martinez et al. (2009)
Pulse Electric Field (PEF)	21	16	60		x	OpenCEL (Rittmann et al. 2008)
	23	15	50		x	PowerMod (Zhang et al. 2009)
	24	33	12,5	x		Lee and Rittmann (2011)
	25	10,5	6,5	x		Salerno et al. (2009)
High pressure homogenizer	26	53,6	53		x	Microsludge (Stephenson et al. 2005)
	27	40	60	x		Onyeche and Schafer (2003)
Ball mills	28	50	60	x		Boehler and Siegrist (2006)
	29	360	80	x		Perez-Elvira (2011)
	30	21	65		x	Muller et al. (2004)
Lysate centrifuge	31	12	65		x	Muller et al. (2004)
Microwaves	32	37,5	20,6	x		Qiao et al. (2008)
	33	75	52	x		Kuglarz et al. (2013)
	34	93	40,5	x		Appels et al. (2013)
	35	150	20	x		Solyom et al. (2011)
	36	100	5.9	x		Wang et al. (2009a)
	37	116	25,7	x		Ahn et al. (2009)
	38	37,5	14,4	x		Yu et al. (2009)

Table 4. Energy consumption by different pretreatments

Pretreatments consuming heat

In order to address this kind of pretreatments, different approaches can be considered. First, it has to be said that equation 10 leads to an inequality where a thermal energy term is added to an electrical energy term, what is a priori inconsistent. However, the resulted energy is the total amount of energy that could be recovered back to the pretreatment to satisfy its needs, either electrical or thermal, and is equivalent to the equation 9 for electric pretreatments.

$$\mathbf{E.PT \leq (0.81\ c)\ kWh/m^3_{sludge}} \quad (12)$$

On the other hand, when a co-generation system (CHP) is considered to recover heat and electricity from biogas, just the thermal fraction (E.G + ΔE.G) can be reused for the pretreatment requirements, since the electric fraction (ΔE.E) will represent a net profit or will be dedicated to satisfy the electric requirements of the process. This way, the inequality would be expressed by the next system of equations 13 and 14:

$$\mathbf{E.PT_{thermal} \leq (E.G + \Delta E.G) = (0.61\ c)\ kWh/m^3_{sludge}} \quad (13)$$

$$\mathbf{E.PT_{electric} \leq \Delta E.E = (0.20\ c)\ kWh/m^3_{sludge}} \quad (14)$$

It is once again remarkable that the first term (13) corresponds to an energy waste from the CHP system and its use will directly suppose heat savings in the pretreatment step. As it is reported by Carrère et al. (2010), this thermal energy is generally in excess as compared to the WWTP needs and is one big advantage of thermal treatments. Then, considering that the thermal requirements are fulfilled with the aforementioned thermal integration, the second electrical term (14) has to be evaluated in order to check that the electrical process consumption is below that limit. Thus, a complete full integration of the pretreatment would be achieved.

Representing both equations 13 and 14 in a graph (Figure 4), it is obtained a very similar plot as for electrical pretreatments in Figure 3, but with two lines of different slope: the thermal one (red) and the electrical one (blue). It is noteworthy that the slope of the former (0.61 kWh/kgTS) is three times greater than the second one (0.20 kWh/kgTS), what implies that the amount of thermal energy available for the pretreatment is triple than the electric one. This shows interesting perspectives concerning energy integration feasibility. Then, in Figure 4, several thermal pretreatments obtained from different sources (lab-scale and pilot scale plants from scientific papers, commercial technologies or theoretical studies) have been plotted by points according to their energy consumption and sludge concentration (shown in Table 5), in the same way as previously. It has to be mentioned that this study has focused in thermal hydrolysis (TH) pretreatment, since it offers a big opportunity to be energetically integrated in a plant because it consumes steam, but also offers a high potential to hydrolyze microbial cellular material from sludge because the steam explosion at high pressure. Moreover, scientific and commercial thermal hydrolysis literature provides a large number of available references and data with which to work. On the contrary, pure thermal processes with sludge have just been applied at lab-scale and scarce research has been done in a higher extent.

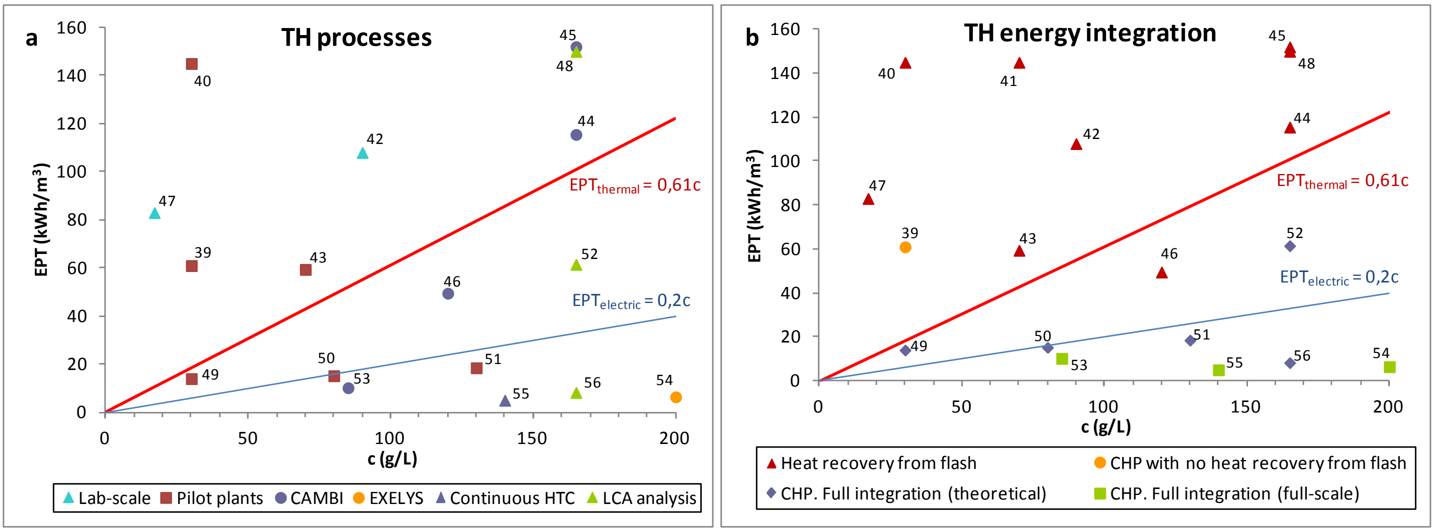

Figure 4. Pretreatments consuming heat according to a) technology b) energy integration

First of all, the data in Figure 4 show very diverse results in spite of talking about the same pretreatment: the range of sludge concentration that could be treated (rising up to 200 g/L) is very wide and the amount of energy needed (from 5 to 145 kWh/m^3) varies considerably. On one hand, different processes have been distinguished (Figure 4a): lab-scale studies (Carrère et al. 2010) present high energy consumptions above the red line, showing a lack of energy integration; pilot plants do not present a clear pattern, there are efficient plants which could treat till 13%TS sludge with a proper energy integration design (Perez-Elvira et al. 2013) or very inefficient processes with huge energy consumptions (Perez-Elvira et al. 2008); finally, industrial plants with commercial technologies are also represented. Among them, there are spread technologies such as Cambi which energy inputs have lead to non-optimized processes (such is the case of Howdon WWTP) (Rawlinson and Oliver 2012), where a support fuel is needed) since a fully integrated system has not been considered. There are also processes with full energy integration, where all the steam required is produced from the biogas in a CHP and the electric energy demand is very low; such is the case of Cambi plant in Dublin WWTP (Abraham et al. 2003) or continuous processes (Exelys in Hillerod WWTP or CTH prototype plant in Valladolid WWTP). A theoretical approach performed by Mills et al. based on life cycle assessment (LCA) clearly shows for a certain sludge concentration (16.5%TS) how energy integration of thermal hydrolysis pretreatment affects on the energy consumption in different scenarios where: biogas is sent to grid (150 kWh/m^3), partial recovery of heat with a support natural gas (62 kWh/m^3), full energy integration with a CHP system (8 kWh/m^3).

In Figure 4b, the same data have been plotted according to the energy integration setup. The simplest configuration is the thermal hydrolysis process with heat recovery from flash to the pre-heating stage, but no thermal energy is recovered from the biogas (no CHP); this is the basic design of Cambi (Ringoot et al. 2012) and all new pilot and industrial plants apply this configuration to reduce the steam requirements. Then, there is one pilot plant in which no heat recovery from the flash took place, but a CHP system was considered to recover heat for calculations (Perez-Elvira et al. 2008). Finally, fully integrated systems consider a CHP engine to burn biogas, produce electricity and recover heat; here we can find full-scale plants (Cambi in Dublin, Exelys in Hillerod or CTH in Valladolid) or theoretical estimations based on pilot plants results (Perez-Elvira et al. 2008) or on LCA studies (Mills et al.). From these results, it is clearly appreciable how energy integration affects: while most of the non-integrated processes are placed above the red line, fully integrated processes (either real plants or theoretical approaches) show very low energy demands and are most of them placed below the blue line. Among them, continuous processes (Exelys and CTH) show the best energy integration results and a wide margin respect to the maximum electrical consumption limit (blue line), spending just 16% and 18% of the extra electrical energy (ΔE.E) produced in the CHP system respectively to treat highly concentrated sludge (20%TS and 14.5%TS respectively). This broad margin will generate a net profit with which overcoming the initial capital cost invested in the thermal hydrolysis plant.

Energy integration	Nº	EC (kWh/m^3)	c (g/L)	Theoretical	Lab-scale	Full-scale	Reference
No heat recovery from flash (CHP)	39	61	30	x			Perez-Elvira et al. (2008)
Heat recovery from flash	40	145	30	x			Perez-Elvira et al. (2008)
	41	145	70	x			*Theoretical calculation*
	42	108	90		x		Carrère et al. (2010)
	43	59,4	70	x			Perez-Elvira et al. (2008)
	44	115,5	165			x	Cambi design value (Ringoot et al. 2012)
	45	152	165			x	Cambi (Howdon WWTP) (Rawlinson and Oliver 2012)
	46	49,5	120			x	Cambi (Tyagi and Lo 2013)
	47	83	17		x		Pérez-Elvira (2006b)
	48	150	165	x			LCA (Mills et al.)
Full integration (CHP)	49	14	30	x			Perez-Elvira et al. (2008)
	50	15,2	80	x			Pérez-Elvira and Fdz-Polanco (2012)
	51	18,5	130	x			Pérez-Elvira et al. (2013a)
	52	61,5	165	x			LCA (Mills et al.)
	53	10,2	85			x	Cambi (Dublin WWTP) (Abraham et al. 2003)
	54	6,4	200			x	EXELYS (Hillerod WWTP)
	55	5	140			x	CTH (Valladolid WWTP) (Pérez-Elvira, 2013b)
	56	8,25	165	x			LCA (Mills et al.)

Table 5. Energy consumption by thermal hydrolysis

<u>Other pretreatments</u>

It has to be mentioned that no attention has been paid to other pretreatments that could be ascribed to different categories, such as the chemical or biological ones. In these cases, an external agent (acid, alkali, enzymes) is added, what entails an associate cost but not an energy requirement. Since this study focuses in energy feasibility and energy integration, it is not possible to introduce these pretreatments unless an economical assessment is performed. However, this is not the aim of this study and therefore these pretreatments were excluded.

4. Pretreatments feasibility limits

To conclude, the limits of the pretreatments feasibility are studied theoretically: working with the same equations previously presented, the values for which the pretreatments begin to satisfy the energy requirements themselves are determined. First, for pretreatments consuming electricity, a standard sludge concentration of 150 g/L has been set. Then, according to equation 11, the maximum energy consumption by the pretreatment is 30 kWh/m^3_{sludge}. This value is the limit below which the pretreatment will start to produce a net benefit for the process and is clearly represented by equation 11. Concerning pretreatments consuming heat, the study is addressed from a different point of view: energy consumptions by thermal pretreatments are determined according to different energy integration configurations and then, the minimum sludge concentration to satisfy the inequality of equation 12 is determined. This way, different approaches have been considered:

- No heat integration: no heat is recovered at all. The sludge is fed at 20ºC and has to be heated up to 170ºC. Energy requirements ascend to 205 kWh/m^3_{sludge}.
- Heat recovery from flash: steam vapours from flash are recycle to a preheating stage, where sludge is heated to 105ºC. The energy demand is reduced to 116 kWh/m^3_{sludge}.
- Thermal heating: the sludge is just heated to 170ºC, with a heat exchanger to recover heat from the output to the input. Thermal requirements are just 65 kWh/m^3_{sludge}. It is not anymore a thermal hydrolysis process, but a thermal heating pretreatment (no pressure) and no steam explosion takes place.
- CHP full integration: complete energy integration is achieved with a CHP system. All heat requirements are satisfied by the exhaust gases from CHP and electrical requirements, estimated around 10-15 kWh/m^3_{sludge}, have to be satisfied by the CHP electricity co-generation. In this case, equation 14 has to be evaluated instead of equation 12, due to the electrical nature of the energy demand.

As it is observed in Figure 5 and Table 6, the minimum sludge concentrations to satisfy the previous energy demands drop down as the energy integration level rises. For the non-integrated system, a minimum sludge concentration over 250 g/L has to be achieved, what is certainly unviable from an operational point of view. When heat is recovered from the flash, the sludge must contain at least 143 g/L total solids, being much more attainable with a conventional centrifuge. A thermal heating process looks a priori more advantageous since just 80 g/L have to be reached to satisfy the energy demand. However, heating sludge does not offer the same advantages as thermal hydrolysis does (high disintegration power by steam explosion). Moreover, if a thermal hydrolysis plant includes a CHP system efficiently integrated, sludge has to be thickened just over 50 g/L, although a higher concentration would increase linearly the net profits of the plant by the extra electric energy output (with a rate of 0.2 $kWh/kgTS_{increase}$).

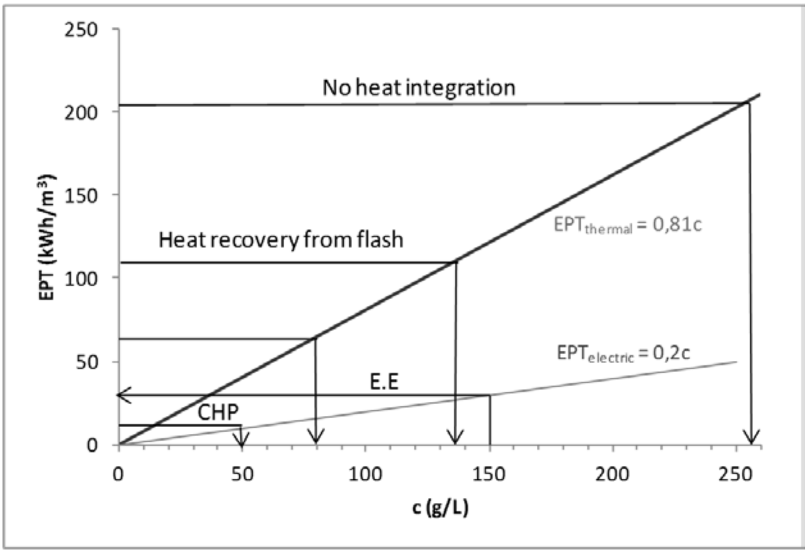

Figure 5. Pretreatments feasibility limits

Pretreatments consuming...	**Energy integration**	**Energy demand**	**Sludge concentration**
		kWh/m$^3_{sludge}$	g/L
Electricity	-	**30**	150
Heat	No heat integration	205	**253**
	Heat recovery from flash	116	**143**
	Thermal heating	65	**80**
	CHP full integration	10-15	**50**

Table 6. Pretreatments feasibility limits

5. Conclusions

Not all the pretreatment technologies have an energy self-sufficiency to be implemented in a WWTP. Generally, pretreatments consuming electricity do not satisfy its energy demands from the biogas production in the same process, except ultrasounds applied in full-scale plants (Sonix, Biosonator). In the case of thermal pretreatments, the potential to be implemented with full energy integration in WWTP is much higher, since they can recover heat from the biogas engine. This way, full energy integration can be achieved in thermal hydrolysis plants (Cambi, Exelys) and theoretical approaches set a minimum sludge concentration of 5%TS, as the main key factor to assure energy self-sufficiency.

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INITIAL TRIALS

CHAPTER 3. THERMAL HYDROLYSIS TO DIFFERENT SOLID WASTES AND MODELLING TOOLS

Experimental work starts with some initial trials to check different aspects of the study considering one pretreatment (thermal hydrolysis) applied to raw substrates. In this chapter, thermal hydrolysis to different solid wastes is studied and modelling tools are evaluated. The effect of this pretreatment is studied by biodegradability lab-scale tests for five solid substrates: biological sludge, the organic fraction of municipal solid waste, grease waste, spent grain and cow manure. Four simple models (a first order equation, the Modified Gompertz equation, the Transference function and the Logistic function) were applied to both pretreated and raw substrates biodegradability tests. The modelling of the biodegradation curves has resulted to be a reliable method to determine kinetic parameters and methane potentials from experimental data with high accuracy. The Modified Gompertz equation has the best results of fine-tuning (average R^2 over 0.98), even with the most complex kinetics. Thermal hydrolysis pretreatment has improved significantly methane productions (over 30%) and kinetics (double), especially in substrates which have a high fibre content (cow manure, spent grain) or microbial cellular material (biological sludge).

Keywords: anaerobic digestion, kinetic, model, pretreatment, solid waste, thermal hydrolysis

Anaerobic biodegradability tests modelling to study the effect of thermal hydrolysis pretreatment in different solid wastes

INTRODUCTION

Anaerobic digestion as a treatment of solid substrates has become a new clean technology based on energy recovery from waste. It is a biological process in which the organic matter is transformed into biogas by the action of specific bacteria in the absence of oxygen in several consecutive steps. Thus, the degradation rate of the overall process is limited by the slowest step, in this case the hydrolysis, which is the first stage in which complex organic matter (proteins, lipids, carbohydrates...) becomes simple soluble matter (amino acids, sugars, fatty acids...). In order to accelerate the hydrolysis step, thermal hydrolysis (TH) pretreatment is one of the most efficient techniques, leading to high solubilisation, pathogen reduction, good dewaterability and an increase in biogas production (Schieder et al. 2000).

Modelling biological processes with mathematical equations helps the understanding of the processes and represents the main aspects of the systems. Several mathematical models of anaerobic digestion have been proposed in the last two decades and a wide variety of methods have been used for parameter estimation and model validation (Donoso-Bravo et al. 2011a). The first modelling approaches focused on describing the limiting step of the process, considering that anaerobic digestion is a multistep process where one slower step controls the global rate: hydrolysis step in the case of solid substrates degradation (Batstone et al. 2009). These models, which are the simplest ones, are a useful and very simple tool to study the degradation of substrates and determine the main parameters to model the complex system with a simple equation.

Thermal hydrolysis effect on anaerobic degradation of substrates can be studied by the performance of biochemical methane potential tests in lab-scale, but few studies have applied mathematical models in order to obtain its kinetic parameters (Donoso-Bravo et al. 2010). Therefore, in this study, the application of four simple models to pretreated and raw solid substrates biodegradability tests is evaluated.

METHODS

Solid substrates

Five different solid substrates were chosen considering three main aspects: their importance in real scale plants, their availability, and their diversity of composition and origin. These substrates are: thickened biological sludge from a municipal WWTP; the organic fraction of municipal solid waste (OFMSW), which is a synthetic mixture of basic foods in an appropriate proportion as their presence in household waste; grease waste from a dissolved air flotation tank (DAF) from a WWTP; spent grain from brewery industry; and cow manure from slaughterhouse. The characterization of all the substrates was performed at the University of Valladolid following an internal protocol for solid substrates based on the Standard methods (Apha, 2005). Its characterization is presented in *Table 1*.

Parameter	Units	Biological sludge	OFMSW	Grease waste	Spent grain	Cow manure
TS	g/kg	71.2	109.9	505.2	243.6	221.6
VS	g/kg	54.9	105.1	468.2	233.4	208.5
CODt	g/kg	83.9	150	648.3	303.4	258.8
CODs	g/kg	6.3	91.8	nd	70	81
TKN	N-g/ kg	5.75	3.79	3.27	8.73	27.46
NH_4^+	N-g/ kg	0.24	0.82	0.24	1.22	0.75
Grease	g/kg	1.16	2.68	128.0	6.66	4.65
Carbohydrates	%	0	6.28	nd	nd	nd
Starch	%	0	3.44	nd	nd	nd
Fibre	%	0.21	0.82	nd	nd	nd
Proteins	%	3.83	2.43	2.04	4.69	16.7
C/N	g/g	8.87	21.10	39.00	16.96	15.67

Table 1. Substrates characterization (nd: no determined)

Thermal hydrolysis pretreatment

The hydrolysis plant is made up of a 2L reactor fed with a substrate and heated with steam until the desired temperature, and a flash tank where the steam explosion takes place after the hydrolysis reaction time has elapsed. The operational conditions remained constant: 170ºC and 30 minutes hydrolysis time, which are the optimized conditions obtained by Fdz-Polanco et al. (2008), except for the OFMSW (120ºC and 10 minutes), since some inhibitory behaviours were observed at 170ºC for OFMSW in previous tests.

Biochemical methane potential tests

Biochemical methane potential (BMP) tests allow determining kinetics and methane potentials of the substrates. The assays were performed by triplicates following an internal protocol based on standardized assays (Angelidaki et al. 2009). The reactors volume was 300 mL and a substrate-inoculum ratio of 1:1 in terms of VS was applied. The incubation temperature was 35ºC and reactors were stirred in a horizontal shaker. The inoculum was WWTP mesophilic digested sludge. Periodical monitoring analyses of biogas production by pressure meter and biogas composition by gas chromatography (Varian CP-3800) were performed during the tests. Methane potentials are expressed as average values of the net volume of methane per gram of initial substrate VS content.

Modelling

A set of four models, next presented in equations 1-4, was considered in order to fine-tune the experimental data to theoretical equations so to estimate their parameters with a certain degree of confidence. All models, despite differing mathematically from each other, have common features: simplicity (two or three parameters), an exponential character, a kinetic parameter (R_m or μ_{max}) which indicates the initial slope of the curve ($mLCH_4/gVS/d$), a maximum biogas production parameter (P) expressed as $mLCH_4/gVS$, and, in some cases, a lag-phase parameter (λ), in days. B is the calculated methane production ($mLCH_4/gVS$) for time t. Therefore, a comparison between the four models and their estimated parameters could be made.

- First order equation (FO): a negative exponential equation can model the simplest kinetics with just two parameters: the maximum biogas yield (P) and a kinetic parameter (μ_{max}) that represents the microorganisms' growth specific rate. (Pavlostathis and Giraldo-Gomez 1991)

$$B = P \times [1 - exp(-\mu_{max} \cdot t)] \quad (1)$$

- Modified Gompertz (MG) equation (Lay et al. 1997): describes the cumulative methane production in batch assays assuming that the methane production is a function of bacterial growth. (Nopharatana et al. 2007)

$$B = P \times exp\left\{-exp\left[\frac{R_m \times e}{P}(\lambda - t) + 1\right]\right\} \quad (2)$$

- Transference function (TF) or Reaction curve model: this function has been used mainly for control purposes, since it considers that any process may be analyzed as a system receiving inputs and generating outputs (Donoso-Bravo et al. 2011b). It has been implemented in anaerobic digestion by Redzwan and Banks (2004); Donoso-Bravo et al. (2010); Donoso-Bravo et al. (2011b).

$$B = P \times \left[1 - exp\left(\frac{-R_m(t - \lambda)}{P}\right)\right] \quad (3)$$

- Logistic function (LF) (Donoso-Bravo et al. 2010): this model assumes that the rate of gas production is proportional to the amount of gas already produced, the maximum production rate and the maximum capacity of biogas production. It fits the global shape of the biogas production kinetics: an initial exponential increase and a final stabilization at a maximal production level. In this case a modified version of the logistic function was used (Altaş 2009):

$$B = \frac{P}{1 + exp\left[\frac{4R_m(\lambda - t)}{P} + 2\right]} \quad (4)$$

The fine-tuning of each model to the experimental data was achieved by least squares methodology, by minimising the next objective function:

$$OF(\varphi) = min \sum_{t=1}^{N} \left(B_{exp}(t) - B_m(t, \varphi)\right)^2$$

where B_{exp} is the consumption velocity obtained from measurements (plotted in BMP results graphs as points), B_m is the corresponding velocity calculated by the model (plotted with continuous curves) and N is the number of measurements. The correlation factor (R^2) was then calculated to assess the accuracy of each model with respect to the experimental data.

Analytical methods

Substrates characterization was partially performed in the University of Valladolid, following an internal protocol based on Standard methods (Apha, 2005) to determine the next parameters: TS, VS (total and volatile solids); COD (chemical oxygen demand); TKN (total Kjeldahl nitrogen); NH_4^+ (ammonium). The other parameters were determined in an external laboratory: grease (EPA Method 1664), carbohydrates (CE Regulation 152/2009), fibre content (Weende, CE Regulation 152/2009), proteins (IT-MA-014, AOAC Official Method) and elemental content (IT-MA-014, AOAC official method).

Statistical analysis

All BMP tests were carried out by triplicates. The experimental methane productions are always referred to average values and standard deviations are calculated and represented in BMP curves with vertical lines. Moreover, deviations between experimental and model methane productions are determined and compared.

RESULTS AND DISCUSSION

Modelling results

The presented modelling procedure has been successfully applied to all the pretreated and raw samples previously proposed. In *Table 2*, all the modelling results can be consulted and *Figure 1* represents BMP curves: experimental results are represented by points and modelling results by continuous lines.

The estimated parameters were determined in most cases with a high degree of confidence: 80% of the fine-tuning equations reach R^2 values over 0.95. On the other hand, FO and TF estimated values for grease waste with a poor correlation factor (R^2 below 0.9). Since grease waste is the only substrates with a considerable lag-phase (between 15 and 20 days, see *Figure 1*), it was deduced that these models did not fit with lag-phase kinetics. Nevertheless, the irregular behaviour of the raw OFMSW curve has been successfully modelled by the four models, although FO lead to much lower R^2 value than the other models, probably due to its bi-parametric character.

