Hydrothermal Processes as an Alternative to Conventional Sewage Sludge Management

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- Data collection and laboratory analysis: I conducted all the experimental work and data analysis described in the publications. Mr. Grasham contributed to computer modelling in ASPEN Plus presented in Chapter 5.
- Writing the paper: I was lead author of all the publications. I defined the structure of the paper and wrote all the sections, which were reviewed by my supervisors and other co-authors. Their comments were added accordingly.

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Abstract

Sewage sludge management is one of the biggest concerns to the wastewater industry due to the increasing volumes produced and new stringent environmental regulations. Hydrothermal Treatments (HT) are a good option for converting wet biomass such as sewage sludge into high value products. However, HT are still not well developed when compared with other waste processing treatments. One of the most promising areas for developing hydrothermal processing applications is in sewage sludge treatment facilities. Sewage sludge has been identified as a potential feedstock for hydrothermal processing that could make use of existing facilities currently in place in wastewater treatment works (WWTWs). In order to look for options aimed at reducing the costs of the WWT process and digestate management by delivering a sustainable and novel approach, the aim of this project is to assess alternatives to enhance the way sewage sludge is handled in WWTWs, by focusing on the use of hydrothermal processes and the potential of recovering energy and nutrients. The potential of integrating HT Processes with AD for sewage sludge treatment was evaluated. Hydrochar yields ranged from 38 to 68% at 160°C and from 29 and 40% at 250°C for all thermal treated sewage sludge samples. The soluble fraction of organic carbon increased in primary sludge digestate (525%), secondary sludge digestate (808%) and sewage digestate sludge (675%) after thermal treatments compared with the untreated digestates. Figures from Biomethane Potential (BMP) tests showed that hydrothermal treatment enhanced methane production in all non-AD and AD sludge samples processed. Mass and energy balances were carried out from six proposed process configurations from different sewage sludge feedstocks and their digestates (primary, secondary and 1:1 Mix) in order to evaluate the waste generation, nutrients potential fate, net energy production and potential profit. The results showed the HTC at higher temperatures (250°C) seems to have more economic and environmental benefits. Scenarios that involved primary and mix sludge seemed to be the most suitable options in terms of the organic matter removal, energy harnessing and economic feasibility.

Table of Contents

List of figures

List of Tables

List of Acronyms and Abbreviations

AD	Anaerobic digestion
ADPS	Anaerobic digested primary sludge
ADSS	Anaerobic digested secondart sludge
ATH	Advance thermal hydrolysis
BMP	Biomethane Potential
CHP	Combine heat power
COD	Chemical oxygen demand
CSTR	Continuous stirred reactor
DEFRA	Department of Environmental Food and Rural Affairs
EU	European Union
FIT	Feed in Tariff
GEMA	Gas and Electricity Markets Authority
HT	Hydrothermal treatment
HTC	Hydrothermal carbonisation
HTL	Hydrothermal liquefaction
HTG	Hydrothermal gasification
HTP	Hydrothermal process
HHV	High Heating Value
MAD	Mesophilic anaerobic digestion
MSW	Municipal solid waste
PW	Process water
PS	Primary sludge
SS	Secondary sludge
ROI	Return of investment
SCOD	Soluble chemical oxygen demand
SVS	Suspended volatile solids
TCOD	Total chemical oxygen demand

TKN	Total Kjeldahl nitrogen
TS	Total solids
VFA(s)	Volatile fatty acid(s)
VS	Volatile solids
UK	United Kingdom
WWTW(s)	Waste Water treatment work(s)

Chapter 1. Introduction

1.1. Background

Over the past decade, sludge management at Waste Water Treatment Works (WWTWs) has been considered one of the biggest concerns for water companies and environment protection agencies. In the UK, over 16 billion litres of waste water per day are collected and treated in 9,000 WWTWs before they are discharged to inland waters, estuaries or the sea (DEFRA, 2012a). That implies the need for suitable treatment processes to be carried out in order to reduce potential risks to the environment and public health. As a result of that, around 1.4 million tonnes (dry weight) of sewage sludge are produced annually in the UK (DEFRA, 2012b).

Sewage sludge can be used for the production of energy due to its large organic matter content (Kim et al., 2014). Anaerobic digestion (AD) has been commonly used for sewage sludge treatment as this feedstock does not need to be dried or dewatered before treatment, which reduces net operational costs. In the UK, around 75% of the total sewage sludge produced undergoes anaerobic digestion (DEFRA, 2012b). The main purpose of the anaerobic digestion process is to stabilise the organic matter present in sewage sludge before disposal and to produce bioenergy in the form of methane to reduce net energy costs. Sewage sludge contains complex biodegradable organic compounds that must be solubilised and broken down into smaller monomers before being assimilated by anaerobic bacteria (Gunnerson and Stuckey, 1986). According to Abelleira-Pereira et al. (2015) and Hindle (2013) only one half of the organic matter in sewage sludge is susceptible to anaerobic biodegradation, resulting in biogas formation. Anaerobic digestion is considered as an economical and sustainable technology for sewage sludge stabilisation, considering the beneficial production of methane that can be used to produce electricity and heat at WWTWs (Abelleira-Pereira et al., 2015, Hindle, 2013).

After anaerobic digestion, the treated sludge contained in AD reactors (digestate) requires proper disposal. Currently, the main routes for the disposal of digestate in the UK includes some pre-treatment processes to reduce moisture (thickening, dewatering, centrifugation, filtration, etc.), before final disposal on agricultural land (79%), incineration (18%) or landfilling (0.6%) (DEFRA, 2012b).

However, the large quantities and characteristics of sewage sludge that are being produced, treated and disposed, have induced changes into the European Directive regarding requirements for sewage sludge application on agricultural land. Currently, the EU Sludge Directive 86/278/ECC only limit the presence of seven heavy metals for sewage sludge intended for agricultural use and sludge treated-soils. According to Dichtl et al. (2007), the European Commission is assessing whether the current Sludge Directive should be revised in order to set additional requirements, including the presence of organic compounds and more stringent limits for hazardous substances, which will demand higher quality requirements for treated sludge if the current disposal route to land is used. Because of these imminent changes, it is expected that the disposal of sewage sludge and digestate on land will no longer be accepted despite their valuable nutrient and organic material content.

As a consequence, WWTWs will have to face the very difficult task of finding alternatives to current sewage sludge treatment and final disposal routes and therefore, there is a clear opportunity for developing innovative solutions that simultaneously help to deal with this emerging challenge and delivering sustainable targets set by the wastewater industry in terms of energy efficiency, renewable energy generation and nutrient recovery. Furthermore, the increasing amounts of sludge being produced in WWTWs encourage researchers and engineers to pay more attention to particular aspects of the current management of sewage sludge, especially considering the opportunities for bioenergy generation and resource recovery and reuse. The challenge here is to achieve an effective and sustainable approach delivering three important targets: (a) reduce the amount of “waste” returning to the environment; (b) generate an income stream from the recovery and reuse of valuable resources embedded in waste streams; and (c) reduce the overall treatment costs by considering the implications of new sewage management options and the changes in the water, carbon and nutrient cycles within WWTWs (Abelleira-Pereira et al., 2015).

Therefore, it is important to investigate new technologies capable of treating sewage sludge and change perceptions about using sewage sludge as a future energy resource (Almeida, 2010, Danso-Boateng et al., 2015, He et al., 2013, Kim et al., 2014).