SUBST.	MODEL	RAW					THERMAL HYDROLYSIS				
		P	R_m	μ_{max}	λ	R^2	P	R_m	μ_{max}	λ	R^2
		$mLCH_4/gVSin$	$mLCH_4/gVSin/d$	d^{-1}	d	-	$mLCH_4/gVSin$	$mLCH_4/gVSin/d$	d^{-1}	d	-
Biological Sludge	FO	204	-	0.149	-	0.975	296	-	0.193	-	0.983
	MG	184	24.0	-	0.0	0.934	278	41.1	-	0.0	0.956
	TF	189	35.6	-	0.0	0.973	283	62.5	-	0.0	0.983
	LF	183	23.0	-	0.0	0.916	276	39.1	-	0.0	0.941
OFMSW	FO	291	-	0.238	-	0.949	327	-	0.141	-	0.987
	MG	308	11.9	-	6.6	0.997	318	31.5	-	0.2	0.992
	TF	349	20.4	-	9.2	0.998	326	47.1	-	0.1	0.988
	LF	311	11.1	-	5.9	0.995	315	33.6	-	0.9	0.991
Grease waste	FO	54287	-	0.0002	-	0.898	4870	-	0.0024	-	0.852
	MG	488.6	30.3	-	17.6	0.990	524	43.4	-	15.8	0.994
	TF	3331	12.0	-	6.3	0.899	1049	18.2	-	6.1	0.872
	LF	471	32.1	-	18.1	0.988	517	44.3	-	16.3	0.993
Spent grain	FO	249	-	0.110	-	0.990	356	-	0.205	-	0.997
	MG	251	18.7	-	0.8	0.994	352	45.5	-	0.0	0.991
	TF	272	25.8	-	0.5	0.992	359	72.8	-	0.1	0.997
	LF	246	18.9	-	1.2	0.984	350	42.2	-	0.0	0.982
Cow manure	FO	337	-	0.086	-	0.996	427	-	0.186	-	0.992
	MG	317	19.6	-	0.0	0.981	408	54.3	-	0.0	0.982
	TF	345	28.0	-	0.0	0.996	416	82.9	-	0.0	0.992
	LF	313	18.5	-	0.0	0.968	405	52.0	-	0.0	0.973

Table 2. Estimated parameters by the four models for raw and hydrolysed substrates

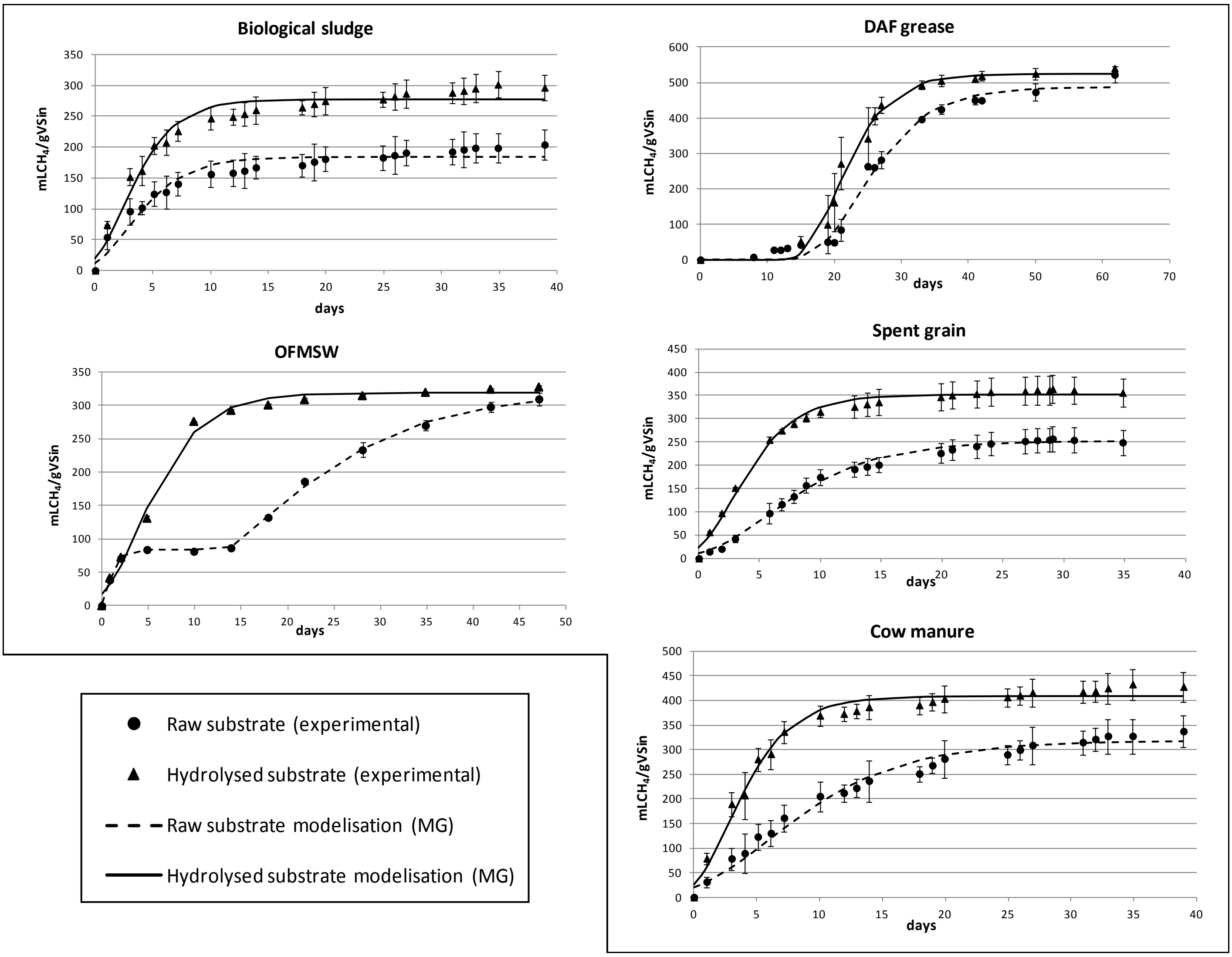

Figure 1. Experimental and estimated biodegradability curves by the Modified Gompertz equation (MG)

As it can be appreciate in *Table 2*, the four models estimate similar values of the maximum methane production for each substrate; among them, the grease waste methane potential is remarkable because its high value (over 470 $mLCH_4/gVSin$). However, talking about kinetic parameters, the diversity of the results rises. FO estimates the *microorganisms' growth velocity* (μ_{max}), which cannot be compared to the *maximum methane production rate* (R_m) that is estimated by the other models. While TF tends to overestimate this parameter, LF and MG estimate similar lower values. In spite of this variability, its application as a tool to determine TH kinetics improvement is a reliable method, since kinetics improvements are consistent between models. Lag-phase time (λ) is determined by all the tri-parametrical models (MG, TF, LF), but just MG and LF fine-tune correctly this kind of kinetic, as it can be appreciate in the grease waste results.

Model	FO	MG	TF	LF
Average R^2	0.962	0.981	0.969	0.973

Table 3. Average correlation factors for all models

Among all the models, the Modified Gompertz equation (MG) has resulted to be the most appropriate and accurate model to fine-tune these solid substrates kinetics (average R^2 higher than 0.98, *Table 3*). In *Figure 1*, the biodegradability curves from experimental data and the modelling ones obtained with this model are plotted. It is appreciable that the model curves follow accurately the tendency of the experimental points.

Statistical Analysis

To assess the accuracy of the model parameters determination with respect to the error from BMP experimental data, standard deviations have been calculated and compared (Table 4): on one hand standard deviations of BMP tests (carried out by triplicates) quantify the variability associated to experimental errors, and on the other hand the standard deviations of model parameters associated to different models. As it was already observed in *Table 2*, the four models have estimated similar values of the maximum methane production (P) for each substrate, what leads to standard deviations below 5% in most of the cases (Table 4). These values are lower than the standard deviations from the experimental data (over 10% in some cases), what means that the variability associated to different models is lower than the experimental error. Comparing the experimental methane final productions with the average values obtained by modelling, the errors (enclosed in Table 4) are still low (below 8%) and do not surpass the experimental uncertainty, except for grease waste, due to its low experimental standard deviation. Observing the negative values of errors, it can be outlined that the tendency of the models is to underestimate the experimental final productions. However, the degree of accuracy between both values is acceptable. In contrast, if a similar statistical analysis to the kinetic parameter (R_m) were performed between MG, TF and LF models, the results would claim a lack of consistency in the model standard deviations as it was previously aforementioned (especially because TF values). For example, standard deviations of the kinetic parameter associated to different models (average for all substrates, not shown) rises till 24%, which is considerably higher than the experimental errors associated to triplicates. However, when excluding TF values for this analysis, standard deviations drop down below 3%, showing similar values from MG and LF. Therefore, it must be concluded that not all models lead to an accurate determination of kinetic parameters, but they do for methane productions. Again, MG and LF are considered the most appropriate models to estimate BMP parameters with an acceptable degree of accuracy.

Substrates		Methane final production		Standard Deviations				Error
		P exp.	**P model***	**Exp. SD****		**Model SD**		**Model-Exp.**
		$mLCH_4/gVSin$	$mLCH_4/gVSin$	$mLCH_4/gVSin$	%	$mLCH_4/gVSin$	%	%
Biological Sludge	raw	204	190	25	12.3	8.4	4.4	-6.9
	TH	296	283	21	7.1	7.8	2.8	-4.3
OFMSW	raw	307	315	9	2.9	21.2	6.7	2.5
	TH	327	322	2	0.6	5.1	1.6	-1.7
Grease waste	raw	522	480	1	0.2	8.8	1.8	-8.1
	TH	540	521	11	2.0	3.5	0.7	-3.6
Spent grain	raw	250	255	27	10.8	10.3	4.0	1.8
	TH	356	354	29	8.1	3.5	1.0	-0.5
Cow manure	raw	337	328	45	13.4	13.4	4.1	-2.7
	TH	427	414	31	7.3	8.5	2.1	-3.0

Table 4. Standard Deviations (SD) and error between experimental (exp.) and model methane productions (P). (*average values from the four models, ** from triplicates)

Thermal hydrolysis effect

Thermal hydrolysis pretreatment has a significant effect on the anaerobic digestion kinetics and methane productions of solid substrates, as it had been already tested in several studies (Carlsson et al. 2012). But the quantification of this improvement is difficult to be measured by the observation of the curves and the information that could be extracted can be inexact. Therefore, by the application of these models, the % of improvement that is reached by thermal hydrolysis can be calculated: *Table 5* compiles the values obtained by MG model. Moreover, disintegration factors (DF) are determined to evaluate the solubilisation effect that TH produces in the substrates; from solubleCOD/totalCOD ratio of raw and hydrolysed samples, the disintegration factor is calculated as the relative increase of the previous ratio after TH (*Table 5*).

Among the substrates, biological sludge has suffered the highest methane production increase after TH (more than 50%) despite it contains the highest water content and the lowest C/N ratio (Table 1 for substrates characterisation). However, its initial low soluble content has lead to the highest disintegration factor (over 400%), probably due to the cell disruption that takes place during the pretreatment and especially in the steam explosion. The liberation of the intra-cellular material from microbial cells of the biological sludge can be the main mechanism that causes the biogas production improvement, as it was also concluded by Perez-Elvira et al. (2010). In the case of the OFMSW there is a considerable improvement of kinetics and a lag-phase reduction of almost 7 days; nevertheless its methane productivity was barely surpassed. The initial high soluble matter that this substrate contains (over 60% COD is soluble) and the fact that it is composed by high amounts of easily degradable sugars (3.44% starch and 6.28% carbohydrates) are the main causes of the lack of effectiveness of TH in this substrate and the low solubilisation that is achieved. However, OFMSW digestion has provided an acceptable methane production (over 300 $mLCH_4/gVSin$). The remained three substrates (grease waste, spent grain and cow manure) represent substrates rich in lipids, carbohydrates and proteins respectively. While TH has played an essential role in improving anaerobic digestion of spent grain and cow manure (40 and 30% more biogas respectively and kinetics have doubled), grease waste has not been remarkably influenced by the pretreatment. Its lag-phase after TH is still an important limitation (just 2 days reduction, surpassing 15 days lag-phase) although its methane production can be slightly improved and the kinetics speeds up 40%. In this case, the contained lipids and slow degradable materials of the grease waste could not be subjected to significant alterations during the pretreatment (low solubilisation after TH, just 14% soluble COD). Nevertheless, its high lipid content (128 g/kg) leads to the highest methane production (524 $mLCH_4/gVSin$ after TH), converting this substrate in an interesting co-substrate for anaerobic digestion. Coming back to cow manure, it is remarkable that its high nitrogen content (27.5 N-g/kg) has not lead to ammonia overloading and refractory compounds formation after the thermal pretreatment, what has been reported to be common (Cuetos et al. 2010). It is probable that the high content of lignocellulosic material of this substrate has suffered a high disruption after TH and is the main responsible mechanism that has taken part to improve its degradation.

SUBSTRATES		MODEL PARAMETERS				IMPROVEMENTS			SOLUBILISATION	
		P	**R_m**	**λ**	**R^2**	**P**	**R_m**	**λ**	**CODs/CODt**	**DF**
		$mLCH_4/gVSin$	$mLCH_4/gVSin/d$	d	-	%	%	d red.	%	%
Biological sludge	raw	184	24.0	0	0.934	51	71	0.0	7.5	432.1
	TH	278	41.1	0	0.956				40.0	
OFMSW	raw	308	11.9	6.6	0.997	3	164	6.4	61.2	5.2
	TH	318	31.5	0.2	0.992				64.4	
Grease waste	raw	489	30.3	17.6	0.990	7	43	1.8	-	-
	TH	524	43.4	15.8	0.994				14.0	
Spent grain	raw	251	18.7	0.8	0.994	40	144	0.8	23.1	69.7
	TH	352	45.5	0	0.991				39.1	
Cow manure	raw	317	19.6	0	0.981	29	177	0.0	31.3	15.7
	TH	408	54.3	0	0.982				36.2	

Table 5. Thermal Hydrolysis improvement in the estimated parameters by MG respect the raw substrates and disintegration factors (DF)

As it is reported by Carlsson et al. (2012), two main components can be identified among substrate categories that cause low bioavailability and/or biodegradability: microbial cells/flocs such as those found in waste activated sludge from WWTP and lignocellulosic material from plants and vegetables found in energy crops and harvesting residues, in manure and to some extent in household waste (Carlsson et al. 2012). In fact, in this study, the biological sludge is the only substrate that is mainly composed by microbial cells, which is one of the two causes of a low bioavailability which could be overcome by the application of pretreatments. The other cause is a high content of lignocellulosic material, which, in this study, is represented by cow manure and spent grain. Then, it can be affirmed that substrates with high content of fibre or microbial cells are more susceptible to be pretreated in order to improve its degradation capacity.

CONCLUSIONS

Modelling the biodegradation of solid substrates by simple equations has resulted to be a reliable method to determine kinetic parameters and methane potentials from experimental data with a high degree of accuracy. The Modified Gompertz equation has the best results of fine-tuning (average R^2 over 0.98), even with the most complex kinetics. Thermal hydrolysis pretreatment has improved significantly methane productions (over 30%) and kinetics (double), especially in substrates which have a high fibre content or microbial cellular material. However, thermal hydrolysis has not showed remarkable effects in substrates rich in lipids or with a high content of easily degradable carbohydrates.

ACKNOWLEDGEMENTS

The presented work has been carried out under the financial support of R+i Alliance. This research was supported by the Spanish Ministry of Science and Innovation project CONSOLIDER-CSD 2007-00055.

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OPTIMIZATION OF PRETREATMENT TECHNOLOGIES TO SOLID WASTES

Considering all the previous works, either bibliographic or experimental, the main body of the thesis lies in the **optimization of pretreatment technologies to different solid wastes**, focusing on two different areas which are based in two different research private projects that financed the research:

- *Alliance* project: focused on the co-digestion of sewage sludge with other solid co-substrates. The main co-partners of these projects are Cetaqua and Suez Environment, which were looking for the optimisation of WWTP anaerobic digestion processes. Then, the effect of the pretreatments was always addressed considering sewage sludge and pretreatment technologies always pointing to its application in WWTP. Different co-substrates were selected according to internal decisions in the project; among them, cow manure and grease waste were deeply investigated in a lab-extent and the results are here enclosed in Chapters 4 and 5.

- *Topbio* project: belongs to Urbaser, which is a MSW management company, and then the central area of research is the study of the anaerobic digestion of the organic fraction of MSW in view of a full-scale implementation. First, Chapter 6 compiles lab-scale tests where ultrasounds and thermal hydrolysis pretreatments are applied to a synthetic mixture of the organic fraction of MSW. Then, in Chapter 7, thermal hydrolysis pretreatment is optimised using a preselected MSW from a real full-scale MSW treatment plant in order to simulate more real conditions.

CO-DIGESTION OF SEWAGE SLUDGE ENHANCED BY PRETREATMENTS

Chapters 4 and 5 focus on the **enhancement of sewage sludge co-digestion**. This section corresponds to the results from *Alliance* project, which focused on the selection of potential co-substrates to carry out its co-digestion with sewage sludge. Three co-substrates were initially tested (grease waste from WWTP, cow manure from slaughterhouse and spent grain from brewery industry), from which two of them were selected in order to optimize their co-digestion by pretreatments: cow manure and grease waste (next developed in Chapter 4 and 5). This study pays attention on the configuration of how the pretreatments are implemented in a co-digestion process of a WWTP, considering the optimized operational conditions for sewage sludge.

CHAPTER 4. OPTIMIZATION OF COW MANURE AND SEWAGE SLUDGE CO-DIGESTION

Cow manure is a common waste which is produced worldwide in the cattle farming sector and has a high methane potential, but its high fibre and protein content could cause certain limitations in the anaerobic digestion process. Then, its anaerobic co-digestion with sewage sludge is an interesting alternative for energy recovery. However, the traditional co-digestion process presents some limitations (no synergistic effects), which could be overcome by the application of pretreatments. This chapter studies the optimization of cow manure and sewage sludge co-digestion using several disintegration technologies: thermal hydrolysis, ultrasounds and enzymatic pretreatments. Results have first shown that thermal hydrolysis and ultrasounds applied to raw cow manure can increase 28% its methane potential. Moreover, when pretreatments are applied to the co-digestion mixtures, more than 60% methane production respect to the non-pretreated one and hydrolysis rates 4 times higher were observed. Finally, thermal hydrolysis optimization resulted in the highest biogas production (365 $mLCH_4/gVS$) so long as biological sludge was pretreated. Moreover, digestate´s hydrodynamic properties were considerably improved, offering interesting perspectives for a further study in view of real scale application.

Keywords: co-digestion; cow manure; enzyme; sewage sludge; thermal hydrolysis; ultrasound

Optimization of cow manure and sewage sludge co-digestion by using disintegration technologies

1. INTRODUCTION

Manure production is one of the most problematic environmental concerns of waste management in cattle farming sector. Nearly three-quarters of the manure is from dairy and cattle, with the remainder coming from swine and poultry operations (Zhiyou et al. 2003). Currently, the disposal of manure is predominately done through land application, which causes greenhouse gas emissions, ecological system eutrophication, and groundwater contamination (Ying et al. 2009). However, recent environmental and regulatory restrictions in the animal sector such as the decreasing availability of land for manure disposal are forcing the development of new waste management strategies. An alternative is to change manure, a waste with an energy content of about 13.4 MJ/kg, from a disposal problem to a bioresource for value-added products (Klass 1998).

Anaerobic digestion is an attractive treatment of organic wastes such as cow manure, since it produces biogas, a renewable energy source, and a stabilized digestate that can be reused as organic fertilizer (Neves et al. 2008). Moreover, the anaerobic digestion technology can also be used to control malodorous emissions (Comino et al. 2009). The importance of this technology results in considerable environmental benefits and can be an additional income source for farmers (Chynoweth et al. 2004). However, cow manure biodegradation presents some limitations: the high content of fibre contained in the manure limits the overall efficiency of anaerobic digestion because the degradation of recalcitrant fibre is very slow (Ying et al. 2009). In the other hand, ammonia toxicity can cause inhibition at concentrations of 3 g/L. Thus, anaerobic digestion of cow manure requires hydraulic retention times greater than 30 days (Borja et al. 1993). Therefore, the application of disintegration technologies to overcome these limitations could be of high interest.

Whereas a lot of works have been focused on the enhancement of anaerobic digestion of sewage sludge by thermal treatments (Valo et al. 2004; Bougrier et al. 2008) or ultrasounds cavitation (Donoso-Bravo et al. 2005) with good results, very few studies concern disintegration of manure to increase their conversion into biogas. The best results for thermal hydrolysis to cow manure were obtained with temperatures in the range of 140-180ºC where the optimum was 170ºC (Yoneyama et al. 2006). This value is in the range of optimal temperature generally reported for thermal hydrolysis of sewage sludge (Bougrier et al. 2008). Among other technologies, enzymatic hydrolysis has been tested with several substrates such as corn stover (Kaar and Holtzapple 1998; Varga et al. 2003), wheat straw (Cacchio et al. 2001), rice hull (Sharma et al. 2001), fruit pomace (Avelino et al. 1997) and sugarcane bagasse (Zheng et al. 2002) but no data has been found on hydrolyzing manure with enzymes (Zhiyou et al. 2003).

On the other hand, the co-digestion of animal manure and other types of organic wastes offers economic and environmental benefits due to cost-sharing by processing multiple waste streams with complementary characteristics in a single facility in order to improve the methane production and prevent inhibition problems. There are several advantages to use animal manure for co-digestion: it is a good substrate for dilution of toxic wastes, it is also a source of nutrients, trace metals, vitamins and other compounds necessary for microbial growth and finally it plays a role in neutralizing pH and improving buffering capacity (Angelidaki and Ellegaard 2005). Several studies have reported the economic and environmental benefits of co-digestion of multiple substrates such as manure and other waste streams (Holm-Nielsen and Al Seadi 1998).

Then, the application of disintegration technologies to the co-digestion of cow manure and sewage sludge could overcome the manure digestion limitations leading to a very profitable process. In this study, several disintegration technologies such as thermal hydrolysis, enzymatic hydrolysis and ultrasounds cavitation have been tested and compared by the assessment of biochemical methane potential tests. A further optimization of the process by different configurations has been also developed to study more deeply the possible implementation of the technology in a continuous plant.

2. MATERIALS AND METHODS

2.1 Substrates

Thickened primary (SS1) and biological sludge (SS2) were sampled from a municipal WWTP and kept refrigerated at 4ºC. Cow manure (CM) comes from slaughterhouse. The characterization of the substrates (*Table 1*) included total and soluble chemical oxygen demand (CODt, CODs), total and volatile solids (TS, VS), total Kjeldahl nitrogen (TKN) and ammonium (NH_4^+).

Parameter	Units	Cow Manure	Sludge	
			SS1	SS2
CODt	g/kg	258.8	188.2	83.9
CODs	g/kg	81.0	10.3	6.3
TS	g/kg	221.6	167.5	71.2
VS	g/kg	208.5	115.6	54.9
TKN	N-g/ kg	27.0*	4.69	5.75
NH_4^+	N-g/ kg	1.02	0.29	0.24
Grease	g/kg	5.3	-	-
MIXTURE RATIOS	Weight %	15.0	42.5	42.5
	COD %	51.9	23.1	25.0
	ST %	53.5	40.4	6.1
	SV %	60.8	33.7	5.6

Table 1. Substrates characterization and mixture ratios
*(*high protein content, 167g/kg estimated)*

SS1 and SS2 were mixed in a 1:1 weight ratio (according to the common ratio in the WWTP) and then cow manure was added in a proper ratio (15% weight basis). These mixtures have been previously studied considering different COD ratios: 15/85%, 25/75% and 50/50% (expressed as CODmanure/CODsludge%). The selected ratio, after carrying out different biochemical methane potential (BMP) tests, was 25/75%COD (CM represents a 15% in weight basis, consult *Table 1* for equivalences). It was identified a decrease in the methane production for this ratio in comparison with the one obtained for mixtures with lower ratios. Therefore, the assessment of the application of pretreatments to this type of mixture is a challenge in order to know if its application can overcome this limitation.

2.2 Pretreatments

Three disintegration technologies (thermal hydrolysis, enzymatic hydrolysis and ultrasounds cavitation) were studied. The pretreatments were selected based on COD solubilisation, increase in biogas production, pathogen reduction and dewaterability, as well as the availability to carry out the test at lab-scale. A brief description of the equipments is enclosed:

- *Thermal Hydrolysis:* the hydrolysis plant is made up of a 2L reactor fed with a substrate and heated with steam until the desired temperature, and a flash tank where the steam explosion takes place after the hydrolysis reaction time has elapsed. The operational conditions of temperature and hydrolysis time for these tests were 170ºC and 30 minutes, which are the optimized conditions obtained by Fdz-Polanco et al. (2008).
- *Ultrasounds:* electrical energy is converted in mechanical vibrations (cavitations), which are transmitted to the sample by a sonotrode during 20 minutes with a 200W power device *Hielscher UP400S*.
- *Enzymatic treatment:* The substrate, the enzymatic solution (commercial protease from *Aspergillus oryzae,* 500 U/g activity) and a buffer solution are introduced in 300 mL closed bottles and stirred for 12 hours under controlled conditions (37ºC and pH 5.3).

2.3 Biochemical methane potential tests

Biochemical Methane Potential (BMP) tests allow to determine kinetics and methane potentials of the substrates. The assays were performed by triplicates following an internal protocol based on standardized assays (Angelidaki et al. 2009). The reactors volume was 300 mL and a substrate-inoculum ratio of 1:1 in terms of VS was applied. The incubation temperature was 35ºC and reactors were stirred in a horizontal shaker. The inoculum was WWTP mesophilic digested sludge. Periodical monitoring analyses of biogas production by pressure meter and biogas composition by gas chromatography (*Varian CP-3800*) were performed during the tests. Methane potentials are expressed as average values of the net volume of methane per gram of initial substrate VS content.

2.4 Modelling

The Modified Gompertz equation (Lay et al. 1997), next presented in equation 1, was considered in order to fine-tune the experimental data from BMP tests to a theoretical equation:

$$B = P \times exp\left\{-exp\left[\frac{R_m \times e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

The model has three parameters: the kinetic parameter (Rm) which indicates the initial slope of the curve ($mLCH_4/gVS/d$), the maximum biogas production (P) expressed as $mLCH_4/gVS$ and the lag-phase (λ), in days. B is the calculated methane production ($mLCH_4/gVS$) for time *t*. The model fine-tuning to the experimental data was achieved by least squares methodology, by minimising the next objective function (2):

$$OF(\varphi) = min\sum_{t=1}^{N}\left(B_{exp}(t) - B_m(t,\varphi)\right)^2 \quad (2)$$

where B_{exp} is the consumption velocity obtained from measurements (plotted in BMP results graphs as points), B_m is the corresponding velocity calculated by the model (plotted with continuous curves) and N is the number of measurements. The correlation factor (R^2) was then calculated to assess the accuracy of the model with respect to the experimental data.

2.5 Analytical methods

Standard methods (Apha 2005) for substrates characterization were applied to determine the next parameters: TS,VS total and volatile solids; COD chemical oxygen demand; TKN total Kjeldahl nitrogen; NH_4^+ ammonium; VFA volatile fatty acids; grease.

2.6 Hydrodynamic characteristics

To assess the dewaterability and hydrodynamic properties of pretreated and raw mixtures for the last set of experiments, filterability, centrifugability and rheology tests were performed following an internal method established from the experiments in sludge characterization in the *Department of Chemical Engineering and Environmental Technology,* at the University of Valladolid (Donoso-Bravo et al. 2011). *Filterability* is measured by forcing the sludge to pass through a filter under a 1 barg pressure and then the filtration constant (*FC*) was calculated. *Capillary suction time* (CST) was determined using a Triton Electronics Ltd. *Centrifugability* assesses the liquid and solid phase separation after 5 minutes centrifugation at 5000 rpm by the next parameters: % separated liquid, % solid recovery in cake and solid concentration in cake (%TS). *Rheology* is evaluated by viscosity curves, obtained with a *Brookfield Digital Viscometer DV*-I.

2.7 Statistical analysis

All BMP tests were carried out by triplicates. The experimental methane productions are always referred to average values and standard deviations are calculated and represented in BMP curves with vertical lines. For the hydrodynamic tests, duplicates were measured and the results were averaged.

2.8 Experimental procedure

The experimental setup is divided in four consecutive stages, next described:

- *Phase 1*: Pretreatments to cow manure.
- *Phase 2*: Co-digestion of cow manure and mixed sludge.
- *Phase 3*: Pretreatments and co-digestion of mixtures. Each pretreatment is applied to mixtures following the same procedure: the cow manure and SS2 were pretreated and then mixed with SS1 following the ratios previously defined.
- *Phase 4*: Thermal hydrolysis optimization for co-digestion. Thermal hydrolysis was applied to three different configurations: cow manure, secondary sludge or mixture of cow manure and secondary sludge. In each case, the pretreated sample was then properly mixed with the non-pretreated substrates to obtain the desired mixing ratio for co-digestion of cow manure, SS1 and SS2.

Primary and biological sludge were used to make the final mixture and reproduce real conditions, but, from them, only biological sludge was pretreated in all cases. The reason for which pretreatments are only applied to biological sludge is that it is mainly composed of biomass, hardly degradable carbohydrates added to the sludge particles and easily degradable proteins, only available with a break of the cellular wall. Hydrolysis breaks these cells and help to the biodegradation of biological sludge (Pérez Elvira et al. 2006).

3. RESULTS AND DISCUSSION

3.1 Phase 1: Pretreatments to cow manure

In a first phase the influence of the three pretreatments applied to the raw cow manure was compared. *Figure 1* shows the specific methane production evolution for raw cow manure and after the application of each pretreatment, and *Table 2* compiles the parameters obtained by the fine-tuning of the experimental data to the modified Gompertz model. Results indicate that both ultrasound and thermal hydrolysis increase the methane production of the raw substrate (P 27% and 28% higher respectively). Moreover, it can be observed that the rate of the biogas production is higher during the first seven days, where ultrasounds and thermal hydrolysis presented a higher biogas production increase, which leads to kinetic parameters (Rm) 43% and 177% higher than the raw substrate one respectively. This means there is a first stage in cow manure degradation that could be improved by the application of these pretreatments (thermal hydrolysis especially), probably due to the solubilisation of organic matter that converts slow degradable materials, such as fibre and proteins, in more available matter in the soluble phase for the bacteria (more than 20% CODs/CODt increase after thermal hydrolysis). Enzymatic hydrolysis scarcely improves the final methane production and the hydrolysis rate, so the effect of this pretreatment is not appreciable (BMP errors are higher, as it is shown in curves from *Figure 1*). Possible reasons could be the low reaction time for the enzymatic reactions, or maybe a lack of activity of this commercial protease with this specific substrate.

Therefore, thermal hydrolysis pretreatment seems to be the most efficient technology to improve the biogas production of cow manure, with a 28% more biogas and 177% faster kinetic. However, the application of this pretreatment to a mixture of cow manure and sewage sludge in a same facility would be of great interest in view of a real application. Therefore, the next step of the study will focus on co-digestion processes.