Hydrothermal processing is currently being considered as an alternative technology to further harness energy from sewage sludge and digestate (He et al., 2013, Zhao et al., 2014) and to reduce the issues related to current disposal of final solid products. Hydrothermal processing involves the treatment of biomass in hot compressed water and depending upon process severity, can produce either a solid hydrochar, a biocrude or a syngas. The main aim of the hydrothermal processing routes is energy densification, which is produced largely by the removal of oxygen. Hydrothermal pre-treatment can also be used to enhance the sludge solubilisation and subsequent biogas production when processed by anaerobic digestion (Wirth et al., 2015, Wang et al., 2010). Conventional Thermal Hydrolysis (TH) is carried out at 170°C and produces a sludge that is more biodegradable than the raw sludge (Shana et al., 2013). When it is applied at lower temperature in the presence of hydrogen peroxide, it is referred to as Advanced Thermal Hydrolysis (ATH) (Abelleira et al., 2012).

Depending on the temperature and pressure that it is applied, the products from hydrothermal processes are different. At temperatures ranging from 200°C to 250°C, the process is referred to as HT carbonization (HTC) and predominantly produces a solid biocoal like product called hydrochar; at intermediate temperatures of approximately 250–375°C, the process is known as HT liquefaction (HTL), primarily producing an oil referred to as biocrude; at the higher temperature range (i.e., greater than 375°C), the process is called HT gasification (HTG), predominantly producing a gas product containing CO, H_2 and methane (syngas). The hydrochar produced from HTC can be co-fired with coal or used as soil amendment; the biocrude from HTL can be upgraded to a variety of fuels and chemicals, while the syngas from HTG can be used for combustion or converted to hydrocarbons by either biological or catalytic processing (Biller and Ross, 2012).

It is known that the digestate (i.e., sewage sludge following anaerobic digestion) still has large amounts of organic matter (Kim et al., 2014) and converting this organic matter by hydrothermal carbonisation into bio-coal may be possible, which in return would bring alternative disposal routes to digestate. Hydrothermal processing also generates a “process water" that is rich in organic compounds and cannot be directly disposed into the environment (Almeida, 2010, Becker et al., 2014, Kim et al., 2014, Stemann et al., 2013, Wirth et al., 2015, Zhao et al., 2014). The treatment of this “waste stream” is essential and it has been proposed that it can be treated anaerobically enhancing net biogas yields.

According to Mumme et al. (2015) and Sridhar Pilli et al. (2015) the integration of the HT step into the waste water systems is suggested to be energy positive. In fact, CAMBI® and BIOTHELYS ® are commercial high-temperature processes that have been successfully developed as pre-treatment steps for hydrothermal hydrolysis of sewage sludge, resulting in extra methane production to up to 43%, when compared with conventional AD processes without pre-treatment (Sridhar Pilli et al., 2015). However, HT as a post-treatment step after AD is an approach that is still under research and development, but preliminary findings have shown that this approach could be even more effective with regard to overall energy production from sewage sludge. Aragón-Briceño et al. (2017) found that thermal treatment of sewage sludge as a post-treatment step can improve the overall energy production up to 179% compared with the 43% extra energy of the thermal hydrolysis as pre-treatment. Therefore, further research on process conditions and overall benefits from hydrothermal processes as a post-treatment step after AD is still needed.

In this research project, it is considered that the use of Hydrothermal Treatments is not only a suitable option to effectively handle sewage sludge, considering future vetoes on sludge-to-land practices, but it can also help to obtain valuable by-products (i.e., biochar, bio-oils, syngas, bio-fertilisers, etc.).

1.2. Aim, scope and objectives

Due to the increasing amount of digestate produced in WWTWs, and a potential ban on the current final disposal route on agricultural land, there is a need to look for options aimed at reducing operational costs at WWTW, including digestate stabilisation and disposal, by delivering a sustainable approach. Therefore, the aim of this project is to assess alternatives to enhance the way sewage sludge and digestate is handled in WWTWs, by focusing on the use of hydrothermal processes and the potential of recovering energy and nutrients. The scope of this project is to assess at lab scale such alternatives by introducing hydrothermal processes in sewage sludge management in modern WWTWs.

The specific objectives for this research project are:

- To evaluate the effect of temperature during HTC processing conditions of sewage digestate on product yields and the characteristics of the different by-products.
- To evaluate the influence of solid loading on hydrochar and process water characteristics from HTC of sewage digestate.
- To investigate the changes that occur in sewage sludge samples collected at various stages along treatment process units in a conventional WWTW, when subjected to hydrothermal processes at different temperatures.
- To assess the integration of HTP with AD through mass and energy balances from proposed process configurations from different sewage sludge based on the results obtained from experimental analyses.