Sample: Cow manure	Parameters				% increase		lag-phase reduction
	P	Rm	λ	R^2	P	Rm	
	$mLCH_4/gVS$	$mLCH_4/gVS/d$	d	-	%	%	days
Raw CM	317.4	53.3	0.00	0.981	-	-	-
Thermal Hydrolysis	407.8	147.7	0.00	0.982	28.5	177.1	0
Ultrasounds	403.2	72.0	0.00	0.975	27.0	35.1	0
Enzymatic	318.6	58.1	0.00	0.973	0.4	9.0	0

Table 2. Results of the pretreated cow manure samples (Gompertz modelling)

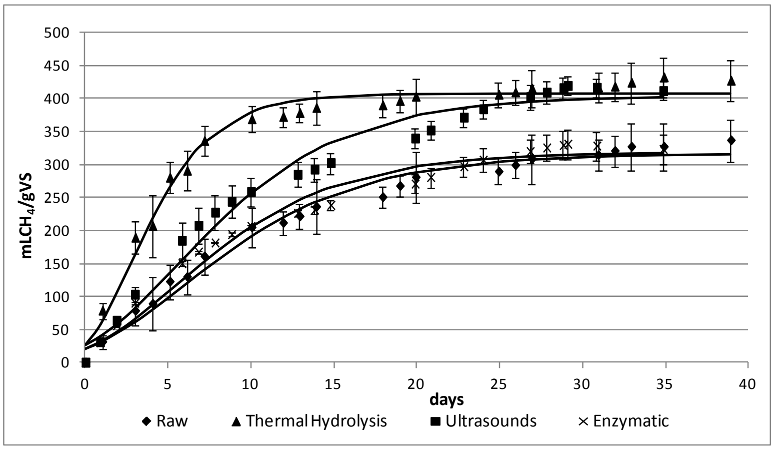

Figure 1. BMP tests results of raw and pretreated cow manure (Phase 1)

3.2 Phase 2: Co-digestion of cow manure and mixed sludge

In this phase, co-digestion of cow manure and mixed sludge for the specified mixture ratio has been tested. Co-digestion factors (α) indicate the ratio between the experimental methane potential of the co-digested mixture and the theoretical value calculated according to the mixture ratio from the individual co-substrates methane potentials. Analysing the raw substrates biodegradability potentials (see *Table 3* and *Figure 2*), it can be deduced that the co-digestion of cow manure and mixed sludge with the selected mixture ratio do not offer any advantage in terms of biogas production, as it was expected from previous studies. Co-digestion factor of the raw mixture presents a value of 0.87, what means the methane potential of the mixture is 13% below than the expected theoretical value. The application of pretreatments is therefore needed to solve this limitation.

Sample		Parameters				Co-digestion factors (α)
		P	**Rm**	**λ**	**R^2**	
		$mLCH_4/gVS$	$mLCH_4/gVS/d$	d	-	-
Substrates	Cow manure (CM)	317.4	53.3	0.00	0.981	-
	Primary sludge (SS1)	325.4	52.7	0.00	0.984	-
	Biological sludge (SS2)	184.1	65.2	0.00	0.934	-
Mixture	CM+SS1+SS2	273.4	52.9	1.39	0.991	0.87

Table 3. Results of the co-digestion of the mixture (Gompertz modelling)

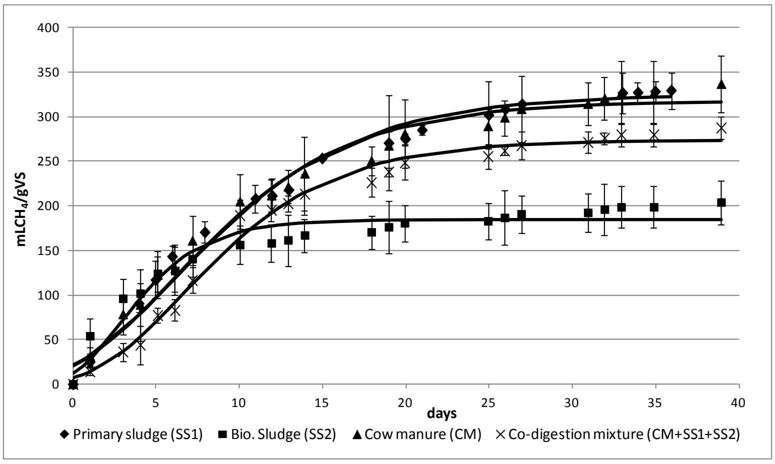

Figure 2. BMP tests results of substrates and co-digested mixture (Phase 2)

3.3 Phase 3: Pretreatments and co-digestion of mixtures

In order to compare the effect of pretreatments in the co-digestion process, each pretreatment is applied to a mixture of cow manure and secondary sludge and then mixed with non-pretreated primary sludge, according to the ratios described in the *Materials and Methods* subsection *2.1 Substrates*. The methane potentials of the raw and pretreated mixtures are shown in *Figure 3*. In *Table 4*, the results of Gompertz equation modelling and co-digestion factors are shown.

All the pretreated co-digestion tests considerably improved the biogas productivity respect to the non-pretreated one (273.4 $mLCH_4/gVS$). In all cases the methane potentials reached values over 440 $mLCH_4/gVS$, increasing the raw mixture's one more than 60%, which means co-digestion factors between 1.4/1.5; kinetics speeded up more than 4 times and the lag-phase was eliminated (see *Table 4*). An increase of the easily degradable matter content in the soluble phase could be the major reason (Pérez Elvira et al. 2006): the liberation of amino acids from cow manure's proteins during the hydrolytic process, the size reduction of fibres and a cell disruption of the biological sludge could be the main responsible mechanisms. Then, disintegration factors were determined as the increase of *soluble COD/total COD* ratio before and after pretreatments: 30.8% thermal hydrolysis, 13.2% enzymatic hydrolysis, 82.8% ultrasounds. In general, higher solubilisations were reached after pretreatments, which mean that a high solubility of the organic matter takes place in all of them, especially in the ultrasounds pretreatment. This explains the high production rate that takes place during the first five days of the tests in the case of pretreated samples, reaching about 75 % of the total methane production. This offers interesting perspectives for a continuous process application, leading to a fast hydrolysis step and providing a lower hydraulic retention time.

Sample		**Parameters**				**% increase**		**lag-phase reduction**	**α**
		P	**Rm**	**λ**	**R^2**	**P**	**Rm**		
		$mLCH_4/gVS$	$mLCH_4/gVS/d$	d	-	%	%	days	-
Raw Mixture	CM+SS1+SS2	273.4	52.9	1.39	0.991	-	-	-	0.87
Pretreated Mixtures	Thermal Hydrolysis	440.3	235.0	0.07	0.978	61.0	344.0	1.3	1.41
	Ultrasounds	474.0	220.4	0.00	0.966	73.4	316.4	1.4	1.51
	Enzymatic	455.8	218.6	0.00	0.971	66.7	313.0	1.4	1.46

Table 4. Results of the co-digestion and pretreatments to mixtures (Gompertz modelling)

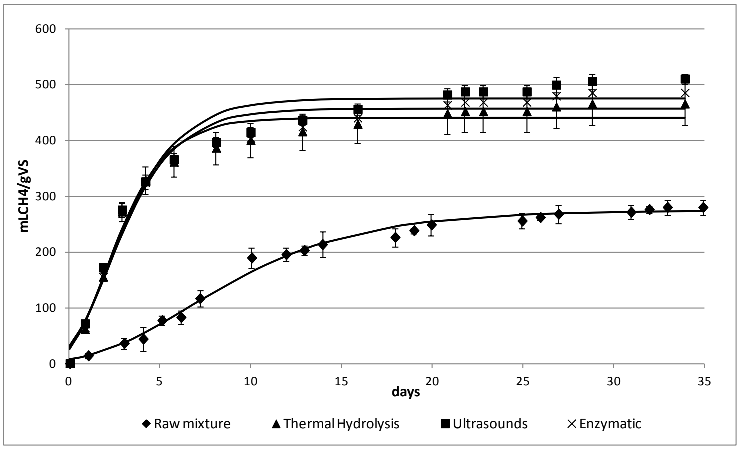

Figure 3. BMP tests results of raw and pretreated mixtures (Phase 3)

Relating phases 1 and 3, it can be observed that co-digestion assays presented a better effect by the action of pretreatments than the cow manure ones, what could be explained by the high efficiency that pretreatments have in biological sludge.

Among ultrasounds and thermal hydrolysis, which have reached the highest improvements (faster kinetics and higher methane potentials) in both phases 1 and 3, the last one also presents some operational and economical advantages, such as: high energy-efficiency, foaming problems reduction, better sludge dewaterability, guarantee of pathogen removal, odours emission control (Pérez Elvira et al. 2006). Therefore, thermal hydrolysis offers more possibilities to be the best pretreatment option for a further study in next phase.

3.4 Phase 4: Thermal hydrolysis optimization for mixtures co-digestion

According to previous results it was decided to use the thermal hydrolysis pretreatment for an optimization of the co-digestion of cow manure and mixed sludge. Three configurations have been tested in order to identify which is the best option to optimize the process: (1) thermal hydrolysis applied to the raw cow manure; (2) thermal hydrolysis applied to the biological sludge; (3) thermal hydrolysis applied to the mixture of cow manure plus biological sludge.

BMP tests results of co-digested mixtures, shown in *Figure 4* and *Table 5*, indicate that all the configurations lead to an improvement regarding the non-pretreated mixture in terms of methane production (at least 16% more methane), kinetics (more than double in some cases) and lag-phases (reduced to 0). The most promising mixtures are the ones applied to the secondary sludge or to the mixture of secondary sludge and cow manure, with increases over 30% of the final methane production (P). Even though hydrolyzed cow manure presented a significant increase in the kinetics during the first seven days, the final biogas production is lower than the other ones. Thus, the important effect that thermal hydrolysis has on the biological sludge is again noted.

Sample (CM+SS1+SS2)		**Parameters**				**% increase**		**lag-phase reduction**
		P	**Rm**	**λ**	**R^2**	**P**	**Rm**	
		$mLCH_4/gVS$	$mLCH_4/gVS/d$	d	-	%	%	days
Raw mixture		273.4	52.9	1.39	0.991	-	-	-
Thermal	CM (1)	318.8	126.7	0	0.977	16.6	139.4	1.4
Hydrolysis	SS2 (2)	357.5	94.2	0.04	0.987	30.7	77.9	1.3
to…	CM + SS2 (3)	364.6	112.1	0.61	0.941	33.3	111.9	0.8

Table 5. Results of different configurations of thermal hydrolysis to mixtures (Gompertz modelling)

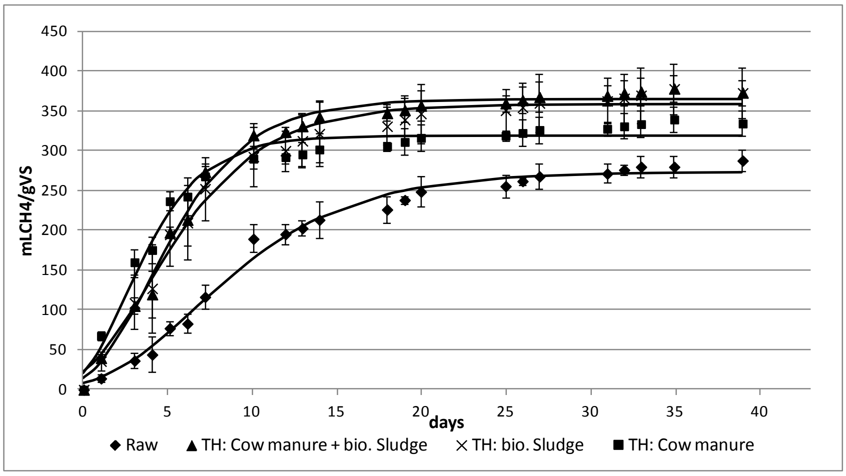

Figure 4. BMP tests results of raw and thermally hydrolyzed mixtures with different configurations (Phase 4)

The hydrodynamic characteristics of the hydrolyzed mixtures indicate that thermal hydrolysis improves the filterability, capillarity (higher FC and lower CST) and viscosity (curves not shown), especially in the hydrolyzed cow manure mixture: FC=280m^2/s; CST=112s versus FC=21m^2/s; CST=5222s of non-pretreated sample. Meanwhile, the mixture without pretreatment presents good results for centrifugability: good separation of liquid and solid phases (70% separated liquid and 100% solid recovery in cake) and higher solid concentration in cake (25%TS). These results indicate that hydrolyzed mixtures have better hydrodynamic properties for a continuous operation: mixing properties, dewaterability, and viscosity of sludge become more favourable.

Then, in order to choose the best option between these alternative configurations, the ones in which biological sludge is thermally hydrolyzed seem to be most suitable. Pretreating the cow manure with the sludge or not would be a question of interest in view of choosing the best biodegradability parameters (both pretreated, see *Table 5*) or avoiding operational problems such as blocking, associated with pretreating a solid substrate (just biological sludge pretreated). However, if a high quality digestate for land application is desirable as a sub-product, the application of the thermal hydrolysis to the cow manure would have especial interest (at least 133ºC for 20 minutes), according to the European regulation 1774/2002.

Anyway, a further continuous operation study of this pretreatment would be interesting to optimise the co-digestion process and confirm all the previous results.

4. CONCLUSIONS

Cow manure methane potential is increased 28% by the application of thermal hydrolysis and ultrasounds pretreatments. The co-digestion of cow manure and mixed sewage sludge does not lead to synergistic effects. However, when pretreatments are applied to cow manure and biological sludge, a considerable improvement of methane production takes place, providing a faster hydrolysis process (4 times faster) and over 60% more biogas yield. Thermal hydrolysis optimization resulted in the highest biogas production so long as biological sludge was pretreated. The assessment of hydrodynamic tests indicates dewaterability and rheology were also improved by the pretreatment.

5. ACKNOWLEDGEMENTS

The work presented has been carried out under the financial support of R+i Alliance and special acknowledgements to Consolider.

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CHAPTER 5. OPTIMIZATION OF SEWAGE SLUDGE AND GREASE CO-DIGESTION USING DISINTEGRATION TECHNOLOGIES

This chapter deals with the optimization of grease waste and sewage sludge co-digestion, focusing on thermal hydrolysis pretreatment. It is divided in two sections (corresponding to two different articles): a previous study, which was partially developed in the University of Valladolid, where co-digestion mixtures were optimized and different pretreatments were tested (O*ptimization of municipal sludge and grease co-digestion using disintegration technologies*); and a second part where thermal hydrolysis was optimized and tested in a semi-continuous reactor, fully developed in University of Valladolid (*Grease waste and sewage sludge co-digestion enhancement by thermal hydrolysis: batch and fed-batch assays)*. Next, both papers are included, but special attention has been paid to the second part of the study since it compiles a complete sequence of tests which results in semi-continuous trials and evaluates in depth the thermal hydrolysis effect on the co-digestion process.

Grease waste is an adequate substrate for sewage sludge co-digestion since, coming both from waste water treatment plant, it has a high methane potential (489 $NmLCH_4$/gVSin); however, no synergistic effect takes place when co-digesting with 52%VS grease. On the other hand, thermal hydrolysis improves the anaerobic digestion of grease waste (43% higher kinetics) and biological sludge (29% more methane potential). Therefore, the application of thermal hydrolysis to a co-digestion process was further studied. Firstly, biochemical methane potential tests showed that the best configuration to implement the thermal hydrolysis to the co-digestion process is pretreating the biological sludge alone, providing a 7.5% higher methane production (398 $NmLCH_4$/gVSin), 20% faster kinetics and no lag-phase. Its implementation in a fed-batch operation resulted in a considerable methane production (363 $NmLCH_4$/gVSin) and thermal hydrolysis improved the rheology and dewaterability properties of the digestate. This leads to important economical savings when combining with co-digestion, reducing final wastes management costs and showing interesting perspectives for full-scale application.

Keywords: co-digestion; fed-batch reactor; grease waste; pretreatment; sewage sludge; thermal hydrolysis

The next articles have been published in Water Science & Technology:

Optimization of municipal sludge and grease co-digestion using disintegration technologies. (2012) L. Bouchy, A. Pérez, P. Camacho, P. Rubio, G. Silvestre, B. Fernández, R. Cano, M. Polanco and N. Díaz (Water Science and Technology)

Grease waste and sewage sludge co-digestion enhancement by thermal hydrolysis: batch and fed-batch assays. (Accepted for publication) (2014) Cano R., Nielfa A., Pérez A., Bouchy L., Fdz-Polanco M. (Water Science and Technology)

Optimization of municipal sludge and grease co-digestion using disintegration technologies

L. Bouchy, A. Pérez, P. Camacho, P. Rubio, G. Silvestre, B. Fernández, R. Cano, M. Polanco and N. Díaz

ABSTRACT

Many drivers tend to foster the development of renewable energy production in wastewater treatment plants as many expectations rely upon energy recovery from sewage sludge, for example through biogas use. This paper is focused on the assessment of grease waste (GW) as an adequate substrate for co-digestion with municipal sludge, as it has a methane potential of 479–710 LCH_4/kg VS, as well as the evaluation of disintegration technologies as a method to optimize the co-digestion process. With this objective three different pre-treatments have been selected for evaluation: thermal hydrolysis, ultrasound and enzymatic treatment. Results have shown that co-digestion processes without pre-treatment had a maximum increment of 128% of the volumetric methane productivity when GW addition was 23% inlet (at 20 days of HRT and with an OLR of 3.0 kg COD/m^3d), compared with conventional digestion of sewage sludge alone. Concerning the application of the selected disintegration technologies, all pre-treatments showed improvements in terms of methane yield (51.8, 89.5 and 57.6% more for thermal hydrolysis, ultrasound and enzymatic treatment, respectively, compared with non-pretreated wastes), thermal hydrolysis of GW and secondary sludge being the best configuration as it improved the solubilization of the organic matter and the hydrodynamic characteristics of digestates.

Key words | co-digestion, disintegration, enzymatic treatment, grease, sewage sludge, thermal hydrolysis, ultrasound

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INTRODUCTION

At present, many drivers tend to foster the development of renewable energy production in wastewater treatment plants (WWTPs): for example strong incentives are being implemented at the European and national levels, and the aim for independence regarding energy providers. The final ambition is energy self-sufficiency.

In WWTPs several types of waste are produced and are usually disposed of, disregarding their energy potential: this is the case for grease. Furthermore, grease is a waste produced by many other industries and economic activities (biofuel-producing industry, food industry, restaurants, …) and therefore it is an interesting market opportunity. On the other hand, grease is one of the most studied substrates to be co-treated with sewage sludge, but some limits have been detected for its application, such as degradation limits for high grease additions or inhibition problems due to their degradation products (Davidsson *et al*. 2007; Luostarinen *et al*. 2009).

Within this context, amongst several approaches to be considered, many expectations rely upon energy recovery from sludge, for example through biogas use. To date biogas production and use has not been optimized, as in many cases it was designed and operated as a means of stabilizing sludge, and not recovering energy. Anaerobic co-digestion is reported to offer several benefits over conventional digestion, such as increased cost efficiency and increased degradation of the treated substrates due to possible synergistic effects (Luostarinen *et al*. 2009).

doi: 10.2166/wst.2012.660

Previous studies have shown that there are different wastes with different origins that can be co-treated with sewage sludge obtaining promising results (Corti & Lombardi 2007; Bouchy *et al.* 2009). Various authors reported increases in the methane yield during the co-digestion of sewage sludge (SS) with different types of fats. Davidsson *et al.* (2007) reported an increase in the methane yield of 9–27% when 10–30% grease (on volatile solid, VS, basis) was added to a SS reactor. Luostarinen *et al.* (2009) reported an increase of 60% when co-digesting SS with the grease trapped from a meat-processing industry (46% VS added), and Kabouris *et al.* (2009) found methane yields 2.6 times higher when adding fat, oil and grease from restaurants and food services (48% total VS load). A good option for WWTPs is to use intermediate wastes, generated inside the plant, such as the grease waste (GW) of the dissolved air flotation (DAF) unit, whose management costs will be reduced (Silvestre *et al.* 2009).

However, the addition of solid wastes could decrease the methane production as hydrolysis becomes the rate limiting step at a given hydraulic retention time. A strategy to overcome this is the selection of an adequate pre-treatment technology to ensure that the organic matter could be more accessible to the anaerobic microorganisms. Most of the pre-treatment studies evaluate their efficiency through the solubilization ratio (soluble to total chemical oxygen demand (COD) ratio) and the increment of the methane yield, but fewer have included the dewatering capacity (Gavala *et al.* 2003) as it is an important parameter for industrial scale implementation. The main pre-treatments at WWTPs are thermal and ultrasound processes (Valo *et al.* 2004; Bougrier *et al.* 2008) at industrial scale, but some research has been done with enzymatic pre-treatment.

Within the framework of a larger project on anaerobic co-digestion, the aim of this paper is focused on overcoming the detected limitation on hydrolysis rate of the grease-sludge co-digestion by using three different disintegration technologies.

MATERIALS AND METHODS

Preliminary co-digestion trials (Phase 1)

In a first phase, four different samples of grease waste (GW) were taken from the dissolved air flotation (DAF) unit of four different WWTPs (Barcelona, Spain). A sewage sludge mixture (SS1) was taken from a WWTP, located in Barcelona (Spain). It was composed of a 70/30 (%weight) mixture of thickened primary and biological sludges, according to the common ratio in this WWTP.

Grease samples were characterized in order to select one with the best properties to be co-digested in a continuous anaerobic digester of sewage sludge. Then, a continuous trial with different ratios of mixture (GW and SS) was carried out, increasing gradually the organic loading rate of the co-digestion mixture, maintaining the same sludge input but with increased GW quantities in order to define the optimal biogas production and biodegradability performances, as well as the kinetics and limits. These continuous experiments were carried out in a 7 L continuous stirring tank reactor (CSTR) with a working volume of 5.5 L. The CSTR was operated at mesophilic temperature range (35 °C), with a hydraulic retention time (HRT) of 20 days and with an organic loading rate (OLR) between 2.2 and 3.6 kg COD/m^3 d, during 302 days. The reactor was fed twice a day with a temporized peristaltic pump. The biogas production was measured with a volumetric gas counter (Ritter Apparatebau GMBH & Co KG). The influent and effluent characteristics were measured twice a week and biogas composition once a week.

Optimization assays (Phase 2)

Based on the results obtained in phase 1, second phase trials were carried out focusing on overcoming the identified limitations. These were carried out through the use of several disintegration technologies (thermal hydrolysis, enzymatic and ultrasound) and several configurations (pre-treatments were applied to the GW, to the secondary sludge alone or to the grease-secondary sludge mixture).

For this second phase, thickened primary (SS2) and biological sludges (SS3) were sampled separately in a WWTP (Spain), and mixed in a proper ratio (in that case 50/50 according to the common ratio in the WWTP) after the pre-treatment process. All SS were sampled every two weeks and kept refrigerated at 4 °C, while the grease waste was sampled once and kept frozen at −20 °C.

The pre-treatments were selected based on COD solubilization, increase in biogas production, pathogen reduction and dewaterability, as well as the availability to carry out the test at lab-scale. Next, a brief description of the available equipment to carry out these pre-treatments is given:

- ***Thermal hydrolysis***: The hydrolysis plant (home-built) is made up of a 1 L reactor where the hydrolysis of the substrate/sludge takes place for 30 min, which is fed by an 8 bar steam. It is connected to a flash tank where the decompression is carried out and the final product is obtained (Figure 1).

- ***Cavitation by using ultrasound***: The equipment used is an ultrasound homogenizer that converts electrical energy in to mechanical vibrations (ultrasound), which are transmitted to the sample by a sonotrode. The equipment is shown in Figure 2.
- ***Enzymatic treatment***: In 300 mL closed bottles, the substrate, the enzymatic solution and the buffer solution (for a pH control) are introduced and stirred at a desired temperature. An accurate temperature and pH control is required. In that case, the process is carried out by the addition of a commercial lipase (Biolipase L – Biocon) which assures a higher activity but requires an accurate temperature and pH control.

Figure 1 | Thermal hydrolysis plant.

Figure 2 | US homogenizer.

Analytical and characterization methodologies

Characterization of samples

The different standard methods used for substrate characterization are shown in Table 1.

Biochemical methane potential assays

The batch methane potential (BMP) assays, carried out in both phases 1 and 2, were performed following standardized assays for research purposes (Angelidaki & Sanders 2004; Angelidaki et al. 2009) and adapted to the equipment available in each laboratory involved. The vial volume was 100–1,000 mL and the initial pH was between 7.2 and 7.5 with 5 g COD/L and 5 g VS/L as initial concentration of substrate and inoculum, respectively. The incubation temperature was 35–37 °C. The inoculums were WWTP mesophilic digested sludge (after a pre-incubation period of 2 days at 35 °C). The stop criterion for all tests was a daily methane production below 5% of accumulated production or maximum test duration of 30–35 days. Methane potential or BMP was expressed as the net volume of methane per kg of initial VS content.

Assessment of physical properties

In order to assess the implementation of co-digestion mixtures and pre-treatments in an industrial plant, other tests

Table 1 | Standard methods used for substrate characterization

Parameter	Method	Source
TS, VS, VSS, TSS	SM 2540 Solids	SM (1997)
COD	SM 5220 Chemical Oxygen Demand	SM (1997)
C_T/TOC	5310 B High Temperature Combustion Method, TOC	SM (2000)
TKN	4500 – NB Macro-Kjeldahl Method	SM (1997)
NH_3-N	4500 – NH_3 Nitrogen	SM (1997)
VFA	SM 5560 B Organic and Volatile Acids	SM (2001)

Nomenclature: TS/VS, total and volatile solids; TSS/VS, total and volatile suspended solids; COD, chemical oxygen demand; CT/TOC, total carbon and total organic carbon; TKN, total Kjeldahl nitrogen; NH_3-N, ammonia nitrogen; VFA, volatile fatty acids.

such as filterability tests (filtration constant, SRF, CST), settling test (SVI), centrifugability test (% separation, solids concentration) and rheology test (viscosity curves) were performed in the second phase in order to study the hydrodynamic characteristics of the pre-treated mixtures.

RESULTS & DISCUSSION

Preliminary co-digestion trials (Phase 1)

The characterization of the four GW from four different WWTPs showed the influence of the raw wastewater characteristics and the efficiency of the DAF units of each WWTP on the grease waste (Table 2): samples showed differences in the concentration of main parameters, but all of them presented a high organic matter content (177–335 g COD/kg and 63–143 g VS/kg) and fat also was presented in a large range (15–100 g fat/kg).

Despite the observed differences in physico-chemical parameters, the rate and BMP of the four samples were very similar (432–529 L CH_4/kg VS), showing a clear lag phase of 10 days at the beginning of all assays, followed by the accumulation of volatile fatty acids (VFA) and H_2, for the four GWs studied (Silvestre *et al*. 2009). As the study of codigestion with sewage sludge was the main objective of this work, sample GW2 was selected for the continuous trials because of its high VS and fat concentration, as well as its high C/N ratio.

The co-digestion of GW2 with SS1 (Table 1) in the continuous reactor was performed with different ratios of mixture. The organic loading rate (OLR) was increased up from 2.2 kg COD/m^3 d (fed only with SS) in three steps by adding different amounts of GW2 (2.4, 3.0 and 3.6 kg COD/m^3 d, which corresponded to a grease addition of 4, 23 and 37% of VS inlet, respectively). The results of continuous trials showed an increment of volumetric methane productivity after the GW addition: 36 and 128 for 4 and 23% VS inlet grease addition periods respectively, compared with 0.25 m^3CH_4/m^3d with SS alone. Further OLR increment (37% VS) did not report an increase in volumetric methane production, consistently with the lower methane yield and the COD removal efficiency (Silvestre *et al*. 2009): COD removal when treating SS alone was 35%, while it was 40, 55 and 44% with 4, 23 and 37% VSinlet of grease waste. Although no accumulation of VFA (the total VFA concentration in the effluent was always less than 100 mg/L) or alkalinity imbalance was detected, grease additions higher than 23% VS inlet have not shown an increase of the methane production in the continuous digester, thus suggesting a HRT limitation.

Table 2 | Characterization of grease wastes (GW) and sewage sludges

Waste	TS (g/kg)	VS (g/kg)	tCOD (g/kg)	Fat (g/kg)	C/N	BMP (L_{CH4}/kg_{VS})
GW1	146 ± 1	123 ± 1	298 ± 20	47 ± 1	20	483
GW2*	160 ± 4	143 ± 3	321 ± 30	100 ± 4	39	473
GW3	126 ± 1	101 ± 1	335 ± 64	38 ± 2	23	529
GW4	75 ± 3	63 ± 2	177 ± 5	15 ± 2	10	432
SS1**	32 ± 5	23 ± 4	44 ± 8	0.2 ± 0.0	10	322
SS2***	168 ± 30	116 ± 23	188 ± 38	–	–	337
SS3***	71 ± 14	55 ± 11	84 ± 17	–	–	188

Note: All units are expressed as g/kg wet waste. Nomenclature: SS1-mixture; SS2-primary sludge; SS3-secondary sludge
*GW2 was selected for both phases of this work. **SS1 was used in Phase 1. ***SS2 and SS3 were used in Phase 2.

Optimization assays (Phase 2)

As the main limit suggested from the preliminary co-digestion trials was HRT limitation, in order to reduce the required HRT and enhance the hydrolysis step, within Phase 2 of the research, several pre-treatments were tested. As a first step, a sequence of biodegradability tests has been carried out with GW2 alone to observe the effect of the pre-treatments on the grease waste (Figure 3).

No increase of the methane productivity was observed after the pre-treatment of GW2 alone as final values of methane productivity after pre-treatments are below those corresponding to the raw substrate: 710 L CH_4/kg VS. Methane potential of GW2 was different from that shown in Table 2 due to the fact that Phase 1 and 2 were not carried out at the same time, so the grease was not the same. Nevertheless, the curves' profiles showed that thermal hydrolysis produced acceleration of the biogas production (Figure 3), thus favourably impacting the kinetics which would impact the HRT under continuous operation. While the biodegradation of raw grease and pre-treated grease with enzymes or ultrasound started the biodegradation after 20 days, the methane production of thermally pre-treated grease vials began after 10 days. This was due to the high solubilization of organic matter during the thermal hydrolysis pre-treatment.

Before the biodegradability tests of the co-digestion mixtures, the GW2 and secondary sludge SS3 (see Table 1) were mixed and pre-treated together, and then the primary

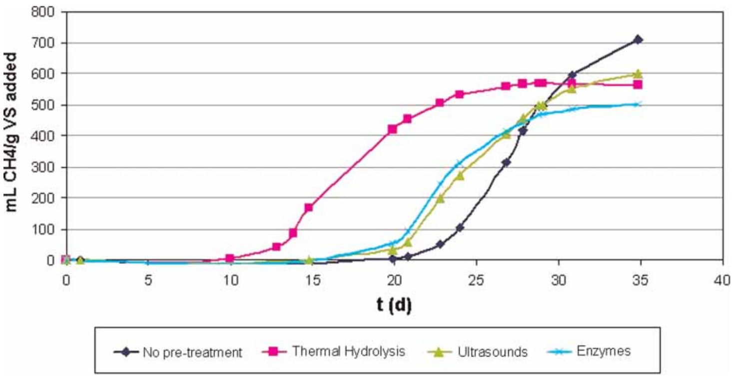

Figure 3 | Biological Methane Potential tests on the grease samples using different disintegration technologies.

sludge SS2 (see Table 1) was added to the pre-treated mixture, thus forming the mixture to be co-digested. This configuration was thought to be the most adequate as former studies (Pérez-Elvira 2006) have shown that the pre-treatment of secondary sludge alone is more effective than together with primary sludge in terms of energy balance (and the use and size of the equipment are then optimized).

Results from Phase 1 showed that a grease addition higher than 23% VS inlet did not report an increase in volumetric methane production. For this reason, a higher rate of VS inlet was selected for the second phase of the research, with the objective of overcoming this limit. So, the final grease waste content in the mixtures to be co-digested was 50% of the initial COD (over 50% VS inlet). The obtained results of co-digestion mixtures, as well as each co-substrate separately, are represented in Figure 4.

While primary and secondary sludges (SS2 and SS3 in Table 1, respectively) methane productivities reached average values of 337 and 188 L CH_4/kg VS, respectively, the pre-treated co-digestion mixtures increased considerably up to values of 600 or 700 L CH_4/kg VS, in the same magnitude as the raw grease yield. Moreover, all the curve profiles of the co-digested mixtures showed much better kinetics, allowing for a quick start during the first 5 days (reaching 60–70% of the total production in this period). This suggests that pre-treatments have allowed high solubilization of the organic matter, which is confirmed by the disintegration factors after pre-treatments (Table 3).

In this trial, ultrasound showed the best results in terms of methane productivity increment (89.5%), which is also consistent with the disintegration results (Table 3). Table 3 summarizes the final productivities of biodegradability tests. BMP increases have also been calculated to show the effect of each pre-treatment with regard to the

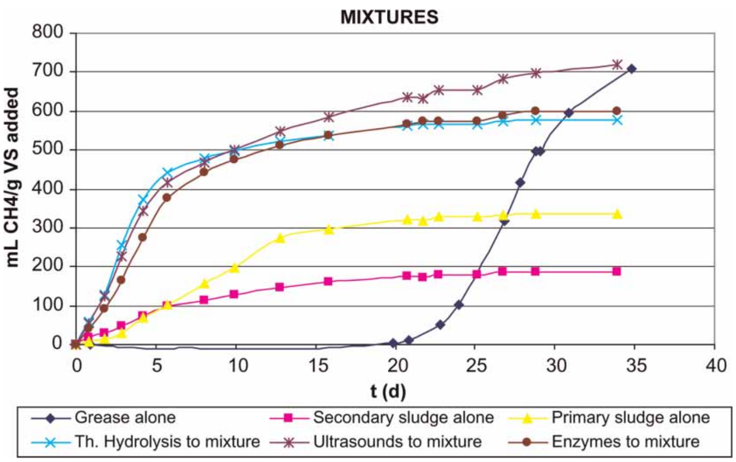

Figure 4 | Biological Methane Potential tests on the sludge and on the mixtures.

Table 3 | Methane productivities and solubilization: increment after pre-treatments

		Solubilization (CODs/CODt)		Methane yield (LCH_4/kg SV)	
Substrate	Pre-treatment	Value	% increase	Value	% increase
GREASE	None	–	–	710	–
	Thermal hydrolysis	–	–	583	−20.7%
	Ultrasound	–	–	601	−15.4%
	Enzymes	–	–	500	−29.6%
SLUDGE	Primary	–	–	337	–
	Secondary	–	–	188	–
MIXTURES	None	6.7%	–	379	–
	Thermal hydrolysis	10.4%	+55%	575	+51.8%
	Ultrasound	12.2%	+82%	718	+89.5%
	Enzymes	12.9%	+92%	597	+57.6%

non-pre-treated samples. In the case of mixtures, results show the improvements in the methane yield after the application of pre-treatments when they are compared with results obtained in previous studies on co-digestion with grease and SS without pre-treatments (Luostarinen *et al.* 2009).

As it was explained in the analytical methodology, other tests such as filterability tests, settling test, centrifugability test and rheology test were performed in this second phase to study the hydrodynamic characteristics of the pre-treated mixtures (Table 4). Unfortunately, not all the parameters for all samples have been determined due to the impossibility of carrying out some tests with certain samples or because of the lack of sample volume obtained.

Considering these monitoring parameters, the thermal hydrolysis samples presented the most convenient hydrodynamic characteristics for a continuous operation in a reactor: lower viscosity, easy filterability (high filtration constants, low CST), good centrifugability (high liquid separation, high solid recovery in cake) and an acceptable solubilization of the organic matter (55%). At full-scale, these advantages may be even more relevant than the CH_4 production increase (this remains to be quantified further).

CONCLUSIONS

Grease waste is an adequate substrate for anaerobic co-digestion of sewage sludge. Despite variable characteristics between samples, their high organic matter and fatty content resulted in high methane potential (479–710 L CH_4/kg VS), compared with municipal sewage sludge (322 L CH_4/kg VS). Continuous experiments showed that the co-digestion of the two materials together was feasible, with 138% increase of the methane yield when grease waste addition was 23% VS inlet (at 20 days of HRT and with an OLR of 3.0 kg COD/m^3 d).

The selected disintegration technologies applied to a mixture of grease and municipal sewage sludge to be co-digested have shown great improvements in terms of methane productivity. Analyses of other parameters related to the hydrodynamic characteristics of the samples have been carried out as well. Ultrasound showed higher biogas productivity than thermal hydrolysis and enzymatic treatment, reaching an increment of 89.5% compared with sewage sludge methane productivity. However, for continuous full-scale operation, the most promising option would be the thermal hydrolysis pre-treatment configuration, as it presented the best hydrodynamic characteristics improvements and a considerable increment of methane productivity. This is a preliminary conclusion after carrying out different batch trials. The assessment in continuous mode should be the next step to confirm the utility of the application of these disintegration technologies to the co-digestion process.

Table 4 | Results from physical properties assessment in Phase 2

Test	Filtration I	Filtration II	Centrifugability		
Parameters	Filtration constant	Capillary suction time	Separated liquid	Solid recovery in cake	Solid conc. in cake
Units	cm^2/s	s	%	%	%
Thermal hydrolysis	0.017	285.6	63.4	98.4	16.3
Ultrasound	–	2,179.8	31.7	95.9	20.4
Enzymes	–	701.7	57.4	88.9	19.2

ACKNOWLEDGEMENTS

The work presented is based on the results of projects carried out under the financial support of CDTI (Sostaqua project) and $R+i$ Alliance.

Thanks to the two anonymous reviewers who contributed to improving the content of the paper.

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First received 9 February 2011; accepted in revised form 15 April 2011

Grease waste and sewage sludge co-digestion enhancement by thermal hydrolysis: batch and fed-batch assays

INTRODUCTION

Anaerobic digestion of sewage sludge has been applied at wastewater treatment plants (WWTP) for decades. It is a well-known, efficient and environmentally sustainable technology which enables green energy production, as well as stabilization of sludge. The co-digestion of organic wastes with sludge offers several benefits over conventional digestion such as increasing cost efficiency and improving the degradation of the substrates due to possible synergistic effects (Luostarinen et al. 2009). The use of an intermediate waste generated in the WWTP, such as the grease trapped in the dissolved air flotation (DAF) unit, would lead to an optimization of the entire plant because its availability on site. The cost of managing the grease waste to landfill will be eluded and its high fat content will increase the biogas yield since lipid-rich materials are known to have high methane potentials (Silvestre et al. 2011). However, its degradation products, long-chain fatty acids (LCFA), may be severely inhibitive to methanogenesis and a lag-phase is usually noticed. Then, co-digestion of fats can be more profitable than used as a single substrate, what is also uneconomical considering the low amounts of grease waste produced in WWTP (7.3kg/person/year according to Noutsopoulos et al. (2013)). Previous works have shown interesting results using this waste for sludge co-digestion at lab-scale (Luostarinen et al. 2009; Silvestre et al. 2011; Davidsson et al. 2008) showing high synergistic effects. On the other hand, the production of grease waste in WWTP could be reinforced by the addition of FOG (fat, oil and grease waste) collected in grease traps from different sources (food industry, restaurants...) with a production rate of 7.1L/person/year, which co-digestion with sewage sludge has also been studied (Kabouris et al. 2009; Long et al. 2012).

When dealing with solid wastes, the degradation rate of the overall digestion process is limited by the first hydrolytic step. In order to accelerate it, thermal hydrolysis (TH) pretreatment is one of the most efficient techniques, leading to high organic matter solubilisation, pathogen reduction, dewaterability and rheology improvement and an increase in biogas production. Thermal hydrolysis technology has been widely tested with sewage sludge and even applied in full-scale processes in several WWTP (Carrère et al. 2010). Nevertheless, pretreating co-digestion mixtures with grease has been hardly studied and need further research for its implementation in a full-scale plant: Li et al. (2013) pretreated FOG and sewage sludge applying ultrasounds and thermo-chemical techniques; Donoso-Bravo and Fdz-Polanco (2013) studied enzymes (lipase) addition to grease trapped from WWTP and sewage sludge co-digestion.

In this study, the implementation of thermal hydrolysis pretreatment in a co-digestion process of grease waste and sludge, both from WWTP, is tested in progressive laboratory scales: from initial batch tests with raw substrates to a fed-batch co-digestion assay; with the aim of checking the possibility for a full-scale application.

MATERIALS AND METHODS

Substrates

Thickened primary (SS1) and biological sludge (SS2) were sampled from a municipal WWTP (Spain). Grease waste (GW) comes from the dissolved air flotation unit of another WWTP located in Spain. Characterization values are summarized in Table 1.

Parameter	Units	GW	Sludge	
			SS1	SS2
CODt	g/kg	648.3	174.2	77.1
CODs	g/kg	-	3.62	1.20
TS	g/kg	505.2	198.3	69.9
VS	g/kg	468.2	99.1	52.8
TKN	N-g/ kg	3.27	4.69	5.75
NH_4^+	N-g/ kg	0.24	0.29	0.24
Grease	g/kg	128.0	15.5	1.2
MIXTURE RATIO (GW+SS1+SS2)	Weight %	15	42.5	42.5
	COD %	47.6	36.3	16.1
	TS %	39.9	44.4	15.7
	VS %	52.1	31.2	16.7

Table 1. Substrates characterization and mixture ratio for co-digestion

SS1 and SS2 were firstly mixed in 1:1 weight ratio (according to the common ratio in the WWTP) to obtain mixed sludge and then GW was added to it according to a specific ratio in the final co-digestion mixture: 48%COD, over 50%VS or 15% weight basis. This ratio was set in accordance from a previous study (Bouchy et al. 2012): for this ratio, there was no increase in the methane production (no synergy by co-digestion) when compared with lower GW addition, being the final objective overcoming the identified limits.

Thermal hydrolysis plant

The hydrolysis plant is made up of a 2L reactor, fed with a substrate and heated with steam until the desired temperature, and a flash tank where the steam explosion takes place after the hydrolysis reaction time has elapsed. TH was only applied to biological sludge rather than to primary because it is mainly composed of biomass, hardly degradable carbohydrates and easily degradable proteins, only available with a break of the cellular wall; hydrolysis breaks these cells and helps to the biodegradation of biological sludge (Perez-Elvira et al. 2010). The operational conditions for these tests were 170ºC and 30 minutes, which were the optimized conditions for biological sludge obtained by Fdz-Polanco et al. (2008). Different conditions could be tested for grease in order to optimise its hydrolysis, but the interest in this study is to integrate grease and sludge TH in an already operating sludge TH plant. In fact, many full-scale plants have implemented TH technology at 170ºC leading to considerable benefits (Carrère et al. 2010).

Fed-batch digesters

The fed-batch experiments were carried out in two cylindrical reactors of 20L of useful capacity and 10L of gas chamber. Both reactors were operated at mesophilic temperature (35ºC±1ºC). The biogas production was continuously measured by a pulse electrical system and analyzed by gas chromatography (Varian CP-3800). Biogas internal recycle assured a correct mixing. Feeding was carried out once per day.

Biochemical Methane Potential tests

The Biochemical Methane Potential (BMP) assays were performed by triplicates following an internal protocol based on standardized assays (Angelidaki et al. 2009). The reactors volume was 300 mL and a substrate-inoculum ratio of 1:1 in terms of VS was applied. The incubation temperature was 35ºC. The inoculum was WWTP mesophilic digested sludge. Periodical monitoring analyses of biogas production by pressure meter and biogas composition by gas chromatography (Varian CP-3800) were performed during the tests. Methane potentials were expressed as average values of the net volume of methane per gram of initial substrate VS.

Modelling

The Modified Gompertz equation (Lay et al. 1997) -equation 1- was considered in order to fine-tune the experimental data from BMP tests to a theoretical equation:

$$B = P \times exp\left\{-exp\left[\frac{R_m \cdot e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

The model has three parameters: the methane yield rate (*R_m*) which indicates the initial slope of the curve ($mLCH_4$/gVS/d), the maximum biogas production (*P*) expressed as $mLCH_4$/gVSin and the lag-phase (λ) in days. B is the calculated methane production ($mLCH_4$/gVSin) for time t. The model fine-tuning to the experimental data was achieved by least squares methodology, by minimising the next objective function (2):

$$OF(\varphi) = min\sum_{t=1}^{N}\left(B_{exp}(t) - B_m(t,\varphi)\right)^2 \quad (2)$$

where B_{exp} is the consumption velocity obtained from measurements (plotted in BMP results graphs as points), B_m is the corresponding velocity calculated by the model (plotted with continuous curves), *N* is the number of measurements, *t* is time and φ represents the Gompertz parameters. The correlation factor (R^2) was then calculated to assess the accuracy of each model with respect to the experimental data.

Hydrodynamic and dewaterability tests

To assess the dewaterability and hydrodynamic properties of the fed-batch reactors, filterability, centrifugability and rheology tests were performed following an internal method for sludge characterization of the University of Valladolid. These tests were very relevant in terms of assessing the impact on mixing requirements, digestate dewaterability and handling properties. *Filterability* was measured by forcing the sludge to pass through a 1.2µm filter under a 1 barg pressure and then the filtration constant (FC) was calculated. *Capillary suction time* (CST) was determined using a Triton Electronics Ltd. and Whatman 17 filter paper. *Centrifugability* assessed the liquid and solid phase separation after 5 minutes centrifugation at 5000 rpm by % separated liquid, % solid recovery in cake and solid concentration in cake. *Rheology* was evaluated by viscosity curves obtained with a *Brookfield Digital Viscometer DV*-I.

Experimental procedures

The experimental setup in this study was composed of three consecutive stages:

- ***First BMP trials*** to study the effect of TH pretreatment in raw substrates (GW and SS2) by BMP tests.
- ***Co-digestion BMP tests*** of GW and mixed sludge and then study the implementation of thermal hydrolysis to co-digestion.
- ***Fed-batch operation***: co-digestion of GW and sludge with and without pretreatment in two identical reactors to study the effect of the pretreatment in a fed-batch operation. Hydrodynamic tests were applied to digestates to study their dewaterability and the rheology of the reactors.

Analytical methods

Internal protocols for solid substrates characterization based on the Standard methods (Apha, 2005) were applied to determine the next parameters: total and volatile solids (TS, VS), total and soluble chemical oxygen demand (CODt/s), volatile fatty acids (VFA), total Kjendhal nitrogen (TKN), ammonium (NH_4^+) and grease content.

Statistical analysis

All BMP tests were carried out by triplicates. The experimental methane productions are always referred to average values and standard deviations were calculated and represented in BMP curves with vertical lines. For the hydrodynamic tests, duplicates were measured and the results were averaged.

RESULTS AND DISCUSSION

First BMP trials: effect of thermal hydrolysis to substrates

As a first approach, BMP tests to raw substrates with and without pretreatment were carried out. As it can be observed in Figure 1a-b and Table 2, the behaviour of the raw substrates biodegradation is completely different: while SS2 has a fast start-up (λ=0) and a low final methane potential (215 $mLCH_4/gVS$), the GW presents a long lag-phase (almost 18 days) but a high methane potential (488.6 $mLCH_4/gVS$), quite similar as the one reported by Silvestre et al. (2011) in batch assays (432-529 $mLCH_4/gVS$). However, TH leads in both cases to an improvement of those limitations: SS2 and GW methane potentials are increased by 29.2% and 7.2% and their methane yield rates gets 43.3% and 25.4% higher respectively. Moreover, TH on GW has reduced by almost 2 days its lag-phase. The application of TH to SS2 leads to great improvements of its biodegradation parameters, because the liberation of easily degradable material during the cells disruption, as it has already been tested by Perez-Elvira et al. (2010). On the other hand, TH to GW presents slight improvements but its long lag-phase (over 15 days) is still an important drawback for its biodegradation in spite of its high methane yield and high kinetic rate. In this case, its high lipid content and slow degradable materials could not be subjected to significant alterations during the pretreatment.

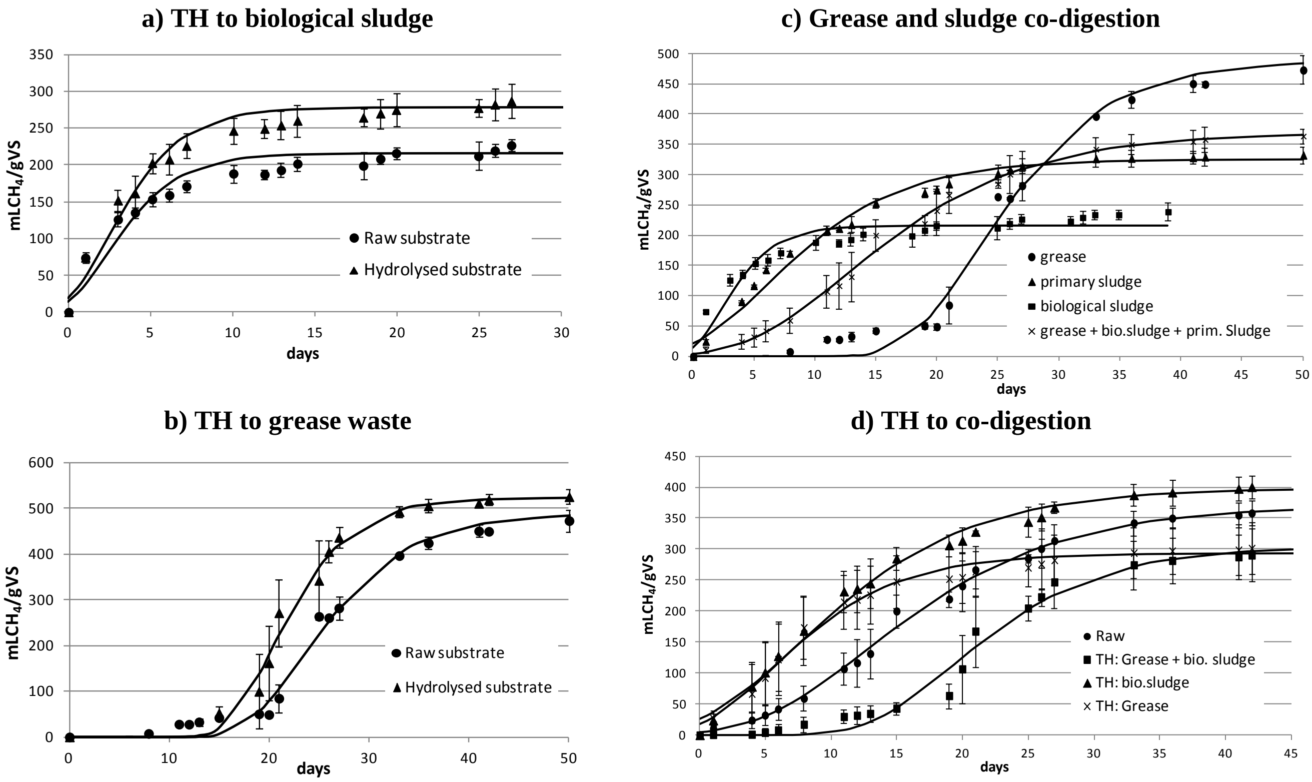

Figure 1. BMP tests results:

a) Biological sludge (raw and thermally hydrolysed)

b) Grease waste (raw and thermally hydrolysed)

c) Grease and sludge co-digestion: raw substrates

d) Different thermally hydrolysed co-digestion configurations

Co-digestion BMP tests:

<u>*Raw substrates co-digestion*</u>

First, the effect of raw substrates co-digestion has been studied. GW, SS2 and SS1 have been separately and together biodegraded (Figure 1c and Table 2). As well, the co-digestion factor (α) has been calculated, which indicates the ratio between the experimental methane potential of the co-digested mixture (P_{exp}) and the theoretical value (P_{theo}) calculated according to the mixture ratio from the individual co-substrates (*i*) methane potentials according to equation (3):

$$\alpha = \frac{P_{exp}}{P_{theo}} = \frac{P_{exp}}{\sum_i ratio_i\ (VS\ basis) \cdot P_i\ (\mathrm{mLCH_4/gVS})} \quad (3)$$

The final methane potential of the co-digested mixture is 6% lower than the theoretical value (Table 2), so that the mixture does not offer any synergistic effect in terms of methane production, what was already expected from previous work but it is not in accordance with literature: Silvestre et al. (2011) reported an increase of 138% for GW addition of 37%VS and Davidsson et al. (2008) between 9-27% for 10-30%VS addition. This could be explained by the higher GW input in this study (52%VS) that could cause an overload by LCFA. On the other hand, the lag-phase of the raw GW (18 days) decreases till values below 5 days when the three co-substrates are degraded together, what is interesting in view of a continuous process. It is also remarkable that SS1 methane yield rate is lower than SS2 one, what could be due to the high content of lipids, fibres and solids in SS1; however, its methane production is 50% higher than SS2, what justifies the application of the pretreatment to the latest.

Implementation of thermal hydrolysis to grease waste and sludge co-digestion

In order to overcome the co-digestion limitation when adding too much GW to the mixture, TH is applied. Three different configurations to carry out the pretreatment to the co-digestion mixture are tested: TH applied to the GW, to the SS2 alone or to the GW and SS2 mixture. Then, mixtures were subjected to the same ratios explained in Table 1 by adding the non-pretreated substrates before BMP tests. The results are presented in Table 2 and Figure 1d.

In view of the results, TH only improves the raw mixture biodegradation when just SS2 is pretreated. This sample leads to 7.5% higher methane potential, 20% faster kinetics and a null lag-phase. The increase of the methane production in this case rises the co-digestion factor slightly over 1, making the co-digestion process more profitable. The results concerning the two other configurations of pretreatment do not show any improvement respect the non-pretreated sample in terms of methane production. This fact supports the high efficiency that TH has on SS2 rather than on GW, as it was already observed while pretreating raw substrates. However, the efficiency of TH on SS2 is partially overshadowed when co-digesting since SS2 VS content in the mixture scarcely rises till 17% (Table 1). Then, if the GW content in the co-digestion mixture were lower, the effect of TH would be greater and synergies could be more favourable. Therefore, TH to just SS2 seems to be the most appropriate configuration to be implemented in the next step.

Substrates		Gompertz parameters				% increase		lag-phase reduction	Co-digestion factors (α)
		P	R_m	λ	R^2	P	R_m		
		$mLCH_4/gVS$	$mLCH_4/gVS/d$	d	-	%	%	days	-
Grease waste (GW)	Raw	488.6	30.3	17.6	0.990	7.2	43.3	-1.8	-
	TH	524.0	43.5	15.8	0.999				-
Biological sludge (SS2)	Raw	215.0	32.8	0.0	0.917	29.2	25.4	0.0	-
	TH	277.7	41.1	0.0	0.956				-
Primary sludge (SS1)	Raw	324.8	20.1	0.0	0.984	-	-	-	-
Co-digestion mixture (GW+SS1+SS2)	Raw	370.3	16.3	4.3	0.996	-	-	-	0.94
	TH to GW	293.4	20.1	0.2	0.985	-20.8	22.6	4.2	0.75
	TH to SS2	398.1	19.6	0.0	0.991	7.5	19.7	4.3	1.01
	TH to GW+SS2	305.7	17.5	12.8	0.986	-17.4	7.0	-8.5	0.78

Table 2. BMP results: Gompertz parameters, thermal hydrolysis improvements and co-digestion factors

Fed-batch operation: co-digestion of grease and thermally hydrolysed sludge

The study of a fed-batch process aims to simulate a more real operation and foresee the impact that TH would have in a full-scale co-digester. A simultaneous operation of two identical reactors of 20L capacity during five months enables to compare the traditional co-digestion process without pretreatment (R1) with a co-digestion of thermally hydrolysed SS2, raw GW and SS1

(R2). All the operational variables were maintained at the same values for both reactors during the study: 20 days sludge retention time (SRT), 3.4 kg VS/m^3/d organic loading rate (OLR), same mixture ratios (Table 1) and similar feed characterization. Table 3 summarizes all the parameters that were monitored during an operation time of 70 days (because fluctuations during this period, parameter values were averaged and standard deviations are included) after an adaptation period equivalent to 3 SRT (60 days), as well as the main results of biogas production, substrate removal and digestates dewaterability properties. In Figure 2 the methane production during the entire assay (130 days in total) is plotted; as well, the dewaterability properties and rheology of digestates (viscosity curves) are represented.

		Parameter	Units	R1	R2	% Increase R2 vs R1
	DESIGN DATA	Volume	L	20	20	
		SRT	d	20	20	
		OLR	kg VS/m^3/d	3.4	3.4	
	FEED CHARACTERI.	TS	g/L	82.2±4.4	84.4±6.9	
		VS	g/L	65.6±3.2	67.8±6.3	
		CODt	g/L	103.3±13.2	106.2±14.0	
	REACTOR MONITORING	pH	-	7.5±0.2	7.6±0.1	
		Alkalinity	gCaCO$_3$/L	3.68±0.12	4.09±0.16	
		Alkalinity ratio	-	0.20±0.02	0.19±0.02	
		VFA	mgAcH/L	859±170	951±209	
		VFA/Alkalinity	-	0.22±0.08	0.22±0.07	
		TS	g/L	54.0±4.7	44.3±4.3	
		VS	g/L	34.8±4.3	27.2±2.5	
		CODt	g/L	43.5±4.1	41.2±8.1	
		CODs	g/L	2.07±0.37	1.94±0.22	
		TKN	N-g/L	2.47±0.06	2.39±0.11	
		NH_4^+	N-mg/L	682±38	831±41	
	SUBSTRATE REMOVAL	TS	%	34.3±5.5	46.5±6.1	35.4
		VS	%	46.9±6.9	58.8±5.3	25.5
		CODt	%	56.7±5.7	59.1±10.1	4.2
	PRODUCTION EFFICIENCY	BIOGAS	NLbiogas/d	36.7±4.5	38.7±6.6	5.5
			NLCH$_4$/gVSin	0.35±0.04	0.36±0.06	2.3
		% CH$_4$	%	64.9±1.9	63.3±4.1	-2.4
Digestates	Filterability	Filtration constant	m^2/s	48	67	40.0
		Capillary Suction Time	s	545	471	-13.5
	Centrifugability	Separated liquid	%	52	57	4.5
		Solid recovery in cake	%	98	99	1.6
		Solid concentration in cake	%	11	13	2.4

Table 3. Average values of the main parameters in both reactors during the fed-batch operation and dewaterability properties of both digestates (R2 thermally hydrolysed)

Monitoring parameters that were analyzed twice a week (Table 3) show a similar and stable operation of both reactors: correct pH level (between 7 and 8), enough alkalinity content to assure buffer capacity (over 1000 mgCaCO$_3$/L), low VFA level and correct ammonia level (below 1000 mg/L). Substrate removal efficiency is higher in R2, especially in terms of solids removal (35%TS and 25%VS higher than R1), but does not lead to a corresponding increase of methane production, which trends are shown in *Figure 2*. Then, TH results on a significant increase of VS and TS destruction but the improvement in biogas production is not as high. This discrepancy does not occur in the case of COD, for which the removals are very similar in both reactors (57 and 59%) and coincide with the theoretical value estimated with the methane production (considering the conversion factor 0.35 $NLCH_4$/gCOD). Average methane productivities in both reactors scarcely raise over 350 $NmLCH_4$/gVSin (in 20 days SRT), which is a bit lower than the methane potential obtained in BMP tests (370 and 398 $mLCH_4$/gVS respectively after 50 days). Even so, it is an acceptable production to carry out a continuous co-digestion process considering the high stability of the process. Moreover, although kinetics have not been evaluated in the fed-batch process, Table 2 showed an increase of 20% in the methane yield rate after TH, what is interesting in view of reaching a lower SRT in a continuous reactor; this will lead to an increase in the biogas production per unit of reactor volume.