1.3. Structure of Thesis

This thesis is organized in nine chapters with the introduction section constituting the first chapter. In this chapter the background, aim, scope and objectives are highlighted. Chapter 2 presents a thorough literature review that focuses on the problematics of sewage sludge management in the UK, AD as a common option to deal with sewage sludge and opportunities from hydrothermal treatments as potential processes to be integrated with the AD.

Chapter 3 describes the general methodology followed for all the experiments carried out. Nevertheless, more detailed methodology is included in each result chapter.

In chapters 4 to 7, the results are reported for each stage of this project. Every chapter has been written following a style similar to journal papers and hence, they contain several sections including an introduction, materials and methods, results and discussions, conclusions, summary and list of publications and awards derived from each chapter.

Chapter 4: This chapter “Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatmen”t is related with objective 1. This research investigates the effect of process temperature on the characteristics of hydrochars and process waters from hydrothermal processing of sewage digestate and compares the yields and characteristics of the different products including the fate of nitrogen and phosphorus species. In addition, experimental biomethane potential (BMP) tests were conducted on process waters on their own and in combination with hydrochars to assess the effect that hydrochars may have on AD processes. The results from experimental BMP tests were compared to theoretical predictive models.

Chapter 5: “Hydrothermal Carbonization of Sewage Digestate: Influence of the solid loading on hydrochar and process water characteristics” is related with objective 2. In this chapter the influence of solid loading on the composition of the resulting hydrochar and process water from sewage digestate is presented. An evaluation of product yields, solubilisation of organic carbon and biomethane potential of the process water is compared for 2.5-30% solid loadings at a HTC temperature of 250°C with a 30-minute reaction time.

Chapter 6: “Evaluation and comparison of product yields and bio-methane potential from hydrothermally treated sewage sludge” is related with objective 3. In this chapter the potential of hydrothermal processing as a novel alternative for sewage sludge treatment was evaluated. Primary, secondary and digestate sludge were treated using hydrothermal processes. The effect of process temperature was evaluated with regard to product yields, biomethane potential and solubilisation of organic carbon and nutrients. Tests at 160 and 250°C for 30-minute reaction time were carried out.

Chapter 7: “Mass and Energy Integration Study of Hydrothermal Carbonization with Anaerobic Digestion of Sewage Sludge” is related with objective 4. In this chapter the potential of integration of HTC with AD for sewage sludge treatment was evaluated. Mass and energy balances were carried out from six proposed process configurations from different sewage sludge and digestates (primary, secondary and 1:1 Mix) in order to evaluate the waste generation, nutrients potential fate, net energy production and potential profit.

Chapter 8 contains a general discussion that summarizes research findings and a critical analysis against published research in the field. Finally, Chapter 9 presents the general conclusions from this research work and recommendations for further studies.

Chapter 2. LITERATURE REVIEW

2.1. Water Supply in the UK

According to the Drinking Water Inspectorate (2014), there are 53 million people benefiting from water supply services in the UK. That effectively means a total drinking water production of 13,707 million L/day, which is supplied by water treatment plants across the UK. That water comes from different sources including surface waters (64.1%), groundwater (30.1%) and others considered mixed sources (5.8%) (DEFRA, 2012b)

The main role of water companies in the UK is to collect, clean and deliver safe drinking water to their customers and to collect and clean waste water before returning it to the environment.

One of the main ways in which water sources can be affected is by the amount of water abstracted to meet the increasing demand from the UK's fast growing population, and by the quality of the discharged effluent from wastewater treatment systems. "*Pollution imposes not only environmental costs through its effect on aquatic life, but also financial costs from the treatment of water for drinking. The accumulative cost of water pollution in England and Wales has been estimated at up to £1.3 billion per annum*" (NAO, 2010).

According to NAO (2010) , water pollution derives from two sources:

1. Point Source Pollution: It comes from a single identifiable source such as a factory or sewage treatment works.
2. Diffuse pollution: It is caused by excessive or improper use of fertilisers, poor management of waste or livestock on farms, the run-off of chemical from light industry or wrongly connected domestic or commercial drainage systems. It is very difficult to identify where the pollution is coming from the agricultural sector is considered the major contributor of diffuse pollution, but urban sources contributes to diffuse pollution too.

On average, 80% of all drinking water supplied to UK households will become domestic wastewater, and in addition to trade wastewater, it is expected that the production of sewage and sewage sludge will continue increasing as a consequence of population and economic growth (NAO, 2010).

2.2. European Water Framework Directive (WFD)

The European Water Framework Directive came into force in December 2000 and became part of UK law in December 2003. It consolidates a number of pieces of EU legislation.

The directive is designed to help, protect and enhance the quality of:

1. Surface freshwater (including lakes and rivers).
2. Groundwater
3. Groundwater dependant ecosystems
4. Estuaries
5. Coastal waters out to one mile from low-water.

The specific goal of the WFD is for all EU member states to achieve “good” ecological and chemical status for these water courses (Servern Trent Water, 2013).

From the point of view of the UK Water Industry, the requirements of the European Framework are getting more stringent every day, the investment in maintenance is increasing and the profit is getting tight. This is reflected in higher bills for customers, increasing carbon emissions and higher debts to the companies and customers. Therefore, UK water companies have recognised the need to increase the efficiency of their water treatment systems and the production of renewable energy. To continue delivering effective services, the UK water sector has also identified the need to improve their processes through much greater innovation (Servern Trent Water, 2010).

According to Servern Trent Water (2010), the EU framework policies do not consider:

1. Sufficient account of the impact of carbon emissions or costumer bills.
2. Supply issues are addressed using regionally focused, capital intensive solutions. It means that current regulatory framework

encourages the companies to look for a new water sources because the demand is increasing.

3. Economic regulation no longer provides the right incentives. This affect the investment in innovation in the water companies because there are not sufficient money to encourage companies to create new technology. The companies have tended to apply standards, capital-intensive solutions to meet regulatory requirements because that’s represent the “cheaper” option in the short term. It is not sustainable for them invest in long term solutions despite the fact that it may be profitable.

This make believe that now is a critical time for the UK Water Sector with a stake in the industry to question what future direction they should take. Without significant changes to the policy and regulatory framework the sector does not look sustainable. While the framework has delivered higher customer and environmental standards, the consequences have been significant water company debt, higher bills to customers and increased carbon emissions (Priestley, 2015).

In England, 35% of rivers achieved a good or very good status in 2017 under the actual Water Framework Directive, lightly lower compared from 36% in 2012 (DEFRA, 2018). In 2010 in England, when new regulations implemented by the EU Drinking Water Directive for private supplies were introduced, 9.6% of water treatment plants did not pass the tests on public water supplies. In 2013 however , only 0.3% of tests on public water supplies failed to meet both EU and National Standards, due the new technologies that have been implemented (Drinking Water Inspectorate, 2014). However, the European Water Framework Directive requires Member States to achieve “good status” in all natural bodies by 2027. This will not be possible to achieve using current technologies and the strict standards but instead, UK government aimed to set out a longer term goal by 2050 (Priestley, 2015). According to DEFRA and The Environmental Agency (2018), the UK water companies will spend over £5 billion to benefit the natural environment. Neverthless, an assessment made by The Environmental Agengy (2015) showed that cost for meeting the WFD goals, that will benefit from preventing deterioration and improving the water environment, would be around £23 billion.

2.3. Sewage Sludge in the UK

According to DEFRA (2012b), about 11 billion litres of waste water in the UK were collected and treated in 9,000 WWTWs before the effluent was discharged to inland waters, estuaries or the sea. That implies the need for suitable treatment processes to be carried out in order to avoid potential damage to the environment and public health problems.