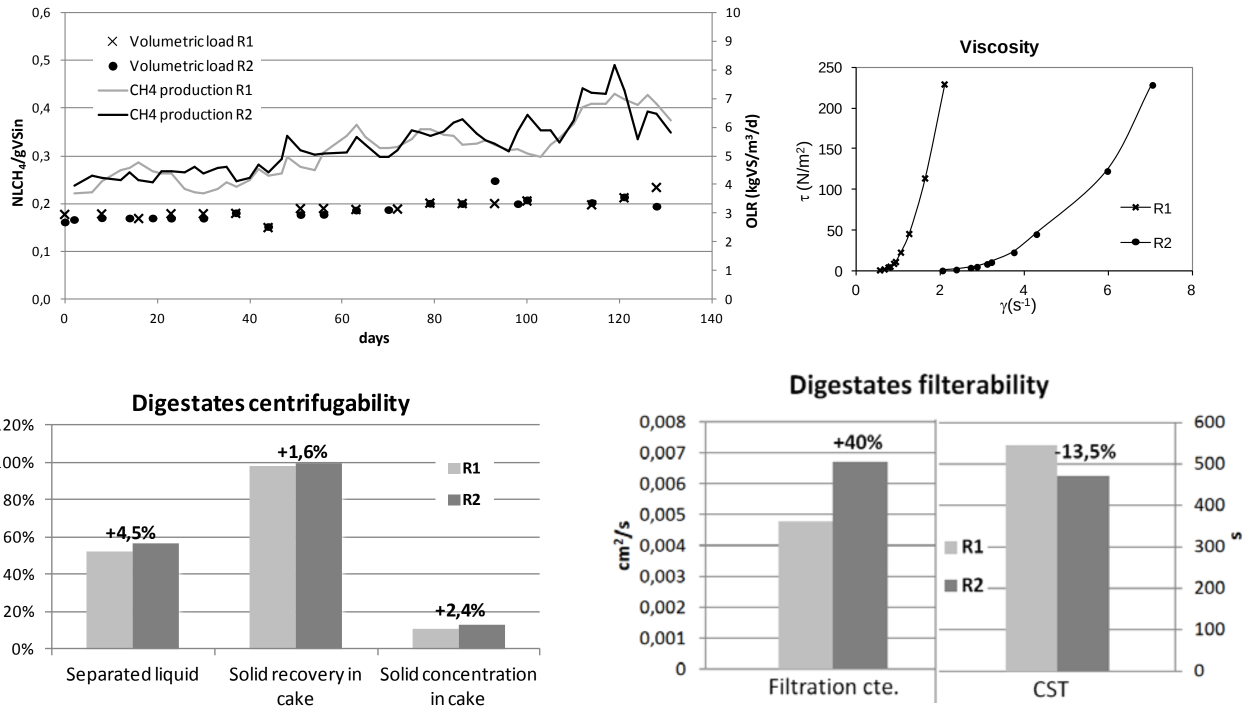

Figure 2. Fed-batch operation results: methane production, organic loading rate. Hydrodynamic parameters results.

Considering the dewaterability and rheological properties from the digestates (*Figure 2*), it is remarkable the high influence that TH presents: filtration constant is 40% higher; capillary suction time decreases 13.5%; and centrifugation is also improved, separating 4.5% more liquid and recovering 1.6% more solids in a 2.4% thicker cake. All these figures result directly in a more energetically efficient dewaterability process with the consequent economical savings: a reduction of $50kg_{biowaste}/t_{digestate}$ will be eluded with TH, what supposes savings of $1.25€/t_{digestate}$ (considering the average landfill tax in Spain: 25€/t). Furthermore, viscosity curves (viscosity corresponds to the slope, which has not a constant value because the non-Newtonian behaviour of these fluids) show that R2 clearly presents a lower viscosity than R1 (approximately 3 times lower). This, in view of a full-scale continuous operation, is an important consideration to facilitate pumping, mixing and avoid operational problems such as blocking or settling and will suppose as well energy savings since mixing and feeding are the main electricity consumers in a digester (Carrère et al. 2010).

According to other reported values from lab-scale semi-continuous reactors, very similar results have been obtained when co-digesting GW and sewage sludge without pretreatment: Silvestre et al. (2011) reached 331 Nm^3CH_4/tVSin for the same SRT but lower GW addition; Davidsson et al. (2008) found a similar production (344 Nm^3CH_4/tVSin) in just 13 days SRT but a lower GW input; Luostarinen et al. (2009) obtained 463 Nm^3CH_4/tVSin when adding 46%VS grease trap sludge from a meat processing plant. It is noteworthy that a more recent study (Noutsopoulos et al. 2013) has doubled these methane yields, reaching 700 Nm^3CH_4/tVSin, in 15 days SRT when adding 60%VS of GW.

Then, despite TH has not presented an improvement in terms of methane production, it leads to important advantages related to dewaterability efficiency (saving 1.25€/$t_{digestate}$) and rheology properties (important energy savings). Moreover, the co-digestion of grease waste and sewage sludge in the same facility eludes the landfill taxes associated to grease waste management. Considering a 500000 equivalent inhabitants WWTP, these savings ascend over 60000€/year (considering a GW production of 7.3kg/person/year in WWTP and without counting FOG wastes from external sources). Therefore, the application of this pretreatment in a co-digestion reactor of grease waste and sewage sludge is an interesting alternative to be considered for a full-scale process.

CONCLUSIONS

- Thermal hydrolysis leads to 29% increase of the methane potential of biological sludge and 43% higher kinetics of grease waste, which also shows a high methane production (489 $NmLCH_4$/gVSin) but a long lag-phase (16 days).
- No synergistic effect of grease and mixed sludge co-digestion was found at the studied mixture ratio (52%VS grease), but the lag-phase was reduced to 4 days.
- The best configuration to implement the thermal hydrolysis to the co-digestion process is pretreating the biological sludge alone, providing 7.5% higher methane production, 20% faster kinetics and no lag-phase. This could be improved if the grease content of the mixture would be lower, since thermal hydrolysis showed higher efficiency on the biological sludge.
- The implementation of this assay in fed-batch reactors resulted in a considerable methane production (363 $NmLCH_4$/gVSin) and thermal hydrolysis improved the rheology and dewaterability properties of the digestate. This leads to important economical savings when combining with co-digestion, reducing final wastes management costs and showing interesting perspectives for full-scale application.

ACKNOWLEDGEMENTS

The work presented has been carried out under the financial support of R+i Alliance and special acknowledgements to Consolider.

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MUNICIPAL SOLID WASTE ANAEROBIC DIGESTION ENHANCEMENT. OPTIMISATION OF PRETREATMENTS CONDITIONS

Chapters 6 and 7 focus on the enhancement of the municipal solid waste anaerobic digestion and the optimization of the pretreatments operational conditions. To that end, different sets of experiments have been performed in BMP lab-scale tests in order to cover a wide range of experimental conditions for different pretreatments and substrates. Chapter 6 deals with ultrasounds and thermal hydrolysis pretreatments to enhance anaerobic digestion of a synthetic mixture of the organic fraction of municipal solid waste (OFMSW). Then, Chapter 7 compiles the trials where thermal hydrolysis optimization of a pre-selected municipal solid waste takes place, where a real MSW is sampled from a MSW treatment plant.

CHAPTER 6. ULTRASOUNDS AND THERMAL HYDROLYSIS PRETREATMENTS TO ENHANCE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE ANAEROBIC DIGESTION

Anaerobic digestion as a treatment of the organic fraction municipal solid waste (OFMSW) is a clean technology based on energy recovery from waste to produce biogas. In order to accelerate the hydrolysis process, two pretreatments (ultrasounds and thermal hydrolysis) were tested in laboratory scale considering a synthetic OFMSW. Biochemical methane potential tests were performed in order to study kinetics and methane potentials and hydrodynamic parameters from digestates were also determined. Ultrasounds were tested at different sonication times and power levels but no improvements were found. Similarly, thermal hydrolysis was tested at four temperature levels for different operation times: while 120ºC resulted in considerable kinetics acceleration (more than double), 6 days lag-phase reduction, reducing biodegradation time to 20 days and achieving high methane production (318 mLCH_4/gVSin); higher temperatures (170ºC) lead to slow biodegradations probably caused by the formation of recalcitrant compounds. Moreover, an improvement of the digestate rheology and dewaterability properties takes place after thermal hydrolysis.

However, it is believed that the fact of considering a synthetic waste which contains high amounts of easily degradable compounds has influenced negatively and overshadowed the effects of pretreatments since the raw mixture already presented an acceptable methane potential and quite favourable kinetics.

Keywords: anaerobic digestion; organic fraction municipal solid waste; pretreatment; thermal hydrolysis; ultrasound

Municipal solid waste anaerobic digestion enhancement by ultrasounds and thermal hydrolysis pretreatments

1. INTRODUCTION

It is considered municipal solid wastes (MSW) those generated in the activities of urban areas, such as homes, offices, shops or other services. In modern societies, the treatment of wastes generated as a result of a high consumption of products has become a significant problem. In the European Union (EU27), it is estimated that each person generates 520 kg of waste per year (Eurostat, 2011), from which the organic fraction constitutes between 35-45% in most of the European countries (Hogg et al., 2002) and a 15% increase of MSW generation between 1995 and 2008 was observed (Gentil et al. 2011). This accounts an overall production over 100 million tonnes of organic wastes in the European Union annually. This problem is due to factors such as the rapid population growth, the concentration of population in the cities or the use of material goods of rapid aging. This situation presents at the same time an opportunity to develop clean technologies based on energy recovery from these wastes, such as anaerobic digestion. Several companies have already invested in these technologies, designed and operated different commercial technologies of MSW anaerobic digesters such as Valorga, Kompogas, Dranco, Arrowbio, Waasa, BTA… (Karagiannidis and Perkoulidis 2009)

Anaerobic digestion is a biological process in which the organic matter is transformed into biogas by the action of specific bacteria in the absence of oxygen. The obtained biogas contains 60-70% methane and is susceptible for energy recovery. In addition, the solid residues of such biogas production can be used as low-grade fertilizers (Hilkiah Igoni et al. 2008). For example, two *Cambi* plants in Norway (Lillehammer and Ecopro) have received permits to use the bio-fertilizer in the agricultural sector and also for land remediation purposes (Sargalski, 2008). The anaerobic digestion process consists in several consecutive steps of biological processes. Thus, the degradation rate of the overall process is limited by the slowest step, in this case the hydrolysis (especially when dealing with solid wastes). Hydrolysis is the first stage in which complex organic matter (proteins, lipids, and carbohydrates) becomes simple soluble matter (amino acids, sugars, fatty acids) more easily assimilated by bacteria in further steps. Therefore, this stage is crucial for the whole process success and for a fast and profitable biogas generation. Then, it is desirable to accelerate and improve the hydrolysis process by pretreatment technologies. These technologies are based on the solubilisation of organic matter by mechanical processes: grinding (Izumi et al. 2010), ultrasounds (Cesaro et al. 2012)**,** microwaves (Shahriari et al. 2012); chemicals: reagents such as NaOH, HCl (López Torres and Espinosa Lloréns 2008); thermal processes: high temperature (Liu et al. 2012) and high pressure (Cuetos et al. 2010); or biological: enzymatic treatment (Fdez.-Güelfo et al. 2011). Pretreatments can also deal with some other problems that take place in anaerobic digesters such as mixing problems, by reducing viscosity, or digestate minimization, by enhancing dewaterability (Neyens and Baeyens 2003).

All these pretreatment technologies have been widely tested with sewage sludge (Pérez-Elvira et al, 2006) and even applied in full-scale continuous processes (such as *Cambi)* in several biosolids plants (Román et al, 2007). Nevertheless, in the area of OFMSW they have hardly been studied and need further research for its implementation in MSW treatment plants. The optimisation of the operating conditions and an evaluation of the efficiency of these techniques at lab-scale is therefore the first stage to assess the potential of each pretreatment.

The aim of this study is to evaluate the effect of two of these pretreatments (ultrasounds and thermal hydrolysis) in the anaerobic digestion process of OFMSW in a laboratory scale by the application of BMP tests. It is also desirable to carry out an optimization of the operational conditions of both pretreatments and evaluate the influence that these pretreatments have on the hydrodynamic properties. Hence, the better pretreatment with its optimal conditions could be selected to a further pilot scale study in order to be finally implemented in a full scale plant with a proper economical and energetic feasibility study.

2. MATERIALS AND METHODS

3.1 Substrate characterization

The substrate used in the tests is synthetically reconstituted solid waste, which pretends to represent the organic fraction municipal solid waste (OFMSW) from real plants. It is composed of a mixture of basic foods in a certain proportion as their presence in household waste, according to real composition data provided by Urbaser. The fact of using a synthetic waste assures a constant composition of the substrate for all the experiments, avoiding external variations. In fact, a reconstituted waste has already been used with similar purposes in other studies to simulate a real waste (Boulanger et al. 2012). After some initial trials, it was decided to reduce its size till 1-2 cm bits in order to facilitate the operation in lab-scale equipment, although full-scale plants use to shred it till 3-4 cm (Sargalski, 2007).

The full characterization of the substrate is presented in *Table 1*: it has a high content of organic matter (96% of the total solids are volatile) and soluble organic matter (over 60% soluble COD). Among the macroscopic characterization, it is remarkable the low fibre and grease content and the high amount of carbohydrates and starch.

TS	g/kg	109.9
VS	g/kg	105.1
CODt	g/kg	150
CODs	g/kg	91.8
TKN	N-g/ kg	3.79
NH_4^+	N-g/ kg	0.82
Grease	g/kg	2.68
Carbohydrates	%	6.28
Starch	%	3.44
Fibre	%	0.82
Proteins	%	2.43
C/N	g/g	21.1

Table 1. Substrate characterization
(TS, VS: total and volatile solids; CODt, CODs: total and soluble chemical oxygen demand; TKN: total Kjeldahl nitrogen; NH_4^+: ammonium)

3.2 Pretreatment equipment

Two disintegration technologies were studied: thermal hydrolysis and ultrasounds. Its selection was based on COD solubilisation, increase in biogas production, pathogen reduction and dewaterability, as well as the availability to carry out the test at lab-scale. Next, a brief description of the equipments is enclosed:

- Thermal hydrolysis: The hydrolysis plant (home-built) is made up with a 2L reactor connected to a flash tank by a decompression valve. The reactor, which is fed with a substrate in a batch mode, is heated with steam and supports high pressures (10 bar). The flash tank is an open-air 5L vessel where the steam explosion takes place after the hydrolysis reaction time has elapsed. Temperature and pressure are manually controlled by the steam injection.
- Cavitations by ultrasounds: The ultrasound homogenizer - *Hielscher UIP 1000 hd, 20 kHz* - converts electrical energy in mechanical vibrations (ultrasounds), which are transmitted to the sample by a sonotrode. The equipment has a nominal power of 1kW and works as well in batch mode. The sample is introduced in a 250 mL stainless steel cell where the sonotrode is completely immersed. It has a water jacket as refrigeration system to control the temperature inside the cell. The power input can be set and the reaction time has to be controlled manually.

3.3 Biochemical Methane Potential tests

The BMP tests were performed following an internal protocol based on standardized assays for research purposes (Angelidaki et al., 2009). In 2L glass bottles, 150 mL of inoculum were introduced in each reactor and the substrate was added according to a substrate-inoculum ratio of 1:1 in terms of VS. The incubation temperature was 35ºC and reactors were stirred in a rotary shaker. The inoculum was mesophilic digested sludge from a waste water treatment plant and was pre-incubated for 2 days at 35ºC. Periodical monitoring analyses (every 2-3 days) of biogas production by pressure meter (*IFM Electronics*, PI-1696) and biogas composition by gas chromatography (*Varian 3800*, sample uptake with a 100µL *Hamilton* syringe) were performed during the tests. Methane potentials are expressed as average values of the net volume of methane per gram of initial substrate VS content.

3.4 Modelling

The Modified Gompertz equation (Lay et al., 1997), next presented in equation (1), was considered in order to fine-tune the experimental data from BMP tests to a theoretical equation:

$$B = P \times exp\left\{-exp\left[\frac{R_m \cdot e}{P}(\lambda - t) + 1\right]\right\} \tag{1}$$

The model has three parameters: the kinetic parameter (R_m) which indicates the initial slope of the curve ($mLCH_4/gVS/d$), the maximum biogas production (P) expressed as $mLCH_4/gVS$ and the lag-phase (λ), in days. B is the calculated methane production ($mLCH_4/gVS$) for time *t*. The model fine-tuning to the experimental data was achieved by least squares methodology, by minimising the next objective function (2):

$$OF(\varphi) = min \sum_{t=1}^{N} \left(B_{exp}(t) - B_m(t, \varphi)\right)^2 \tag{2}$$

where B_{exp} is the consumption velocity obtained from measurements (plotted in BMP results graphs as points), B_m is the corresponding velocity calculated by the model (plotted with continuous curves) and N is the number of measurements. The correlation factor (R^2) was then calculated to assess the accuracy of the model with respect to the experimental data.

3.5 Analytical methods

Substrates characterization was partially performed in the University of Valladolid, following an internal protocol based on Standard methods (Apha, 2005) to determine the next parameters: TS, VS (total and volatile solids); CODt, CODs (total and soluble chemical oxygen demand); TKN (total Kjeldahl nitrogen); NH_4^+ (ammonium). The other parameters were determined in an external laboratory: grease (EPA Method 1664), carbohydrates (CE Regulation 152/2009), fibre content (Weende, CE Regulation 152/2009), proteins (IT-MA-014, AOAC Official Method) and elemental content (IT-MA-014, AOAC official method).

3.6 Hydrodynamic tests and solubilisation

Solubilisation factors (SF) were determined after pretreatments to quantify the increase of soluble matter which takes place for each treatment condition, which is calculated as the % increase of solubleCOD/totalCOD.

To assess the dewaterability and hydrodynamic properties of the digested samples, filterability, centrifugability and rheology tests were performed following an internal method established from the experiments in sludge characterization in the *Department of Chemical Engineering and Environmental Technology,* at the *University of Valladolid* (Donoso-Bravo et al. 2011). These tests were very relevant in terms of assessing the impact on mixing requirements, digestate dewaterability and handling properties. *Filterability*, defined as the viability of sludge to flow through a filter, is measured by forcing the sludge to pass through a filter under a 1 bar pressure. The filtration constant (*FC*) was calculated as a ratio of the slope from plotting filtrate volume (V^2) versus filtration time and the area of the filtering paper. *Capillary suction time* (CST) was measured to evaluate digestate dewatering behaviour: a long CST means a high cake specific resistance. The CST was determined using a Triton Electronics Ltd. (Type 319) and Whatman No. 17 filter paper. *Centrifugability* assesses the liquid and solid phase separation after 5 minutes centrifugation at 5000 rpm. After measuring the separation performance and determining the suspended solids concentration in the supernatant phase, the next parameters are calculated: % separated liquid, % solid recovery in cake and solid concentration in cake (%TS). *Rheology* is evaluated by viscosity curves, as the slope from plotting the shear stress (τ, N/m^2) versus the turning speed frequency of the spin (γ, s^{-1}) obtained with a *Brookfield Digital Viscometer DV*-I. Since digestates are not a Newtonian fluid, there is not a constant value of the viscosity, so the curves have to be evaluated.

3.7 Statistical analysis

All BMP tests were carried out by triplicates. The experimental methane productions are always referred to average values and standard deviations are calculated, enclosed and represented in BMP graphs with vertical lines. For the hydrodynamic tests, duplicates were measured and the results were averaged. ANOVA analyses have been also performed to study the significance degree of the interrelation between different parameters from experimental data.

3.8 Experimental design and procedures

Ultrasounds tests: 200 g of fresh OFMSW are directly placed in the cell where the sonotrode is introduced, remaining the latest at 1-2cm from the bottom of the cell. No water is added to avoid dilution and no stirring takes place. Substrate was subjected to a sequence of trials in which two operation parameters were varied: sonication time and power. Sonication time was manually controlled for each batch, covering a wide range of values: 5, 15, 30, 60 minutes. Power was set at 2 levels for each sonication time: full power efficiency (equivalent to 250W) and 70% (equivalent to 150W). Thus, a total of 7 pretreated samples (pretreatment to the sample with lowest time and power was not possible to be performed) and a raw one without pretreatment were tested (*Table 2*). Energy input in the pretreatment is calculated directly multiplying the power consumption and the sonication time. It is expressed as kJ/kgTS and ranges between 3400-41000 kJ/kgTS, similar as the sludge values reported by Pilli et al. (2011).

Thermal Hydrolysis tests: 250 g of fresh OFMSW were introduced in each trial in the hydrolysis reactor (after a preheating stage with steam). Then, steam is introduced to reach the desired temperature (4 levels: 70, 120, 150, 170ºC) reaching respective pressures 1, 2, 5 and 8 barg. After the hydrolysis time is elapsed (ranging from 2 to 30 minutes), steam injection stops and a sudden decompression takes place in the flash tank (steam explosion) when opening the decompression valve. Different combinations of temperature and time were tested (*Table 2*) according to typical values from literature (Carrère et al. 2010) and trying to cover a wide range of operation conditions, with an overall of 11 pretreatment conditions plus a raw sample without pretreatment. Experiments for the lowest temperature (70ºC) were not able to be performed because the low pressure level attained and just the results for the highest hydrolysis time were obtained. The energy input is estimated theoretically according to the equation of Ringoot (2012), where a typical thermal hydrolysis energy integrated plant is considered (recovery of heat from the flash vapours in a preheating stage). This way, the steam consumption is calculated, which is directly related to the energy demand of the pretreatment (also expressed as kJ/kgTS and estimated theoretically according to Ringoot 2012).

ULTRASOUNDS			
Sample	**Time** min	**Power** W	**Energy input** kJ/kgTS
Raw	0	0	0
1	5	250	3400
2	15	150	6100
3	15	250	10200
4	30	150	12300
5	30	250	20500
6	60	150	24600
7	60	250	41000

THERMAL HYDROLYSIS			
Sample	**Temperature** ºC	**Time** min	**Energy input*** kJ/kgTS
Raw	-	0	0
1	70	30	1900
2	120	5	4820
3	120	10	4820
4	120	15	4820
5	120	20	4820
6	150	5	4780
7	150	10	4780
8	150	20	4780
9	170	2	4770
10	170	15	4770
11	170	30	4770

Table 2. Experimental design and energy consumption

3. RESULTS AND DISCUSSION

4.1 Ultrasounds tests

Figure 1 shows the aspect of the samples after ultrasound pretreatment. In all of them the pieces of the original residue can be appreciated, what shows that the pretreatment did not change substantially the particle size of the sample.

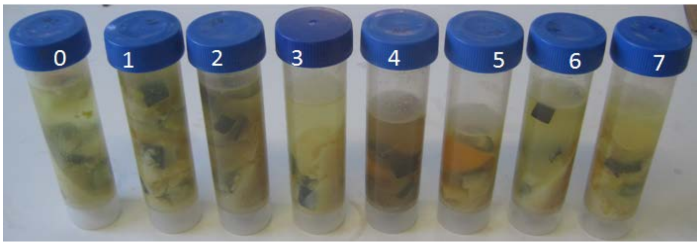

Figure 1: Samples after ultrasound pretreatment

BMP tests were carried out for all these samples during 60 days and the data have been plotted in *Figure 2* showing the evolution of the cumulative methane production and the modelling curves. In all the graphs, the non-pretreated sample is represented with a discontinuous line to compare it with the pretreated samples. *Table 3* shows the parameters obtained by the model fitting and the influence of the pretreatment respect to the raw sample. For the lowest sonication times (5 and 15 minutes, samples 1 to 3), ultrasounds do not show significant effects: favourable kinetics (R_m close to the raw sample) and very similar final methane yields (around 300mLCH_4/gVSin) were obtained. For intermediate time (30 minutes) and higher power (sample 5), kinetic rate improves over 50% the non-pretreated sample one, but final methane production is 15% lower. However, at low power level (sample 4), a lag-phase of 18 days appears, leading to a very slow biodegradation. At higher times (60 minutes) and low power level (sample 6), ultrasounds do not produce improvements, and at high power (sample 7) a considerable lag-phase (12 days) takes place again. It is noteworthy that, in this case, the lag-phase phenomenon coincides with the most aggressive conditions of pretreatment. Finally, from all these tests, the only one whose methane potential slightly exceeds the raw sample one (no significant increase) is the sample that was sonicated for the shortest time (5 minutes, sample 1), what shows that time is not a critical factor, although too long sonication times could favour slow degradations (samples 4 and 7). These slow degradation phenomena could occur because the formation of some non-easily degradable compounds by the effect of high temperatures that takes place during long sonication times in the surroundings of the sonotrode. This behaviour was also observed by Cesaro et al. (2012) when sonicating a mixture of sludge and OFMSW, stating that a disinfection effect could take place or recalcitrant compounds could be formed by high temperatures. This event will be deeper discussed in the next section of thermal hydrolysis tests, where the formation of such refractory compounds has been more evident.

Analyzing the organic matter solubilisation - solubilisation factors (SF) enclosed in *Table 3* - it follows that the major solubilisation is given for samples 4 and 7 (SF 25 and 27% respectively), which are precisely those trials that showed slow biodegradations. Therefore, a high solubilisation after ultrasounds pretreatment can be a sign of low degradation in BMP results. Otherwise, a null solubilisation factor, such as the sample 1, has resulted in an assay with acceptable kinetics and no lag-phase. In general, excluding these three samples, solubilisation factors reach very similar values (average of 9%) as those reported by Elbeshbishy and Nakhla (2011) and Cesaro and Belgiorno (2013) when sonicating food waste at 5000kJ/kgTS and over 15000kJ/kgTS respectively. On the other hand, no correlation was found between the solubilisation factor, the methane production and the energy input.

In view that the ultrasounds did not offer promising results in view of improving OFMSW anaerobic digestion and due to the solid nature of the sonicated samples, hydrodynamic tests were not performed to these samples.

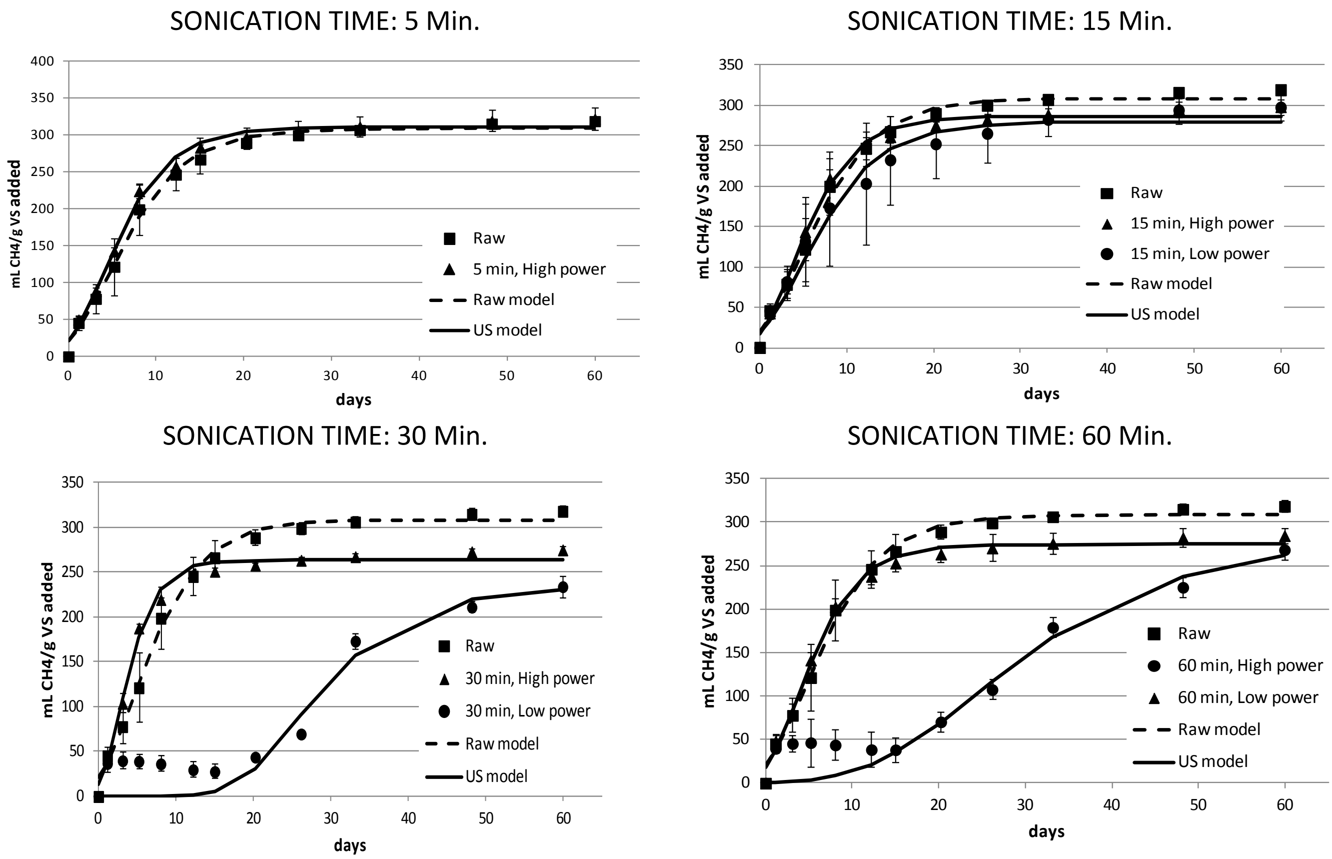

Figure 2: BMP tests evolution of sonicated samples

US samples			SF	Gompertz parameters				% increase		lag-phase reduction
Code	**Time** min	**Power** W	%	**P** $mLCH_4/gVS$	**R_m** $mLCH_4/gVS/d$	**λ** d	**R^2** -	**P** %	**R_m** %	days
Raw	0	0	0	308.1	23.9	0.00	0.994	-	-	-
1	5	250	0	310.7	27.7	0.00	0.992	0.8	15.8	0.0
2	15	150	12.4	279.3	20.9	0.00	0.977	-9.3	-12.7	0.0
3	15	250	12.7	286.4	27.4	0.12	0.994	-7.1	14.6	-0.1
4	30	150	24.8	234.0	10.9	17.9	0.961	-24.1	-54.6	-17.9
5	30	250	5.2	263.4	37.5	0.25	0.991	-14.5	56.8	-0.3
6	60	150	8.2	274.4	26.7	0.00	0.993	-10.9	11.5	0.0
7	60	250	27.0	279.7	7.9	11.6	0.964	-9.2	-66.9	-11.6

Table 3: Results of ultrasounds tests (SF: solubilisation factors)

4.2 Thermal Hydrolysis tests

The appearance of the different hydrolyzed samples (*Figure 3*) differs considerably to ultrasound ones. First, it is remarkable the homogeneity of pretreated samples. Pieces of waste are no longer observed, so that crushing of the residue has been complete. On the other hand, the dark colour of samples 9, 10 and 11 is remarkable and corresponds to the highest hydrolysis temperature: 170°C. These brown samples also came with a burnt or caramelized smell, possibly generated by the application of high temperatures.