The treatment of waste water has the objective of returning cleaner water to the environment. As a consequence large quantities of sewage sludge are generated. The sewage sludge comes from the organic matter used in treatment process or biosolids removed from the waste water being treated. Sewage sludge contains organic matter (i.e., carbohydrates, fats, proteins, faecal material, etc.) and chemicals. (DEFRA, 2002, DEFRA, 2012b).

In the past, part of the sewage sludge was discharged to surface waters or into the sea. However in 1998, the European Directive required the cessation of these practices and made a call to find and use alternatives to re-use or dispose of sewage sludge (DEFRA, 2012b). The changes to re-use and disposal routes are shown in **Table 2.1**, where the baseline of 1992 is contrasted with the situation in 2008 and 2010.

Table 2.1.- Sewage sludge reuse and disposal routes – tonnes dry solids (DEFRA, 2012b).

Reuse or Disposal Route	Sludge Discharged to Surface Waters			Sludge Reused		Sludge Disposed			Total
	Pipelines	Ships	Others	Soil & Agriculture	Others	Landfill	Incineration	Others	
1992	8,340	273,158	-	440,137	32,100	129,748	89,800	24,300	999,673
2008	-	-	-	1,241,639	90,845	10,882	185,890	1,523	1,530,779
2010	-	-	-	1,118,159	23,385	8,787	259,642	2,863	1,412,836

One of the most commonly used alternatives for sewage sludge management is spreading on agricultural land, because the sludge can be used as an alternative soil building-material and fertiliser due to its phosphate content and for being a source of slow– release nitrogen for land restoration (DEFRA, 2012a). Nevertheless, the big quantities of sewage sludge that are being produced and applied have induced changes into the European Directive regarding requirements for sewage sludge application on agricultural land. Because of those changes, it is expected that the disposal of sewage sludge on land will no longer be accepted despite its nutrient and organic material content, as lower limits for hazardous substances and higher quality requirements in general are likely to be imposed. With these new restrictions, sewage sludge will hardly be suitable for agricultural reuse (Dichtl *et al*., 2007). That makes think of new alternatives to deal with sewage sludge in WWTWs.

The focus is on alternative sewage sludge treatment technologies that gain the most economical and ecological benefit from the sludge's valuables. Several technologies for nutrient recovery, especially phosphorus have been developed.

2.3.1.Sewage Sludge Management

The large amount of sewage sludge generated at WWTWs, has made its treatment an important issue not only in the UK, but also worldwide. However, any approach to sludge management always needs to consider legal boundaries and operational costs before making a decision about the selected disposal method.

Today around 1.4 million tonnes (dry weight) of sewage sludge are produced annually in the UK. The disposal methods include spread on farmland (58%), incineration (16%) and power generation via gasification (3.5%) and others (22.5%) including direct application on forrests, compost or another methods (BIOMASS Energy Centre, 2011).

Disposal methods in the UK for sewage sludge are described as follows (ISWA and EEA, 1997, Thames Water Ltd, 2008):

- Agricultural use: The main objective is to utilise nutrients such as phosphorus and nitrogen and partly to utilise organic substances for soil improvement.
- Composting: Composting aims to stabilize biologically the sludge controlling pollution risks in order to develop agriculture or other end

use outlets exploiting the nutrient or organic value. Composting involves aerobic degradation of organic matter, as well as a potential decrease of the sludge water content, the efficiency of which depends on the composting process. Is considered a valuable soil improver.

- Incineration: The process is done at high temperatures (over 800 Celsius degrees) and consists of burning the waste and recovering some heat to reuse in the process. The waste generated is ash that mainly consists of heavy metals.
- Landfilling: the process consists of placing the sewage sludge in the landfill as layers between each level. Landfilling will have the lowest priority in the waste hierarchy and will only be chosen when no other ways to dispose of the sludge exist. It is not an option when the place has a vulnerable geologic media.

Moreover the sewage sludge can be dried and used for energy generation. Methods like combustion, gasification, pyrolysis and anaerobic digestion are often used. However AD is most common because does not need the sludge to be dried or dewatered before treatment (less operation costs).

Researchers like Danso-Boateng *et al*. (2015) and He *et al*. (2013) mention that sewage sludge has attracted great attention as a promising feedstock for the production of renewable biofuels.

2.4. Anaerobic Digestion in UK

In last years, the number of researchers studying anaerobic digestion has increased due to its potential to support the production of valuable products in a biobased economy. The AD treatment of organic wastes decreases the amount of organic solids for final disposal and it is considered a clean technology based on its capacity to support bioenergy production (Wang *et al.*, 2010). That shows the importance of this technology in waste water treatment (Cano *et al*., 2014, Hindle, 2013). A wide range of wastes are susceptible to being degraded anaerobically, as it is reported by Carlsson *et al*. (2012): municipal wastes, organic wastes from food industry, energy crops, agricultural residues, manure and waste water treatment plant residues.

Conventional AD brings economic and environmental benefits. One of the advantages of anaerobic digestion is the production of methane, which can be used as a source of energy for the production of electricity and heat. Furthermore, it can be used just like “natural gas” in many other applications (Abelleira-Pereira *et al*., 2015, Hindle, 2013).

AD of solid residues is commonly practiced in municipal waste management to stabilize organic waste, reduce solid volume and at least partially disinfect solids prior to disposal. Many AD facilities have the added benefit of energy recovery via methane production (Elliott and Mahmood, 2007, DEFRA, 2012b). The majority of anaerobic digesters operating in the municipal sector use single phase mesophilic reactors (Erdal *et al*., 2006). The use of thermophilic digesters has become more attractive due to their performance, better pathogen destruction and higher digestions rates, which allow the anaerobic digestion facilities to operate at higher loading rates with smaller reactor volumes (Erdal *et al*., 2006). Thermophilic digestion can reduce the amount of difficult-to-degrade organic materials, thus improving the overall removal efficiency of organics. Negative aspects of thermophilic digestion include increased operator attention, higher odour release potential, higher susceptibility to process upsets and poorer quality of dewatering filtrate (Erdal *et al*., 2006, Tchobanoglous *et al*., 2003). Two stage digestion systems, which segregate the formation of volatile fatty acids from methanogenesis, have also been developed, improving the overall digester performance (Shana et al., 2011).

According to ADBA (2015) the AD sector in the UK grew 33% from 2013 to 2014. It means that by 2014 in UK there were around 150 non wastewater anaerobic digesters plants and 250 anaerobic digesters plants serving WWTWs. Moreover, DEFRA (2012b) reported that 75% of sewage sludge generated from treatment processes undergoes anaerobic digestion. Anaerobic digestion technology for sewage sludge in wastewater treatment plants (WWTWs) has been widely spread for decades (Cano *et al*., 2014).

During the anaerobic digestion process, sludge constituents are solubilised by bacterial action and accumulated in the aqueous phase (i.e., soluble chemical oxygen demand (COD) increases). Soluble COD is in turn fermented into volatile fatty acids (VFAs), which are ultimately converted into biogas (i.e., methane and carbon dioxide) by methanogens. This highlights the importance of considering sewage sludge as a process by product that can be considered as an income stream for WWTWs. In fact, there are a number of practical examples in which better use of sewage sludge can be made (Servern Trent Water, 2013):

- Energy generation: Water companies can produce around 200GW/h of electricity from sewage sludge, which is about 25% of their total needs.
- Fertiliser production. Sewage Digestate is rich in phosphorous and nitrogen and, when treated, it can be used as a secondary source for commercial fertilisers.
- Phosphorous production. Phosphorous is a scare resource and is used in many other products as well as fertiliser, for steel production and in the manufacture of some detergents.

In summary, recent escalation of energy costs and technical advances in anaerobic technology have subsequently made anaerobic digestion one of the most cost/effective alternatives to sewage sludge disposal, particularly because latest technological advances hold the potential for higher methane recuperation while using smaller reactors (Elliott and Mahmood, 2007).