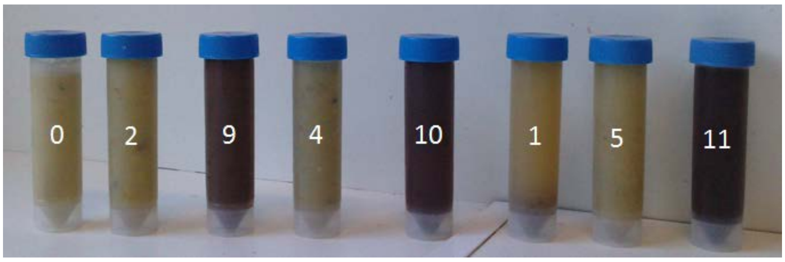

Figure 3: Samples after thermal hydrolysis pretreatment

Figure 4 compiles all BMP results grouped by different hydrolysis temperature. In all of them, the non-pretreated sample (discontinuous line) is represented to compare it with the pretreated samples (continuous lines). Modelling parameters, solubilisation factors and increases are referred in *Table 4*. First, it is especially remarkable that the raw sample in this test presents different results in comparison to the ultrasounds test: in spite of a quite similar final methane production (308.1/308.7 $mLCH_4$/gVSin), the profile of the curve in this case did not follow anymore a first order kinetic, its kinetic rate halved (from 24 to 12 $mLCH_4$/gVS/d) and a lag-phase of 6.5 days grew up. However, since triplicates from BMP worked perfectly (relative standard deviations below 3.2%), this results were assumed as correct to be compared with pretreated samples. In fact, this is a common BMP curve for an heterogenic substrate that contains different fractions of organic matter, which have different individual methane yields and kinetic rates, showing a very similar profile as the one obtained with kitchen waste by Ma et al. (2011).

Concerning BMP tests, the sample at the lowest hydrolysis temperature (70ºC, sample 1) presents a fast kinetic initially, doubling the initial rate of the non-pretreated sample. However, after 10 days its biogas production stabilizes in a rather scarce value: 181 $mLCH_4$/gVSin. For intermediate temperatures (120°C) and hydrolysis times over 10 minutes (samples 3, 4 and 5), the curves show satisfactory results with very similar trends: fast kinetics (kinetic rates around 25-30 $mLCH_4$/gVS/d, more than doubling the raw one), no lag-phase and final methane productions over 300 $mLCH_4$/gVSin. Nevertheless, for lower hydrolysis times (5 minutes, sample 2) and same temperature, the curve shows a slower and lower methane production (22% less methane production than the raw sample). Therefore, times over 10 minutes for 120ºC are more favourable and can enhance the anaerobic digestion kinetics considerably, reducing the digestion time below 20 days with double methane yields (over 300$mLCH_4$/gVSin) respect to the raw sample. For the temperature 150ºC, no significant results are deduced, since the curves show very similar trends as the raw one. All their methane potentials are close to 300 $mLCH_4$/gVSin and no significant kinetics rates increase. Higher temperatures (170°C) have caused important decreases on the biodegradation in all cases, especially for the longest hydrolysis time (15 and 30 minutes, samples 10 and 11) for which long lag-phases are observed (12 and 31 days respectively) and low methane yields are obtained. In the case of the shortest hydrolysis time for this temperature conditions (170ºC, 2 minutes, sample 9), this behaviour is not so pronounced, following a very similar pattern as the raw sample but with a 10% less methane production. This fact could be due because not enough hydrolysis time elapsed to appreciate the effect of the temperature. In all these cases, the tests have lasted much longer (up to 80 days) in order to obtain the final methane yields.

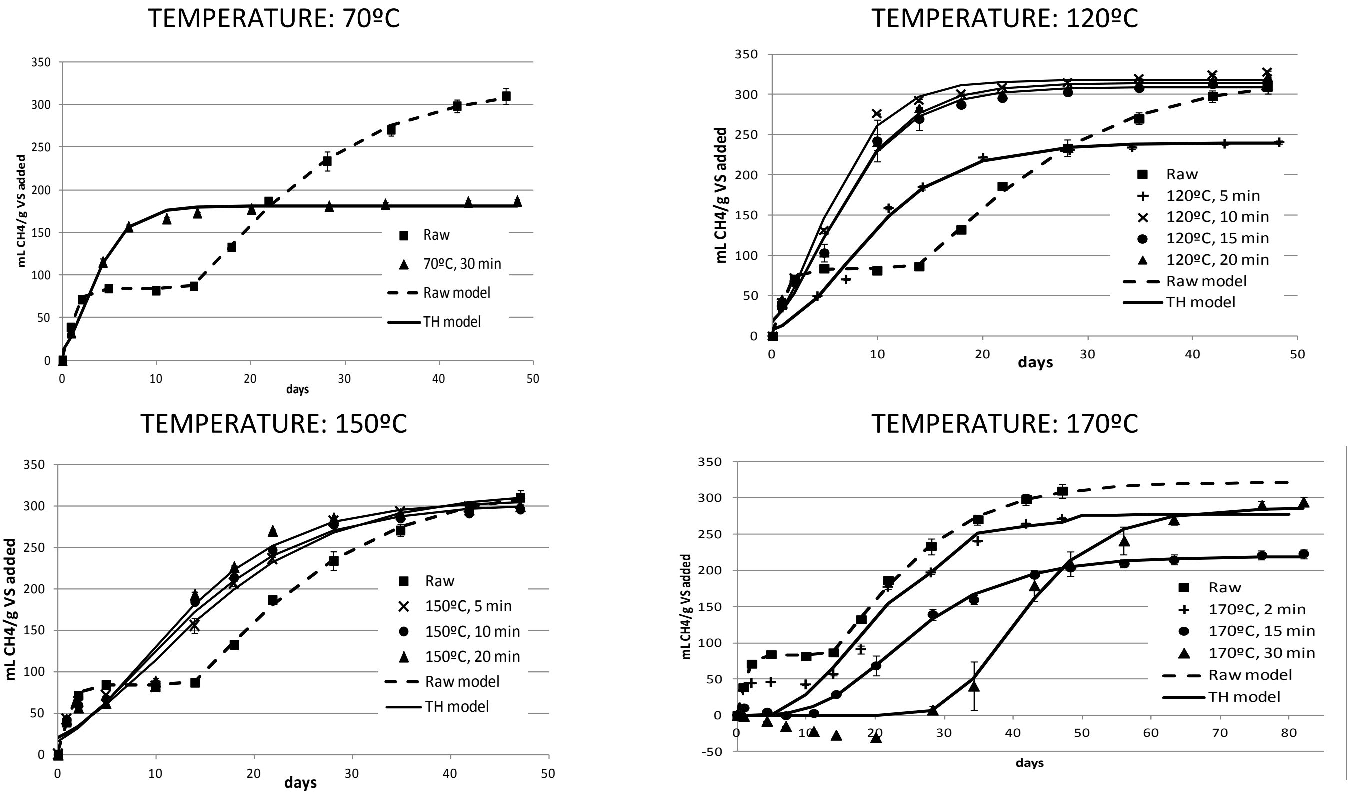

Figure 4: BMP tests evolution of thermally hydrolysed samples

TH samples			SF	Gompertz parameters				% Increase		lag-phase reduction
Code	T ºC	Time min	%	P mLCH$_4$/gVS	R_m mLCH$_4$/gVS/d	λ d	R^2 -	P %	R_m %	days
Raw	-	0	0	308.7	11.9	6.57	0.997	-	-	-
1	70	30	0	180.9	28.3	0.11	0.991	-41.3	137.3	6.5
2	120	5	2.4	239.7	15.8	1.34	0.989	-22.2	32.3	5.2
3	120	10	32.0	318.4	31.5	0.24	0.992	3.4	164.5	6.3
4	120	15	45.1	308.5	25.6	0.17	0.992	0.2	114.7	6.4
5	120	20	14.5	313.9	25.7	0.10	0.991	1.9	115.9	6.5
6	150	5	51.2	317.6	11.5	0.00	0.979	3.1	-3.6	6.6
7	150	10	39.5	303.4	12.5	0.00	0.978	-1.5	4.6	6.6
8	150	20	44.8	307.1	13.9	0.61	0.976	-0.3	16.7	6.0
9	170	2	51.3	277.2	46.4	5.43	0.967	-10.0	289.9	1.1
10	170	15	39.4	219.1	8.2	11.7	0.997	-28.9	-31.3	-5.2
11	170	30	51.5	287.3	13.3	30.7	0.992	-6.7	11.6	-24.1

Table 4: Results of thermal hydrolysis tests (SF: solubilisation factor)

Solubilisation factors (SF) were also determined (*Table 4*). Higher solubilisation of the organic matter took place after thermal hydrolysis than ultrasounds (average SF 34% versus 9% respectively), as it was also observed by Bougrier et al. (2006) with similar reported values. Moreover, there is a correlation between the hydrolysis temperature and solubilisation factors (ANOVA analysis has lead to an F value of 323 versus a critical F value of 4.96), as it was also found by Bougrier et al. (2008) and Donoso-Bravo et al. (2011) working with sludge: the higher the temperature, the factor becomes greater. However, as for ultrasounds, solubilisation factors do not show a direct influence in BMP results and no correlation was found to link them, the same way as in Ma et al. (2011) experiences.

It should be also noted that the samples subjected to the highest temperatures (170°C), coincide with the tins in photo 9, 10 and 11 (*Figure 3*), which happened to be those with dark brown colours. Therefore, it can be hypothesized that under these operating conditions some kind of brown coloured recalcitrant compounds, such as melanoidins, are generated. Melanoidins, which are less readily biodegradable refractory substrates, are produced by Maillard reactions (Wang et al. 2011), whereby long-chain sugars may form such compounds by the effect of high temperature. This kind of phenomenon has been studied since time ago related with thermal processes (Stuckey and McCarty 1984) and can also be associated with other pretreatment technologies such as microwaves (Shahriari et al. 2012) where high temperatures are also reached. In fact, Liu et al. (2012) found evidence of melanoidins in very similar conditions, when pretreating kitchen waste and vegetable and fruit residue thermally at 175ºC for 60 minutes. In the area of sludge, Dwyer et al. (2008) studied how to reduce the temperature of the pretreatment to avoid the formation of such compounds, dropping it down from 170ºC to 140ºC without significant impact on its biodegradation. Wilson and Novak (2009) impute the formation of recalcitrant matter over 220ºC to the caramelization of starch (polysaccharide hydrolysis), which is certainly the main mechanism in the present study due to the high content of starch and carbohydrates that the synthetic OFMSW has (3.44% and 6.28% respectively).

Hence, after the analysis of BMP results, the pretreatment conditions that seem to be the optimum ones are 120ºC and 10 minutes. On the other hand, from the two studied variables, hydrolysis time did not play such an important role in the pretreatment as temperature did. The reason for this could be linked to the important effect of the high pressure decompression that takes place in the flash independently of the hydrolysis reaction time.

Hydrodynamic tests

The hydrodynamic results obtained for some of the digested samples (not performed for all of them) after being subjected to thermal hydrolysis are shown in *Table 5*:

- **Centrifugability**: liquid separation is higher in all the pretreated samples, especially for the highest temperature (170°C), exceeding 80%. The recovery of solids in the cake is quantitative, exceeding in any case 90%, except the non-hydrolysed sample. Finally, the solid cake concentration generally ranges from 10 to 15%. The results also show that the centrifugation is able to separate most of the solids of the digestate, generating a thickened sludge with more than 15% solids.

- **Filtration constant**: it is observed that all pretreated samples again improve the filtration capacity of the non-pretreated one. The sample 11 has the best properties to be filtered, which was pretreated at the highest temperature and time.

- **Capillary Suction Time (CST)**: in this case a higher CST indicates worst hydrodynamic properties. Again, the results are more favourable with the most aggressive pretreated samples.

- **Viscosity**: the results (curves not shown) indicate that the raw sample is the most viscous and sample 11 is less viscous. This is consistent with the trend of other results and it is important to consider if, after anaerobic digestion, the digested waste must be handled. A lower viscosity reduces considerably the cost of pumping and mixing and avoids operational problems such as blockages, accumulations...

SAMPLES			CENTRIFUGABILITY			FILTRATION	
Code	T (ºC)	Time (min)	% Separated liquid mass	% Solid recovery in cake	% Solid concentration in cake	Filtration constant (m^2/s)	CST (s)
Raw	-	0	62.2	86.3	12.0	10	1440
1	70	30	70.4	98.5	12.2	50	454
2	120	5	68.8	97.3	12.0	37	615
4	120	15	71.3	96.5	11.7	33	498
5	120	20	74.8	95.0	11.6	66	426
9	170	2	74.6	94.1	13.7	53	542
10	170	15	78.1	94.3	13.7	49	549
11	170	30	85.7	97.1	16.8	131	342

Table 5: Hydrodynamic tests results for hydrolysed samples

The technique which appears best suited to separate solid and liquid fractions of the digestate is centrifugation, providing a thickened biowaste of 15%TS with more than 95% recovery of solids. The best hydrodynamic properties are linked to the most aggressive hydrolysis pretreatment, due to a greater dilution of the sample by steam, what means higher energy consumption. However, all samples subjected to thermal hydrolysis pretreatment have improved their hydrodynamic properties respect the non-pretreated sample. This means that thermal hydrolysis, whichever the operational conditions, will benefit the dewaterability and rheology of digestates.

Final considerations

Finally, it can be said that thermal hydrolysis has lead, for certain operational conditions (120ºC), to great kinetics improvements in BMP tests, but a low final methane yield increase, in contrast with other studies in which, for example, the final methane yield of sewage sludge from WWTP could be enhanced by 40% at 170ºC (Perez-Elvira et al. 2010). This could be due to the fact that the synthetic OFMSW in this study do not behave as sludge, since it is composed by high amounts of easily degradable sugars (high content of starch and carbohydrates), which are always exposed to bacteria to be degraded with enough time. In fact, Lissens et al. (2004) state that pretreatments effects are usually lower for highly biodegradable wastes. In the contrary, lignocellulosic wastes or with cellular material content (such as biological sludge) are more susceptible to be efficiently pretreated (Carlsson et al. 2012).

4. CONCLUSIONS

Ultrasounds have not generated improvements in either the methanogenic potentials or the kinetic rates of the OFMSW biodegradation. However, thermal hydrolysis has played an essential role in improving kinetics. Among the studied parameters, the hydrolysis time has not presented a great influence but the hydrolysis temperature is critical: while intermediate temperatures (120°C) can improve kinetics (more than double) reducing biodegradation time to 20 days and achieving high methane productions (318 $mLCH_4/gVSin$), higher temperatures (170°C) lead to slow biodegradations probably caused by the formation of recalcitrant compounds. Moreover, digestate properties (viscosity, dewaterability) are improved for all thermally hydrolysed samples.

5. ACKNOWLEDGEMENTS

The presented work has been carried out under the financial support of URBASER with the project *Topbio-Innpacto* and FEDER funds.

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CHAPTER 7. THERMAL HYDROLYSIS PRETREATMENT OPTIMIZATION TO PRE-SELECTED MUNICIPAL SOLID WASTE

According to the previous tests, a further study is now developed to check the effect of pretreatments in a more real waste (just thermal hydrolysis here considered because its higher efficiency from previous tests). Thus, a real MSW from a municipal plant is sampled and, after a pre-selection and cleaning of the organic fraction, it is subjected to a set of experiments where thermal hydrolysis is studied in lab-scale. This chapter compiles the trials where thermal hydrolysis optimization of a pre-selected municipal solid waste takes place. Thermal hydrolysis as a pretreatment to enhance pre-selected MSW anaerobic digestion has resulted a useful and efficient technology not only to increase methane production in the digester (by 30%) and kinetics (by 70%), but also to improve rheological properties and dewaterability, reducing associate costs of the process such as pumping and mixing requirements or digestate management costs. These results show that the effect of thermal hydrolysis in a real MSW is much stronger as for the synthetic OFMSW, as it was suspected. The main responsible mechanism of this fact is thought to be the higher fibre content and lower easily degradable sugars contained in the real pre-selected MSW, what reduces the availability of organic compounds when no pretreatment is applied. The optimum conditions to carry out the pretreatment are set at 15 minutes hydrolysis time at 150ºC, which are below the typical values reported for sewage sludge.

Keywords: anaerobic digestion, pre-selected municipal solid waste, pretreatment, thermal hydrolysis

Thermal hydrolysis optimization of a pre-selected municipal solid waste

INTRODUCTION

In the present study, thermal hydrolysis (TH) pretreatment is applied to a real municipal solid waste (MSW) from a full-scale municipal plant. The aim of the study is the optimization of the operating conditions for TH pretreatment, testing the effects on the MSW methane potential and on the hydrodynamic properties of the pretreated and digested waste.

MATERIALS AND METHODS

Substrate characterisation

The MSW, after being subjected to a separation process (by hand) to remove the bigger inorganic fractions, presents the next characterisation (determined following *Standard Methods APHA 2005*):

TS	VS	VS/TS	COD	TKN	Grease	Inorganics
g/kg	g/kg	%	g/kg	g/kg	g/kg	%
351.4	246.0	70	332.5	5.35	21.01	10

Table 1. Waste characterisation

Inorganics characterisation:

Fractions	%
Plastic	35.8
Glass	53.8
Others	10.5

The reason for which the inorganic fraction was separated previously to TH pretreatment is to avoid bulky materials in the reactor that could cause blockages in pipes rising the risk during the operation at high pressure. It has to be mentioned that in a full-scale plant it would not be necessary this previous cleaning since the blockage risk is lower because the bigger size of the plant, but it would be recommendable to increase the organic fraction content of the waste and avoid the accumulation of inert materials in the reactor.

Equipment

Pretreatment: Thermal Hydrolysis (TH)

The hydrolysis plant (home-built) is made up with a 2L reactor connected to a flash tank by a decompression valve. The reactor, which is fed with a substrate in a batch mode, is heated with steam and supports high pressures (up to 10 bar). The flash tank is an open-air 5L vessel where the steam explosion takes place after the hydrolysis reaction time has elapsed. Temperature and pressure are manually controlled by the steam injection.

Biochemical Methane Potential tests

The BMP tests were performed following an internal protocol based on standardized assays. In 2L glass bottles, 150mL of inoculum were introduced in each reactor and the substrate was added according to a substrate-inoculum ratio of 1:1 in terms of VS. The incubation temperature was 35ºC and reactors were stirred in a rotary shaker. The inoculum was mesophilic digested sludge from a waste water treatment plant and was pre-incubated for 2 days at 35ºC. Periodical monitoring analyses (every 2-3 days) of biogas production by pressure meter (*IFM Electronics*, PI-1696) and biogas composition by gas chromatography (*Varian 3800*, sample uptake with a 100µL *Hamilton* syringe) were performed during the tests. Methane potentials are expressed as average values of the net volume of methane per gram of initial substrate VS content.

Modelling

The Modified Gompertz equation, next presented in equation (1), was considered in order to fine-tune the experimental data from BMP tests to a theoretical equation:

$$B = P \times exp\left\{-exp\left[\frac{R_m \cdot e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

The model has three parameters: the kinetic parameter (R_m) which indicates the initial slope of the curve ($mLCH_4/gVS/d$), the maximum biogas production (P) expressed as $mLCH_4/gVS$ and the lag-phase (λ), in days. B is the calculated methane production ($mLCH_4/gVS$) for time *t*. The model fine-tuning to the experimental data was achieved by least squares methodology, by minimising the next objective function (2):

$$OF(\varphi) = min\sum_{t=1}^{N}\left(B_{exp}(t) - B_m(t,\varphi)\right)^2 \quad (2)$$

where B_{exp} is the consumption velocity obtained from measurements (plotted in BMP results graphs as points), B_m is the corresponding velocity calculated by the model (plotted with continuous curves) and N is the number of measurements. The correlation factor (R^2) was then calculated to assess the accuracy of the model with respect to the experimental data.

Hydrodynamic tests and solubilisation

Solubilisation factors (SF) were determined after pretreatments to quantify the increase of soluble matter which takes place for each treatment condition, which is calculated as the % increase of solubleCOD/totalCOD.

To assess the dewaterability and hydrodynamic properties of the digested samples, filterability, centrifugability and rheology tests were performed following an internal method established from the experiments in sludge. These tests were very relevant in terms of assessing the impact on mixing requirements, digestate dewaterability and handling properties. *Filterability*, defined as the viability of sludge to flow through a filter, is measured by forcing the sludge to pass through a filter under a 1 bar pressure. The filtration constant (*FC*) was calculated as a ratio of the slope from plotting filtrate volume (V^2) versus filtration time and the area of the filtering paper. *Capillary suction time* (CST) was measured to evaluate digestate dewatering behaviour: a long CST means a high cake specific resistance. The CST was determined using a Triton Electronics Ltd. (Type 319) and Whatman No. 17 filter paper. *Centrifugability* assesses the liquid and solid phase separation after 5 minutes centrifugation at 5000 rpm. After measuring the separation performance and determining the suspended solids concentration in the supernatant phase, the next parameters are calculated: % separated liquid, % solid recovery in cake and solid concentration in cake (%TS). *Rheology* is evaluated by viscosity curves, as the slope from plotting the shear stress (τ, N/m^2) versus the turning speed frequency of the spin (γ, s^{-1}) obtained with a *Brookfield Digital Viscometer DV*-I. Since digestates are not a Newtonian fluid, there is not a constant value of the viscosity, so the curves have to be evaluated.

Experimental design

It is desired to study in the process 2 variables at 3 levels:

- Temperature: 133, 150, 170ºC
- Time: 5, 15, 30 minutes

These levels have been selected according to different considerations:

- Temperature: 170ºC is the typical optimum temperature to hydrolyse sludge and municipal solid wastes (*Cambi)*); 133ºC is the minimum temperature to assure sterilization of wastes with biological risk according to European regulations (Regulation 1774/2002); 150ºC is an intermediate temperature.
- Time: it is desired to cover a range of time for the hydrolysis pretreatment till 30 minutes to evaluate the effect of longer times on the simples.

With these departure data, it was decided to set an experimental design in order to obtain more information from the experiments: a *Complete Factorial Design* of 2 factors at 3 levels (3^2 = 9 experiments) without repetitions in the central point was performed. Replicates were conducted (triplicates) in the BMP tests and experiments were carried out randomly. Next, Table 2 shows a summary of the experimental sequence:

Test	Code	Order	t (min)	T (ºC)
1	5H	3	5	170
2	15H	1	15	170
3	30H	6	30	170
4	5M	8	5	150
5	15M	5	15	150
6	30M	2	30	150
7	5L	7	5	133
8	15L	9	15	133
9	30L	4	30	133

Table 2. Experimental design

RESULTS AND DISCUSSION

The appearance of the samples before (raw) and alter TH is considerable different (see Figure 1): while the initial sample is solid, dry and heterogeneous, the hydrolyzed sample is semi-liquid due to the steam dilution, what offers a higher homogeneity, offering advantages for its characterisation and handling.

RAW SAMPLE

AFTER TH

Figure 1. Appearance of the samples before and after TH

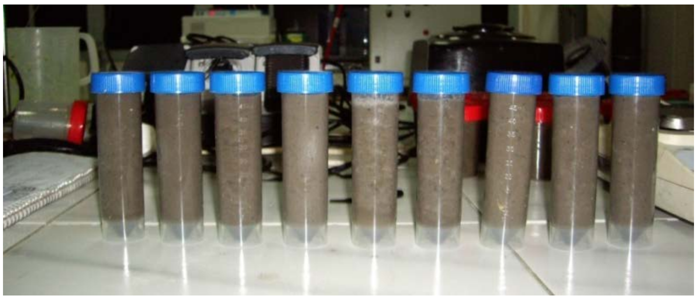


Figure 2. Pretreated samples at different conditions (tests 1 to 9 from left to right)

At a glance at Figure 2, it is remarkable that pretreated samples do not differ so much from each other. However, physic-chemical parameters, hydrodynamic tests and methanogenic potentials will show clear differences between them, as it will be next presented.

BMP tests

After carrying out BMP tests by triplicates to all hydrolyzed samples and one raw sample without pre-treatment (sample 0), the results are next presented in Figure 3 and Table 3:

Code	T	t	Solubilisation	Biogas	Increase
	ºC	min	% CODs/CODt	mLCH$_4$/gVS	%
0	-	-	-	231.2	-
5H		5	**21.7**	209.6	-9.4
15H	170	15	**18.1**	290.9	**25.8**
30H		30	**17.8**	241.9	4.6
5M		5	12.1	244.7	5.8
15M	150	15	**18.5**	297.0	**28.4**
30M		30	15.9	277.9	**20.2**
5L		5	13.8	245.5	6.2
15L	133	15	16.1	266.7	**15.3**
30L		30	12.9	282.9	**22.3**

Table 3. Main results from pretreatments and BMP tests at different conditions

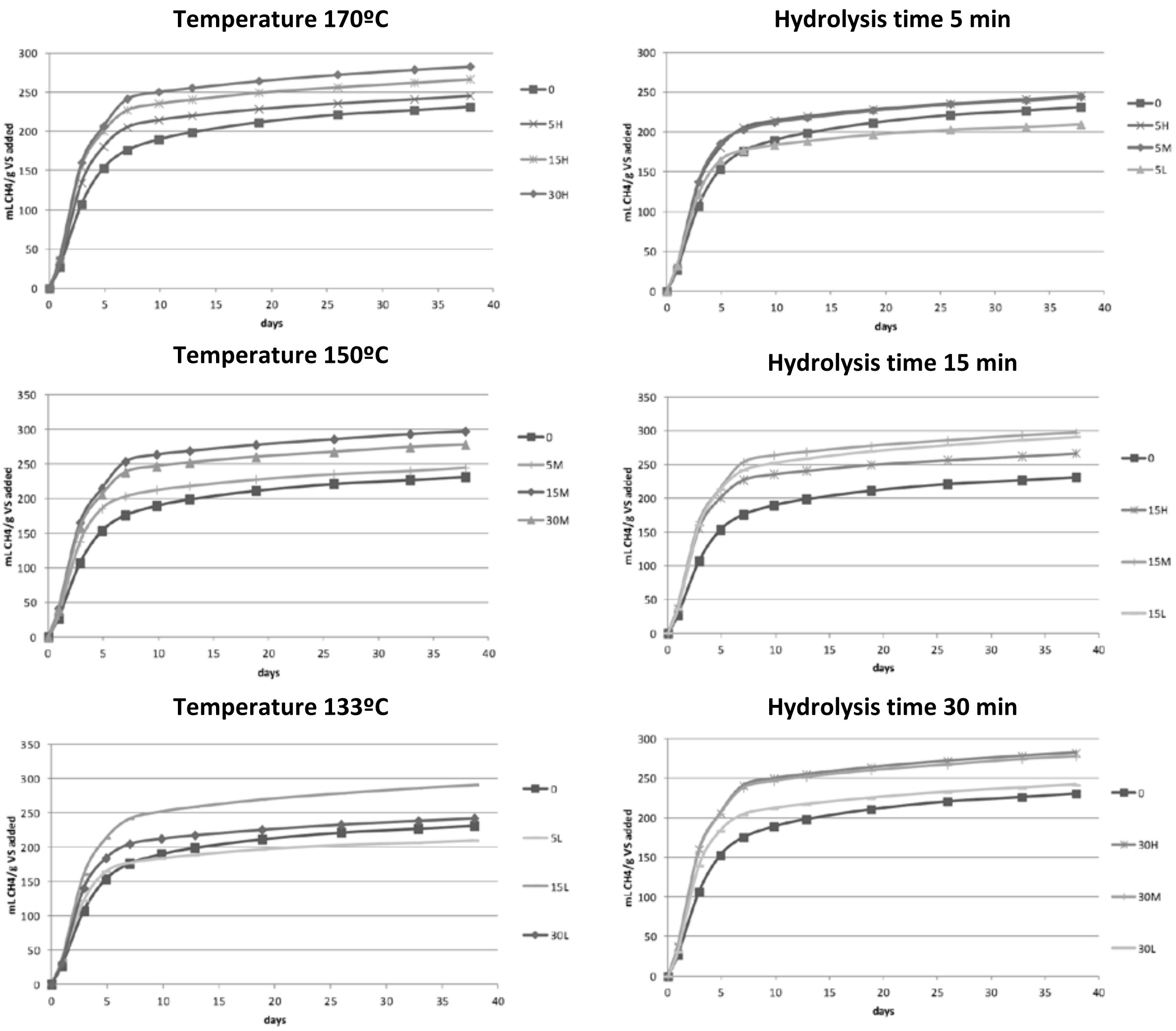


Figure 3. Methane production curves

TH has considerably raised methane potentials of the pretreated samples, reaching over 25% increase respect to the raw sample methane potential. Moreover, the organic matter solubilisation after TH (in terms of COD) is pretty high, reaching values around 18%. However, there is no direct relationship between both variables since for example sample 5H presents the highest solubilisation but the lowest methane potential (even lower than the raw sample).

Modelling of the BMP results

After fine-tuning the previous experimental results to the Gompertz equation, the next parameters are obtained for each curve (Table 4). Again, the highest increases are reached for hydrolysis times of 15 minutes, not only methane potentials (P), but also kinetics parameters (R_m), with increases close to 70%. The lag-phase is for all cases almost 0, even for the raw sample.

Therefore, taking into account just the BMP tests, the best conditions for TH are those from the 15M test: 15 minutes hydrolysis time and 150ºC; leading to increases of 30.2% of methane production and 69.3% of the kinetics.

Sample	Parameters				% increase		Lag-phase reduction
	P	R_m	λ	R^2	P	R_m	
	$mLCH_4/gVS$	$mLCH_4/gVS/d$	d	-	%	%	days
0	215.3	89.7	0.063	0.980	0.0	0.0	0.00
5H	230.0	129.2	0.304	0.986	6.9	44.0	-0.24
15H	250.4	149.7	0.277	0.986	16.3	66.9	-0.21
30H	266.5	149.7	0.243	0.987	23.8	66.8	-0.18
5M	228.2	135.1	0.313	0.984	6.0	50.6	-0.25
15M	280.2	151.9	0.210	0.987	30.2	69.3	-0.15
30M	262.0	148.4	0.219	0.987	21.7	65.4	-0.16
5L	196.7	120.1	0.246	0.986	-8.6	33.9	-0.18
15L	271.7	151.3	0.276	0.984	26.2	68.6	-0.21
30L	226.4	138.0	0.327	0.986	5.2	53.8	-0.26

Table 4. Gompertz model parameters

Statistical study (ANOVA)

After the performance of the Complete Factorial Design, it is desired to study the obtained results with an statistic tool: Analysis of Variance (ANOVA), in order to check if there are critical factors and significant influence of the factors on the response. For all of them, a degree of confidence of 95% has been set (α=0,05). In this study, the effect of both factors (or variables: hydrolysis time and temperature) on different responses is evaluated: steam consumption, model parameters, methane potentials, solubilisation factors. The main results are:

- Steam consumption: higher influence of the hydrolysis time (F=21.8 versus F_{critic}=6.9). On the other hand, the temperature does not present a significant influence (F=3.5), so that the steam consumption (and its associate cost) is directly related to the hydrolysis time.
- Solubilisation factors: in this case neither factor has a significant influence (F values below critical value), although it is usual that a higher temperature leads to a higher solubilisation of the organic matter.
- Gompertz parameters:
    - P (maximum methane production): no significant influence is observed, although hydrolysis time has a higher.
    - R_m (kinetic parameter): the hydrolysis time is clearly the critical factor (F=21.8 versus F_{critic}=6.9). The temperature has no influence on this parameter.
- Experimental methane potentials: so far, ANOVA has been only applied to 2 factors with just one sample per group. But in this case, since replicates (triplicates) have been performed in BMP tests, ANOVA to 2 factors with several samples per group has been applied, so that the interaction between factors can be assessed. Both factors present a significant influence on the methane potentials, especially the hydrolysis time (F=46.1 versus F_{critic}=3.5, while the temperature has an F=11.6). Since both factors are critical, their interaction is significant. Moreover, the noise due to uncontrolled factors represents a 11%, then the effect of the factors is considered significant. It is in this case that it can be concluded that both hydrolysis factors influence significantly in the TH process (especially the hydrolysis time).

Hydrodynamic tests

After BMP tests, different tests have been performed to determine the dewaterability and rheological properties of the digestates and pretreated samples.

- **Viscosity of pretreated samples:**

The viscosity has been determined for the pretreated samples to assess the impact of TH on the mixing properties in the digester. Unfortunately, the raw sample could not be evaluated since it is solid. The pretreated samples have generated different curves (not presented) which indicate that the lowest viscosity is reached in 15M and 30M samples.

- **Dewaterability of the digestates**

Solid-liquid separation properties are carried out in digested samples after BMP tests by centrifugation and filtration tests.

- Centrifugation

The results show the next average values (duplicates are performed): separate liquid %, solid recovery in cake % and total solids concentration in cake (%).

Sample	% liquid separation	% solids recovery in cake	Solids concentration in cake (%)
0	68.7	96.6	12.7
5H	78.6	98.8	14.0
15H	77.7	97.5	13.9
30H	79.8	98.5	13.7
5M	76.3	97.8	14.0
15M	81.0	99.3	14.3
30M	80.1	99.2	13.9
5L	76.4	99.1	13.1
15L	76.7	98.8	13.3
30L	77.2	98.5	13.4

Table 5. Centrifugation results from digestates

It is immediately appreciate a considerable improvement when the pretreatment is performed: the separate liquid is 10% higher than the raw sample, the solid recovery rises slightly and the solids concentration in the cake is also higher, what will suppose a lower dewatered digestate volume to transport to landfill or manage properly. Looking into the results, it is remarkable that again the digestate from sample 15M presents the best results.

- Filtration

Capillary Suction Time (CST)

This assay is also performed by duplicate and generates a CST (in seconds) related with the water transport in a filter, but not with a phase separation. Average results are next presented:

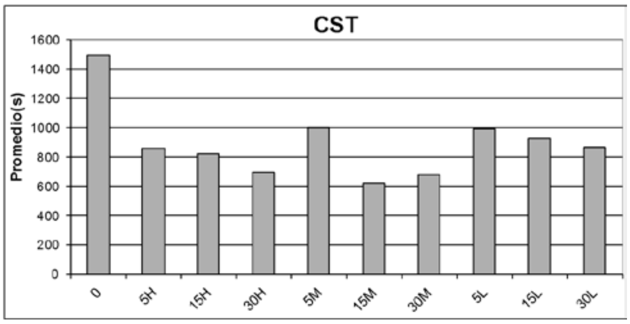


Figure 4. CST results

Samples:	0	5H	15H	30H	5M	15M	30M	5L	15L	30L
Test 1	1551.8	831.9	805.7	693.4	990.6	591.3	664.7	1025	888.6	859.3
Test 2	1440	885.9	839.4	695.7	1007.1	662.1	707.1	957.9	969.4	875.1
Average	1495.9	858.9	822.6	694.6	998.9	626.7	685.9	991.5	929.0	867.2

Table 6. CST results

Again, the lowest CST is reached with the digestate from sample 15M. All CST from pretreated samples present lower values than the raw sample one.

Filtration in column

Filtration curves (not included) let the determination of filtration constants, next presented in Figure 5 and Table 7:

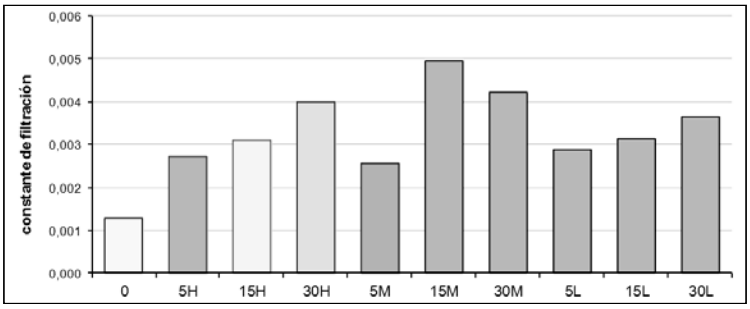


Figure 5. Filtration constants

Samples:		0	5H	15H	30H	5M	15M	30M	5L	15L	30L
Filtration	cm^2/s	0.0013	0.0027	0.0031	0.0040	0.0026	0.0050	0.0042	0.0029	0.0031	0.0036
constants	cm^2/h	4.68	9.73	11.21	14.33	9.19	17.83	15.22	10.34	11.32	13.07

Table 7. Filtration constants

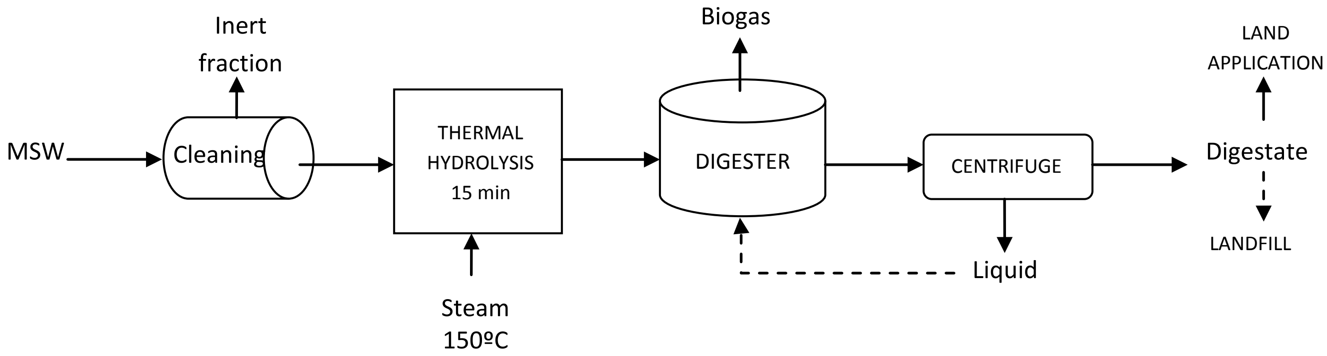
Very similar results are again obtained: all pretreated sample present filtration constants over the raw sample one, and also 15M again presents the highest result, triplicating the value of the raw sample.

Then, all hydrodynamic tests indicate that the sample 15M is the optimum one since it presents the lowest viscosity to be fed into a digester and its digestate also presents the best dewaterability properties so that the final biowaste production would be minimised.

CONCLUSIONS

Thermal hydrolysis as a pretreatment to enhance preselected MSW anaerobic digestion is a useful and efficient technology not only to increase methane production in the digester (by 30%) and kinetics (by 70%), but also to improve rheological properties and dewaterability, reducing associate costs of the process such as pumping and mixing requirements or digestate management costs. The optimum conditions to carry out the pretreatment are 15 minutes hydrolysis time at 150ºC.

Next, a simplified block diagram of the process is enclosed to show the main stages to implement a thermal hydrolysis pre-treatment in a MSW plant:



THERMAL HYDROLYSIS ENERGY INTEGRATION AND ECONOMIC ASSESSMENT

CHAPTER 8. THERMAL HYDROLYSIS ENERGY INTEGRATION AND ECONOMIC ASSESSMENT

Finally, in this chapter, an energy integration and economic assessment of thermal hydrolysis pretreatment has been performed from a more theoretical approach to study its energy and economic feasibility in full-scale plants. Six different substrates have been studied: biological sewage sludge, municipal solid waste (MSW), organic fraction MSW, grease waste, spent grain and cow manure. But special attention has been paid to MSW in order to set the basis for the scale-up of the pretreatment in a MSW treatment plant. Thermal hydrolysis has been tested in laboratory scale with batch tests, from which an energy and economic assessment of three scenarios is performed: with and without energy integration (recovering heat to produce steam in a cogeneration plant), finally including the digestate management costs. Thermal hydrolysis has lead to an increase of the methane productions (up to 50%) and kinetics parameters (even double). The study has determined that a proper energy integration design could lead to important economic savings (5€/t) and thermal hydrolysis can enhance up to 40% the incomes of the digestion plant, even doubling them when digestate management costs are considered. In a full-scale MSW treatment plant (30000 t/year), thermal hydrolysis would produce almost 0.5M€/year of net benefits, with a full refund period of the initial investment of two years.

Keywords: anaerobic digestion, biogas, energy integration, solid waste, thermal hydrolysis

The present Chapter has been accepted for publication in Bioresource Tehcnology for the special issue “Advance Biological Treatment Technologies for Sustainable Waste Management”:

Thermal hydrolysis integration in the anaerobic digestion process of different solid wastes: energy and economic feasibility study. (Accepted February 2014) Cano R., Nielfa A., Fdz-Polanco M. (special issue “Advance Biological Treatment Technologies for Sustainable Waste Management” from Bioresource Technology)

Thermal hydrolysis integration in the anaerobic digestion process of different solid wastes: energy and economic feasibility study

1. INTRODUCTION

Anaerobic digestion as a treatment of solid substrates is a clean technology based on energy recovery from waste gaining importance in a full-scale extent. A wide range of wastes are susceptible of being degraded anaerobically, as it is reported by Carlsson et al. (2012): municipal solid wastes, organic wastes from food industry, energy crops, agricultural residues, manure and waste water treatment plants (WWTP) residues. While sewage sludge anaerobic digestion technology is widely spread in WWTP since decades, other wastes still need more research to be included in anaerobic digestion full-scale plants. In the European Union (EU27), it is estimated that each person generates 520 kg of waste per year (Eurostat, 2011); then, there is a potential opportunity to produce biogas from its organic fraction. Currently, the disposal of manure is predominately done through land application, which causes greenhouse gas emissions, ecological system eutrophication and groundwater contamination (Ying et al. 2009). But new regulatory restrictions are forcing to develop sustainable technologies such as anaerobic digestion for its management. Furthermore, there are further WWTP residues (such as grease waste) with a high energy content which could be treated on-site in sewage sludge anaerobic digesters, saving transport and management costs and increasing biogas production. These are just some examples of different wastes that could be degraded to produce biogas and therefore green energy.

However, anaerobic digestion has a limitation concerning solid substrates. Its degradation rate is limited by the hydrolysis step, which is an especially slow step when dealing with solid substrates. In this process, complex organic matter (proteins, lipids, carbohydrates...) becomes simple soluble matter (amino acids, sugars, fatty acids...). In order to accelerate the hydrolysis step, thermal hydrolysis pretreatment (TH) is one of the most efficient techniques, leading to high solubilisation, pathogen reduction, good dewaterability and an increase in biogas production. As well, the energy input needed for the hydrolysis process is thermal energy and could be satisfied from the energy production of the own process, resulting in an energetically self-sufficient process (Perez-Elvira et al. 2008). In addition, the solid residues of such biogas production (biowaste) after the thermal treatment can be used as low-grade fertilizers (Hilkiah Igoni et al. 2008): for example, two *Cambi* plants in Norway (Lillehammer and Ecopro) have received permits to use the bio-fertilizer in the agricultural sector and also for land remediation purposes (Sargalski, 2008). Thermal hydrolysis has been widely tested with sewage sludge as a cost-effective method (Perez-Elvira et al. 2006) and even applied in real scale continuous processes by *Cambi* in several biosolids plants (Román et al, 2007). But for other substrates, there are just laboratory trials (Valladão et al. 2007; López Torres and Espinosa Lloréns 2008;; Charles et al. 2009; Carrère et al. 2009; Ma et al. 2011; Shahriari et al. 2012; Cesaro et al. 2012; Liu et al. 2012) or pilot scale studies (Zhou et al. 2013) and an economic assessment is required to get closer to full-scale real applications.

In the present study, thermal hydrolysis pretreatment to different solid wastes is evaluated in laboratory scale with batch tests. From them, an energy and economic assessment is performed by the analysis of three different scenarios to set the basis for a process scale-up.

2. MATERIALS AND METHODS

2.1 Solid wastes

Six different solid substrates were selected considering: their importance in real scale plants in order to optimise their anaerobic digestion; their availability; and their diversity of composition, origin, production and biodegradability according to the substrate classification of (Carlsson et al. 2012). These substrates are: biological sludge (thickened to 7% total solids) from a municipal WWTP; the organic fraction of municipal solid waste (OFMSW), which is a synthetic mixture of basic foods in an appropriate proportion as their presence in household waste (Boulanger et al. 2012); municipal solid waste (MSW) previously sorted from a waste treatment plant; grease waste from a dissolved air flotation tank (DAF) from a WWTP; spent grain from brewery industry; and cow manure from slaughterhouse. Their characterization is presented in *Table 1*.

Parameter	Units	**Biological sludge**	**OFMSW**	**MSW**	**Grease waste**	**Spent grain**	**Cow manure**
TS	g/kg	71.2	109.9	351.4	505.2	243.6	221.6
VS	g/kg	54.9	105.1	246.0	468.2	233.4	208.5
CODt	g/kg	83.9	150	332.5	648.3	303.4	258.8
CODs	g/kg	6.3	91.8	-	-	70	81
TKN	N-g/ kg	5.75	3.79	5.347	3.27	8.73	27.46
NH_4^+	N-g/ kg	0.24	0.82	1.049	0.24	1.22	0.75
Grease	g/kg	1.16	2.68	5.80	128.0	6.66	4.65
Carbohydrates	%	0.10	6.28	0.19	-	-	-
Fibre	%	0.21	0.82	7.23	-	-	-
Proteins	%	3.83	2.43	3.67	2.04	4.69	16.7

Table 1. Substrates characterization (TS, VS: total and volatile solids; CODt/s: total/soluble chemical oxygen demand; TKN: total Kjeldahl nitrogen; NH_4^+: ammonium)

2.2 Thermal hydrolysis pretreatment (TH)

The lab-scale hydrolysis plant is made up of a 2L reactor fed with the substrate and heated with steam until the desired temperature, and a flash tank where the steam explosion takes place after the hydrolysis reaction time has elapsed. The operational conditions remained constant: 170ºC and 30 minutes hydrolysis time, which are the optimized conditions obtained by (Fdz-Polanco et al. 2008), except for the OFMSW (120ºC and 10 minutes) and MSW (150ºC and 20 minutes) for which different conditions were found as optimum ones in previous tests.

2.3 Biochemical methane potential tests

Biochemical methane potential (BMP) tests allow to determine kinetics and methane potentials of the substrates. The assays were performed by triplicates following an internal protocol based on standardized assays (Angelidaki et al. 2009). The reactors volume was 300 mL and a substrate-inoculum ratio of 1:1 in terms of VS was applied. The incubation temperature was 35ºC and reactors were stirred in a horizontal shaker. The inoculum was WWTP mesophilic digested sludge. Periodical monitoring analyses of biogas production by pressure meter and biogas composition by gas chromatography (Varian CP-3800) were performed during the tests. Methane potentials are expressed as average values of the net volume of methane per gram of initial substrate VS content. In this study, the results from these tests were taking as a departure point for all calculations.

2.4 Modelling

The Modified Gompertz equation (Lay et al. 1997), next presented in equation 1, was considered in order to fine-tune the experimental data from BMP tests to a theoretical equation:

$$B = P \times exp\left\{-exp\left[\frac{R_m \cdot e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

The model has three parameters: the methane yield rate (R_m) which indicates the initial slope of the curve ($mLCH_4/gVS/d$), the maximum biogas production (P) expressed as $mLCH_4/gVSin$ and the lag-phase (λ) in days. B is the calculated methane production ($mLCH_4/gVSin$) for time t. The model fine-tuning to the experimental data was achieved by least squares methodology, by minimising the next objective function (2):

$$OF(\varphi) = min\sum_{t=1}^{N}\left(B_{exp}(t) - B_m(t,\varphi)\right)^2 \quad (2)$$

where B_{exp} is the consumption velocity obtained from measurements (plotted in BMP results graphs as points). B_m is the corresponding velocity calculated by the model (plotted with continuous curves), N is the number of measurements, t is time and φ represents the Gompertz parameters. The correlation factor (R^2) was then calculated to assess the accuracy of each model with respect to the experimental data.

2.5 Dewaterability test

Centrifugability test was performed following an internal method established from the experiments in sludge characterization (Donoso-Bravo et al. 2011). Centrifugability assesses the liquid and solid phase separation after 5 minutes centrifugation at 5000 rpm in a *Kubota 5100* centrifuge. After measuring the separation performance and determining the suspended solids concentration in the liquid phase, the next parameters are calculated: % separated liquid, % solid recovery in cake and solid concentration in cake (%TS). These parameters enable the quantification of the biowaste that can be separate from the digestate from BMP tests, to estimate the amount of biowaste to deal with after the digestion, which has to be properly managed and will directly influence in the economic assessment.

2.6 Analytical methods

Substrates characterization was performed following an internal protocol based on Standard methods (Apha, 2005) to determine the next parameters: TS, VS total and volatile solids; COD chemical oxygen demand; TKN total Kjeldahl nitrogen; NH_4^+ ammonium. The other parameters were determined according to: grease (EPA Method 1664), carbohydrates (CE Regulation 152/2009), fibre content (Weende, CE Regulation 152/2009) and proteins (IT-MA-014, AOAC Official Method).

2.7 Energy integration and economic assessment

2.7.1 Thermal Hydrolysis integration:

For all scenarios, the thermal hydrolysis process has been integrated energetically (Figure 2a) according to the configuration adopted in commercial processes such as *Cambi*. A recovery of heat from the flash vapours (saturated steam at 105ºC) to the pre-heating stage of the substrate leads to considerable saving in the energy consumption. This way, steam requirements have been estimated with energy and mass balances considering 20% vapour losses in the pre-heating stage and a temperature of the hydrolysed substrate of 105ºC, according to supplied data from a continuous thermal hydrolysis plant from *Aqualogy* in Valladolid WWTP (Pérez-Elvira et al. 2013).

2.7.2 Scenarios evaluation

Thermal hydrolysis implementation in a full-scale plant has been achieved theoretically on three different scenarios (Figure 2) and making the cost-benefit analysis of the process with and without pretreatment, based on a previous study (Perez-Elvira et al. 2008):

1. ***Scenario 1**: **No energy integration.*** The biogas produces green electricity in an engine (EE), which is sold with an extra benefit in case of thermal hydrolysis (higher biogas production). The steam required in the pretreatment is produced in a boiler which is fed with natural gas. The difference between the surplus of green electricity and the cost of natural gas is the net benefit of the process (Figure 2b).

2. ***Scenario 2:* Energy integration**. The biogas is burned in a combined heat and power system (CHP) providing three main streams (Figure 2c):
    - Electrical green energy (EE): to be sold, providing net benefits.
    - Hot exhaust gases (EG): waste stream which heat can be recovered in a boiler to produce steam for the thermal hydrolysis pretreatment (natural gas is not anymore needed if the heat is sufficient).
    - Hot water (HW): it can be used to heat the digester, if necessary; but it is not considered for the energy calculations in the study.

3. ***Scenario 3*: Digestate handling.** Considering the costs of the dewaterability (centrifugation) post-treatment, the biowaste management (taxes and transport to landfill)... This scenario was only studied for MSW substrate because its high potential to be implemented in a full-scale extent, due to the scarce development of its TH application before anaerobic digestion and its high worldwide production, which entails important management problems (Figure 2d).

2.7.3 Energy and economic considerations:

Biogas generation in the anaerobic digester results from the BMP data obtained in laboratory trials. A thermal transfer efficiency of 90% in boilers is considered. When a CHP is considered, electrical efficiency is set to 33% and thermal efficiency to 55% (25% exhaust gases and 30% hot water), with an overall efficiency of 88%, according to typical values of commercial engines. All raw substrates and cold water are considered initially at 20ºC and a constant heat capacity for all of them equal to the water one (4.18 kJ/kg/K) has been ascribed, which is the most unfavourable value. Calorific values of methane and natural gas are 11kWh/Nm^3 and 8.6kWh/Nm^3 respectively (engineeringtoolbox.com). Prices of electrical energy are set at 12c€/kWh (buy) and 15c€/kWh (sell, including bonus from green energy) and natural gas at 35c€/kWh (current prices in Spain according to endesaonline.es). The taxes for landfilling are 25€/t, which is the average cost in Spain according to ateneonaider.com (lower than in the rest of Europe).

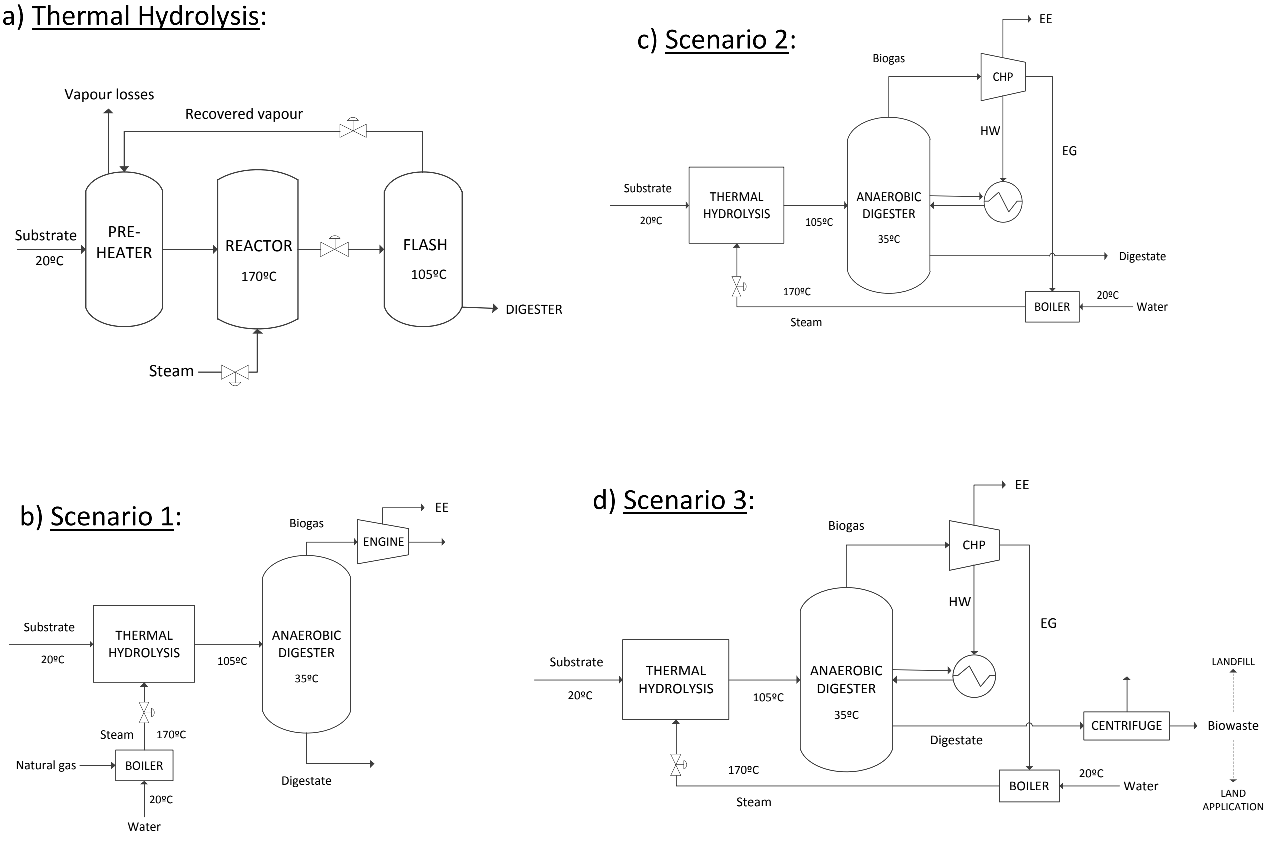


Figure 2. Simplified flow diagrams with different configurations considered in the study:
a) Thermal Hydrolysis pretreatment with heat recovery from the flash vapours in the pre-heater.
b) Scenario 1: No energy integration setup (production of electrical energy EE).
c) Scenario 2: Energy integration design (heat recovery from exhaust gases EG for steam generation).
d) Scenario 3: Digestate handling considerations and biowaste management.

3. RESULTS

3.1 Thermal Hydrolysis evaluation at lab-scale

The results obtained in BMP tests with the Gompertz model fine-tuning for raw and pretreated wastes are enclosed in Table 2 and BMP curves are plotted in Figure 1 (just MSW curves shown as an example). Thermal hydrolysis pretreatment has improved the anaerobic digestion in BMP tests for all the substrates. Gompertz modelling parameters, which have been determined with a high degree of accuracy (average R^2 over 0.98), enable a quantification of these improvements.

SUBSTRATES		MODEL PARAMETERS				IMPROVEMENTS		
		P	R_m	λ	R^2	P	R_m	λ
		$mLCH_4/gVSin$	$mLCH_4/gVSin/d$	d	-	%	%	d red.
Biological sludge	raw	184	65.2	0	0.934	51	71	0.0
	TH	278	111.7	0	0.956			
OFMSW	raw	308	32.4	6.6	0.997	3	164	6.4
	TH	318	85.6	0.2	0.992			
MSW	raw	215	89.7	0.1	0.980	30	69	-0.1
	TH	280	151.9	0.2	0.987			
Grease waste	raw	489	82.4	17.6	0.990	7	43	1.8
	TH	524	118.1	15.8	0.994			
Spent grain	raw	251	50.8	0.8	0.994	40	144	0.8
	TH	352	123.7	0	0.991			
Cow manure	raw	317	53.3	0	0.981	29	177	0.0
	TH	408	147.7	0	0.982			

Table 2. BMP parameters from Gompertz equation modelling and thermal hydrolysis effects

Among the substrates, biological sludge has suffered the highest methane production increase after TH (more than 50%) probably due to the cell lysis that takes place during the pretreatment and especially in the steam explosion. The liberation of the intra-cellular material from microbial cells of the biological sludge can be the main mechanism that causes the biogas production improvement, as it was also concluded by Perez-Elvira et al. (2010). The biological sludge is the only substrate from this study that is mainly composed by microbial cells, which is one of the two causes of a low hydrolysis which could be overcome by the application of pretreatments (Carlsson et al. 2012). The other cause is a high content of lignocellulosic material, which, in the present study, is best represented by the municipal solid waste (MSW) that has a fibre content of 7.2%. Thermal hydrolysis at 150ºC to MSW has also improved considerably its digestion (30% more methane production and 70% faster kinetics), probably caused by the breakdown of its lignocellulosic material into soluble material. On the other hand, the organic fraction of municipal solid waste (OFMSW) has not lead to any biogas improvement by the application of the pretreatment, but just to a kinetic acceleration. The initial high soluble matter that this substrate contains (over 60% COD is soluble) and the fact that it is composed by high amounts of easily degradable sugars (6.28% carbohydrates) are the main causes of the lack of effectiveness of TH in this synthetic substrate. However, OFMSW digestion has provided an acceptable methane production (over 300 $mLCH_4/gVSin$). It is remarkable the higher efficiency that thermal hydrolysis presents when pretreating the real MSW in comparison to the synthetic waste, due to the higher fibre content and lower easily degradable sugars contained in the first one, what reduces the availability of organic compounds when no pretreatment is applied. The remained three substrates (grease waste, spent grain and cow manure) represent substrates rich in lipids, in carbohydrates and in proteins respectively. While TH has played an essential role in improving anaerobic digestion of spent grain and cow manure (40 and 30% more biogas respectively and methane yield rates have doubled), grease waste has not been remarkably influenced by the pretreatment. Although its methane production can be slightly improved and the kinetics speeds up 40%, a considerable lag-phase (over 15 days) is present with or without TH, which could be caused by the inactivation of methanogens because the increase of long chain fatty acids, but this was not experimentally proved. Its high lipid content and slow degradable materials could not be subjected to significant alterations during the pretreatment. In this case, its high lipid content (128g/kg) and slow degradable materials of the grease waste could not be subjected to significant alterations during the pretreatment. Nevertheless, its high lipid content leads to the highest methane production (524 $mLCH_4/gVSin$ after TH), converting this substrate in an interesting co-substrate (Silvestre et al. 2011). Coming back to cow manure, it is remarkable that its high nitrogen content (27.5 N-g/kg) has not lead to ammonia overloading and refractory compounds formation after the thermal pretreatment, what has been reported to be common (Cuetos et al. 2010). It is probable that the high content of lignocellulosic material of this substrate has suffered a high rupture after TH and is the main responsible mechanism that has taken part to improve its degradation.

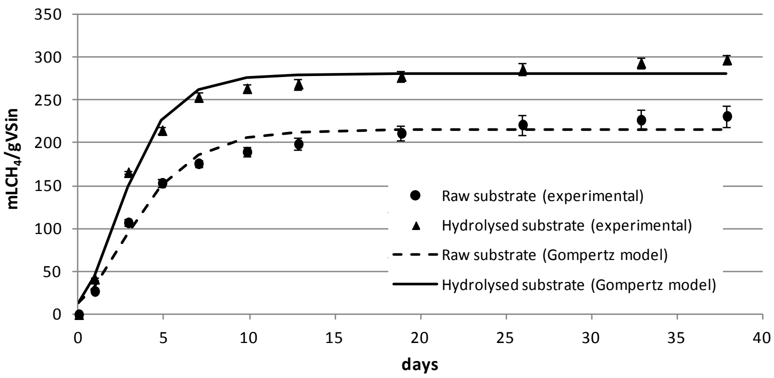


Figure 1. BMP curves of raw and pretreated MSW

As it is reported by Carlsson et al. (2012), two main components can be identified among substrate categories that cause low bioavailability and/or biodegradability: microbial cells/flocs such as those found in waste activated sludge from WWTP and lignocellulosic material from plants and vegetables found in energy crops and harvesting residues, in manure and to some extent in household waste (Carlsson et al. 2012). Then, it has been confirmed that substrates with high content of fibre or microbial cells are more susceptible to be pretreated in order to improve its degradation capacity.

3.2 Energy integration and economic assessment

The feasibility of the thermal hydrolysis pretreatment in a continuous plant has been assessed by different approaches with different configurations, described in Methods and shown in Figure 2. The extrapolation from laboratory trials to a continuous operation has been achieved considering the same biogas productions from BMP tests, but steam consumption, energy balances and equipments characteristics have been determined theoretically considering typical design values from real processes and taking as basis of calculation one tonne of raw waste.

Next, the three scenarios are studied and the main results are enclosed in respective Tables.

Scenario 1:

As a first approach, the simplest configuration is studied, which is the most unfavourable one. No energy integration has been considered, so natural gas requirements for steam generation are high and incomes from green electrical energy are reduced. Table 3 shows the main results for all the raw and hydrolysed substrates. First, it is remarkable that the natural gas consumption for different TH conditions of temperature is almost the same, and even higher for a lower temperature. However, the resulted benefits of TH that have been estimated diverge from each substrate. While most of them show positive balances with net benefits over 3€/t, there are two substrates (biological sludge and OFMSW) with negative incomes. In the case of OFMSW, it is logical since the methane production increase in BMP tests was just 3%, what does not compensate all the steam consumption costs. For biological sludge, the reason is not so obvious since BMP tests showed the highest methane production increase for this substrate (51%). Nevertheless, this increase is determined based in $mLCH_4/gVSin$, and this substrate contains fewer VS (55g/kg) than the others, so the gross methane generation is lower and does not satisfy the steam requirements. In fact, as it has been studied by (Perez-Elvira et al. 2008), the sludge concentration of the biological sludge is the key parameter to satisfy the energy balances and make the process energetically efficient. This way a higher VS content (previous centrifugation)% would lead to positive benefits (VS at least 110g/kg). On the other hand, it is noteworthy the net benefits obtained for grease waste, which rises over 125€/t without pretreatment, what indicates the high potential this substrate offers for anaerobic digestion.

Substrates		Hydrolysis Temperature	GENERATION			CONSUMPTION			BENEFITS		
			Methane	Electrical energy		Steam	Natural gas				
		ºC	$mLCH_4/gVSin$	kWh/t	€/t	kg/t	Nm^3/t	€/t	€/t	**€/t**	**%**
Biological sludge	raw	-	184	37	5.5	0	0	0	5.5		
	TH	170	278	55	8.3	189.2	18.7	5.6	2.7	**-2.8**	**-51**
OFMSW	raw	-	308	118	17.6	0	0	0	17.6		
	TH	120	318	121	18.2	195.7	18.9	5.7	12.5	**-5.1**	**-29**
MSW	raw	-	215	192	28.8	0	0	0	28.8		
	TH	150	280	250	37.5	191.3	18.8	5.6	31.9	**3.1**	**11**
Grease waste	raw	-	489	830	124.6	0	0	0	124.6		
	TH	170	524	891	133.6	189.2	18.7	5.6	128.0	**3.4**	**3**
Spent grain	raw	-	251	213	31.9	0	0	0	31.9		
	TH	170	352	298	44.7	189.2	18.7	5.6	39.1	**7.2**	**23**
Cow manure	raw	-	317	240	36.0	0	0	0	36.0		
	TH	170	408	309	46.3	189.2	18.7	5.6	40.7	**4.7**	**13**

Table 3. Scenario 1. No energy integration. Most results expressed per tonne of substrate fed.

Scenario 2:

In this case, the thermal integration results in the recovery of heat from the exhaust gases from a CHP system (a waste stream) to produce the steam for TH. In Table 4, all the energy streams are calculated for both cases: no TH (raw) and with TH. Electrical output provides net benefits from green electricity, exhaust gases (typically over 400ºC) generate steam, and hot water could be used for any low temperature heat requirement in the plant (such as heating the digester), but it has not been considered for the calculations. In most of the cases, the steam requirements are fulfilled by the steam generated with the exhaust gases, except for biological sludge and OFMSW, for the same reasons explained in *Scenario 1*. In these cases, an extra natural gas is purchased to generate steam and complete the requirements (as states Table 4). The obtained benefits from TH of this scenario are higher than the previous one, but still negative for the last mentioned substrates. The other ones present values from 8€/t to 13€/t, with increases respect the "no TH" till 40% and an extra benefit over 5€/t respect the *Scenario 1*. In this case, it is especially remarkable that TH to grease waste has lead to a net benefit of 9€/t which, considering that TH just increased its methane production by 7%, is an impressive result. This fact is again justified by the VS content of the waste which, in this case, is quite high (468 g/kg) and leads to high gross methane production when calculating per raw weight basis. Spent grain and cow manure are the substrates that lead to the highest benefits (over 10 €/t), although MSW also leads to a very high relative benefit (30%) if it is compared to the raw substrate one. Moreover, this last waste has a very high potential to be implemented in a full-scale extent since it is produced worldwide in high amounts, entailing important management problems. For these reasons, it is has been selected for the last scenario evaluation.

Substrates		**Total energy in biogas**	**GENERATION (CHP system)**					**CONSUMPTION (Boiler)**	**BENEFITS**		
			Electrical output (EE)		**Thermal output**		**Steam produced**	**Steam required**			
					HW	**EG**					
		kWh/t	kWh/t	€/t	kWh/t	kWh/t	kg/t	kg/t	€/t	**€/t**	**%**
Biological Sludge	raw	111	37	5.5	33	28	34	0	5.5		
	TH	168	55	8.3	50	42	51	189*	4.2	**-1.3**	**-24**
OFMSW	raw	356	118	17.6	107	89	110	0	17.6		
	TH	368	121	18.2	110	92	114	196*	15.8	**-1.8**	**-10**
MSW	raw	583	192	28.8	175	146	177	0	28.8		
	TH	758	250	37.5	227	190	231	191	37.5	**8.7**	**30**
Grease waste	raw	2516	830	124.6	755	629	759	0	124.6		
	TH	2699	891	133.6	810	675	814	189	133.6	**9.0**	**7**
Spent grain	raw	644	213	31.9	193	161	194	0	31.9		
	TH	904	298	44.7	271	226	273	189	44.7	**12.8**	**40**
Cow manure	raw	727	240	36.0	218	182	219	0	36.0		
	TH	936	309	46.3	281	234	282	189	46.3	**10.3**	**29**

Table 4. Scenario 2. Energy integration. Most results are expressed per tonne of substrate fed. (*extra natural gas in the boiler has been considered to produce the required steam).

Scenario 3:

In the last scenario, associated costs to digestate handling have been calculated for the municipal solid waste (MSW) substrate. Dewatering and disposal of digestate is considered to be one of the main economic factors in the WWTP operation, representing up to 50% of the total operating costs (Carlsson et al. 2012). A centrifuge has been considered as dewaterability post-treatment to separate the aqueous phase from the solid biowaste. TH effect on the dewaterability process has been assessed by centrifugability tests of the obtained digestates from BMP tests, determining the next parameters: separated liquid (enables the quantification of the biowaste respect to the digestate), solid recovery in cake (indicates the efficiency of the centrifugation) and the solid concentration in cake (total solids of the biowaste). As it is shown in Table 5, TH influences considerably its centrifugability parameters: more than 12% liquid is separated, a full recovery of solids is achieved (99%) and a biowaste with 1.6% more TS is obtained. This will directly influence the associated costs of the biowaste management derived from its volume reduction (35% reduction). In Table 5, these costs are enclosed: they include the landfill deposit taxes and the transport costs. In the case of the thermally hydrolysed digestate, it satisfies the minimum requirements of sterilisation to be used as fertilizer for agricultural purposes (at least 133ºC for 20 minutes) according to the European Regulation 1774/2002. In this case, the associated costs for landfilling are eluded and a null price for selling the fertilizer is ascribed. Other advantages of TH which were not considered in this study but have a high impact in a full-scale plant are: lower viscosity in the digester (reduction of mixing energy requirements in the digester), savings in polyelectrolyte used in centrifugation and no need of a further sterilisation process of the biowaste. This way, in combination with the economic data from *Scenario 2*, total benefits with and without TH have been determined and compared. An extra benefit of 16€/t is reached when TH is applied, what represents an income increase of 96% respect to the conventional configuration.

In Figure 3, all mass flows of the main streams can be consulted for both configurations: with and without TH. Departing with 1 tonne of wet MSW (containing 351 kgTS), it shows the main energy or mass content in each stream of the conventional process and with the TH process implementation. The main differences reside in the biogas and the biowaste generation. While the conventional process recovers 53m^3 CH4 (leading to 192kWh of electrical energy), the TH scenario increases the biogas production to 69m^3 CH4, providing 250kWh of electrical energy and 190kWh (exhaust gases) that can be reused to generate steam. Concerning biowastes, the amount of biowaste generated in the conventional process is 188kg (containing 23kgTS) versus 124kg (with 17kgTS) in the TH scenario, which main advantage is the possibility to be used as fertilizer - instead of lanfilling - as a more sustainable management alternative. On the other hand, both scenarios show the high efficiency that anaerobic digestion offers, since, from 1 tonne of initial waste, just 124/188kg have to be finally managed (apart from the energy recovery advantage), what supposes a reduction of more than 80% of the initial waste mass flow.

MUNICIPAL SOLID WASTE			**RAW**	**TH**
Centrifugability results	Separated liquid	%	65.6	77.9
	Solid recovery in cake	%	96.6	99.3
	Solid concentration	%	12.7	14.3
Biowaste generation		kg/t	188	124
Digestate Costs	Landfill	€/t	4.7	3.1 (0)*
	Transport	€/t	7.5	5.0
	Total	€/t	12.2	5.0
Benefits (Scenario 3)		€/t	16.6	32.6
TH increase		**%**	**-**	**96**

Table 5. Scenario 3. Digestate handling costs, expressed per tonne of substrate fed (* if biowaste is used as fertilizer)

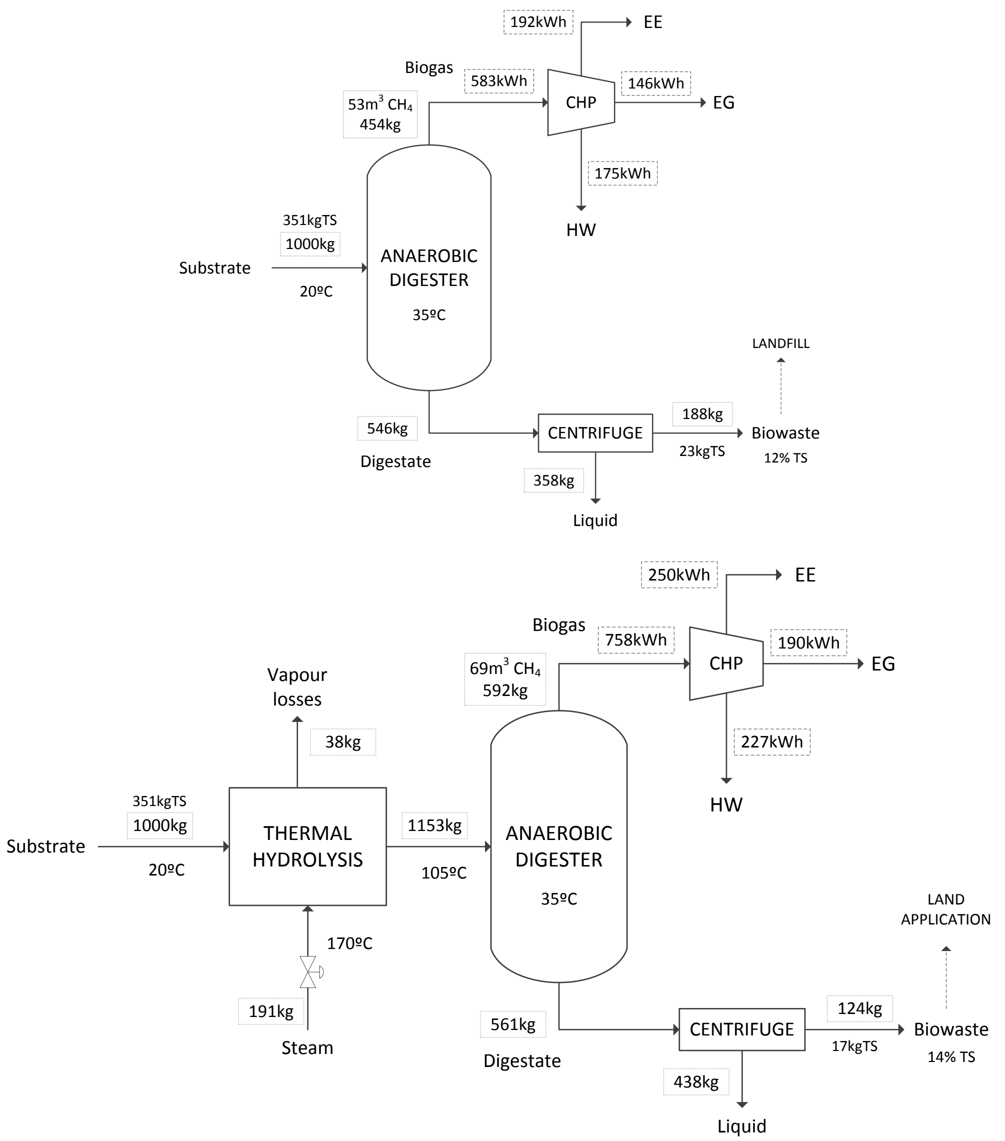


Figure 3. Mass and energy balances of the main streams of *Scenario 3* with and without TH (basis: 1t -wet weight- MSW substrate fed)

3.3 Scenarios comparison

Figure 4 compiles graphically the net benefits obtained by TH in comparison to the conventional digestion process (without TH). It is immediately remarkable that there are positive values for all substrates except for biological sludge and OFMSW, as it has already been explained by the effect of the VS content. In fact, the content of VS is a key parameter to consider when dealing with sludge since it is directly related with the energy efficiency of the TH and it can be easily modified (thickening sludge by centrifugation). As it was observed for the grease waste, a high content of VS leads to high TH benefits in spite of a low methane yield increase.

On the other hand, the energy integration of *Scenario 2* (middle column in Figure 4) improves the profitability of the digestion without energy integration (left column) for every case; thus, the importance a proper energy integration design has on the economic evaluation. Finally, *Scenario 3*, although it was only applied to MSW, increases considerably the incomes (right column) almost doubling the *Scenario 2´*s ones. Therefore, it can be concluded that Scenario 3 is the most economically viable energy integration design.

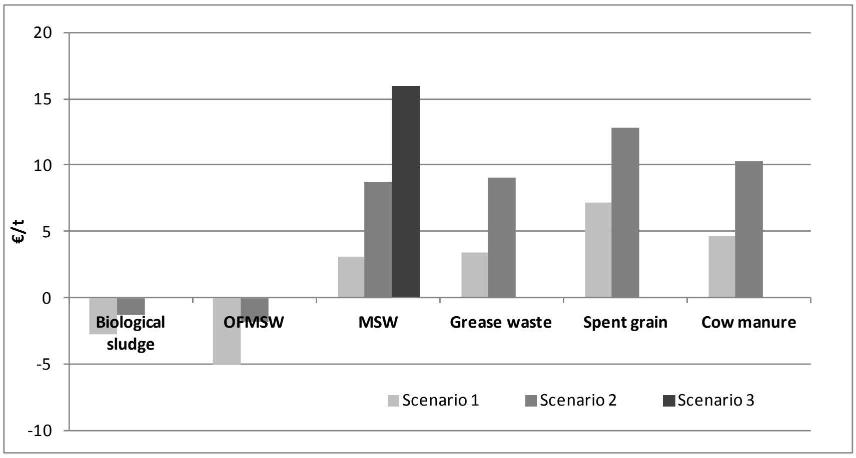


Figure 4. TH net benefits for all substrates in each scenario

3.4 Scale-up forecast

In a last attempt to make a final scale-up and conclude the economic assessment of a thermal hydrolysis plant, it has been considered a MSW flow based in a real plant in order to study the ability of the implementation of this technology in full-scale. The waste treatment plant of Verdal (Norway) treats 30000t/year of waste and has adopted *Cambi* thermal hydrolysis technology as pretreatment since 2008 (Román et al, 2007). Considering this treatment capacity, the benefits obtained in *Scenario 3* (16€/t), a depreciation term of 10 years and fixed equipment costs of the TH plant of 1M€ (rough calculation), the total net benefits ascend to almost 0.5M€/year, providing a full refund of the initial investment of the TH plant after two years operation. Despite this calculation has been carried out as a gross estimate, it provides an idea of the profitability and effectiveness of the thermal hydrolysis in a MSW treatment plant.

4. CONCLUSIONS

Thermal hydrolysis as an anaerobic digestion pretreatment has lead to an increase of methane productions (up to 50%) and kinetics parameters (even double). However, it has not showed remarkable effects in substrates rich in lipids or with high content of easily degradable carbohydrates. The economic assessment has determined that a proper energy integration design could lead to important economic savings (5€/t). Moreover, thermal hydrolysis can enhance up to 40% the incomes of the digestion plant, even doubling them when digestate management costs are considered (Scenario 3). In a real MSW treatment plant, thermal hydrolysis would lead to net benefits of almost 0.5M€/year, with a full refund period of the initial investment of two years.

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CONCLUSIONS AND FUTURE WORK

CONCLUSIONS

According to the chapters sequence and in satisfaction with the objectives presented at the beginning of the thesis, the main conclusions that have been deduced from all the study are next presented:

- **Substrate properties** are very dependent on the kind of waste and on its origin of production. A complete characterization of the matter must be firstly achieved to select the most appropriate pretreatment and specific tests for each one have to be performed.

- Not all the pretreatment technologies have **energy self-sufficiency**: only ultrasounds applied in full-scale plants and thermal pretreatments, which have a higher potential to be implemented with full energy integration since they can recover heat from the biogas engine.

- **Modelling** the biodegradation of solid substrates by simple equations is a reliable method to determine kinetic parameters and methane potentials from experimental data from BMP tests with a high degree of accuracy. The Modified Gompertz equation presents the best results of fine-tuning, even with the most complex kinetics.

- **Thermal hydrolysis pretreatment to different solid wastes** has improved significantly methane productions (over 30%) and kinetics (even double), especially in substrates which have a high fibre content (MSW, spent grain, cow manure) or microbial cellular material (biological sewage sludge). However, it has not shown remarkable effects in substrates rich in lipids (grease waste) or with high content of easily degradable matter (synthetic OFMSW).

- The **co-digestion of sewage sludge** with different solid wastes as co-substrate (such as cow manure or grease waste) offers important advantages concerning management costs and improves anaerobic digesters capacity. However, it does not often lead to synergistic effects at certain mixture ratios (52%VS grease, 61%VS cow manure). When applying **pretreatments to the co-digestion mixture**, higher methane production and faster kinetics are obtained, especially when pretreating just biological sludge from the co-digestion mixture. The implementation of thermal hydrolysis to a grease waste and sewage sludge semi-continuous co-digester resulted in a considerable methane production and an improvement of the rheology and dewaterability properties of the digestate. This leads to important economical savings when combining with co-digestion, reducing final wastes management costs and showing interesting perspectives for full-scale application.

- When pretreating OFMSW (synthetic mixture), ultrasounds have not generated improvements in either the methanogenic potentials or the kinetic rates. On the other hand, thermal hydrolysis at 120ºC has played an essential role in improving kinetics, but at 170°C the formation of recalcitrant compounds lead to slow biodegradations. However, when pretreating a **pre-selected MSW (from a MSW treatment plant) by thermal hydrolysis** great improvements were obtained at the optimum conditions (15 minutes hydrolysis time at 150ºC): a 30% increase of the methane production in the digester and kinetics accelerate by 70%; also rheological properties and dewaterability were improved. It is remarkable the higher efficiency that thermal hydrolysis presents when pretreating the real pre-selected MSW in comparison to the synthetic waste, due to the higher fibre content and lower easily degradable sugars contained in the first one, what reduces the availability of organic compounds when no pretreatment is applied.

- Improving the **rheology and dewaterability properties** of the digestate by pretreatments leads to important economical savings, reducing associate costs of the process such as pumping and mixing requirements or digestate management costs (especially when combining with co-digestion), showing interesting perspectives for full-scale application.

- The **economic assessment** of thermal hydrolysis tests with single substrates has determined that a proper **energy integration** design could lead to important economical savings (5€/t) and thermal hydrolysis can enhance up to 40% the incomes of the digestion plant, even doubling them when digestate management costs are considered. In a real MSW treatment plant, thermal hydrolysis would lead to net benefits of almost 0.5M€/year, with a full refund period of the initial investment of two years.

FUTURE WORK

Considering all the previous work, several routes can be followed to go on with this research:

- **Pretreatment mechanisms**: to go deeper into the mechanistic behaviours when pretreating, further BMP tests can be performed to evaluate the formation of intermediate compounds, kinetics, inhibitions, pathogens... As well, sterilization efficiency or emerging contaminants as monitoring parameters can be considered.

- **Modelling pretreatments**: related with the previous point, mechanistic models can be determined to model a pretreatment process based on conservation principles and dynamics in order to estimate their behaviours. Nowadays, there are also powerful tools such as computational fluid dynamics (CFD) to model these processes.

- **Co-digestion processes**: this area offers several future points. From the optimization of the co-digestion process itself (evaluate other possible co-substrates, optimal mixture ratios, synergies...), to the prediction of mixtures behaviours in anaerobic digestion or the implementation of thermal hydrolysis pretreatment in a pilot scale plant in view of a full-scale process optimization (e.g. grease waste and sewage sludge in WWTP).

- **Thermal hydrolysis to municipal solid waste**: a further pilot scale-up of the process with a semi-continuous reactor would be helpful to understand and optimize the pretreatment, in order to perform a more precise economic evaluation and scale-up. As well, the importance of the pre-selection process (cleaning or separation process) before thermal hydrolysis should be further studied to check its feasibility in full-scale plants.

- **Optimization of thermal hydrolysis technology**: evaluate different configurations to carry out the pretreatment such as partial hydrolysis, hydrolysis to a recycled fraction, hydrolysis between two digestions (inter-stage hydrolysis)... in view of minimising the steam consumption, retention times, operational and capital costs.

SCIENTIFIC OUTPUT

Publications in journals:

Optimization of municipal sludge and grease co-digestion using disintegration technologies. (2012) L. Bouchy, A. Pérez, P. Camacho, P. Rubio, G. Silvestre, B. Fernández, R. Cano, M. Polanco and N. Díaz (Water Science and Technology)

Thermal hydrolysis integration in the anaerobic digestion process of different solid wastes: energy and economic feasibility study. (Accepted for publication) (2014) Cano R., Nielfa A., Fdz-Polanco M. (special issue “Advance Biological Treatment Technologies for Sustainable Waste Management” from Bioressource Technology)

Grease waste and sewage sludge co-digestion enhancement by thermal hydrolysis: batch and fed-batch assays. (Accepted for publication) (2014) Cano R., Nielfa A., Pérez A., Bouchy L., Fdz-Polanco M. (Water Science and Technology)

Papers submitted or in preparation to journals:

Energy feasibility study of sludge pretreatments: a review. (*Review submission*) Cano R., Fdz-Polanco F., Pérez-Elvira S.I. (Chemical Engineering Journal)

Publications in Congress proceedings

- International Water Week (Amsterdam, Netherlands, Nov. 2011). Poster presentation: O*ptimization of cow manure and sewage sludge co-digestion using pre-treatment technologies.*
- ORBIT (Rennes, France, Jun. 2012). Oral presentation: *Optimization of cow manure and sewage sludge co-digestion using disintegration technologies.*
- European Biosolids and Organic Resources conference (Leeds, UK, Nov. 2012): Oral presentation: *Ultrasounds and thermal hydrolysis pretreatments to enhance municipal solid waste anaerobic digestion.*
- 13th World Congress on Anaerobic Digestion (Santiago de Compostela, Spain, Jun. 2013). Poster presentation: *Anaerobic BMP tests modelling to study the effect of thermal hydrolysis pretreatment in different solid wastes.*

ANNEXES

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