2.4.1.Anaerobic Digestion Pre-treatments

In order to improve the AD performance, various technologies has been developed as pre-treatment of the sludge. The benefits of sludge solubilisation prior to anaerobic treatment are twofold; Firstly, the increase in the amount of released soluble substrate significantly increases VFA generation for subsequent improved gas production and secondly, pretreatment reduces the viscosity of the sludge, enabling a greater solids concentration to enter an anaerobic reactor. Higher feed solids either result in increased digestion times in an existing reactor or allow for a smaller reactor volume (Elliott and Mahmood, 2007).

As it is showed in the **Table 2.2**, most of pre-treatments enhance the solubilisation of organic matter (COD), volatile solids reduction and gas production. However, there are not a pre-treatment method that can be determined as being the best all round solution.

Table 2.2.- Different Pre-treatments for enhance the anaerobic digestion.

Pre-treatment	Principle	Effect
Ultrasound	The process consists in appling high-frequency sound waves (generated by a vibrating probe) that makes that the cell walls ruptured due the pressure drop below the evaporating pressure forming gas bubbles. As a result of the gas bubbles, the temperature and pressure gradients increments in the liquid phase which ruptures cell membrane, releasing intercellular matter in the bulk solution.*	COD removal: 11-39%.Volatile solids reduction: 54% (Khanal et al., 2006). Gas production increment: 17% (Muller et al., 2003).
Thermal	It is the exposure of the sludge to high temperatures (105-200°C to enhance the cellular disintegration and thus reduces the time required for hydrolysis step in the anaerobic digestion process.*	COD removal: 60-71%.Volatile solids reduction: 36-59%. Gas production increment: 54-92% (Valo et al., 2004).
Ozone oxidation	Mechanistically ozone reacts with polysaccharides, proteins, and lipids (which are components of cell membranes), transforming them into smaller molecular weight compounds (Bablon et al., 1991). In doing so, the cellular membrane is ruptured, spilling the cell's cytoplasm. If the ozone dose is sufficiently high, mineralization of the released cellular components could also occur (Elliott and Mahmood, 2007).	Volatile solids reduction is about 56% (Sievers et al., 2004).
Alkaline	Heo et al (2003) demonstrated how alkali addition alone is capable of solubilizing Sludge.*	COD solubilisation between 28-38% and gas production was increased between 66-88% (Heo et al., 2003).
Mechanical	The hydrolysis of cellular membranes can also be achieved by mechanical rupturing techniques. The two predominant techniques used are the Kady mill, which uses two counters rotating plates to produce shear (Increases the soluble COD in a 25%), and the wet milling, which is more of a grinding method.*	COD solubilisation until 25%.*
Enzymatic	Enzymes: these products are used for accelerate the cellular degradation.*	

* Elliot and Mahmood (2007)

2.5. Thermal Hydrolysis

AD presents two main concerns in the process: low yield of the organic dry solids degradation efficiency (less than 30-50%) and low methane production at mesophilic conditions (Appels *et al.*, 2011, Hindle, 2013, Ruiz-Hernando *et al*., 2014, Schievano *et al*., 2012, Strong *et al*., 2011, Weiland, 2010).

It is known that the methane production and the organic dry solids degradation are directly related with the methanogenic process. The methanogenic process is limited by the hydrolysis rate of organic matter (i.e., flocs, micro flocs, aggregates of extracellular polymeric substances, recalcitrant compounds of proteins and lipids, as well as component of hard cell walls) and this rate could be limited when the hydraulic retention time is low. That's increase the risk of washing out the methanogens population from digesters (Abelleira-Pereira *et al*., 2015, Carballa *et al*., 2011, Cano *et al*., 2014, Shana *et al*., 2013, Strong *et al*., 2011). Furthermore, the infrastructure has high costs and represents an obstacle for AD development. For these reasons many researchers are looking to improve the methane production throughout the enhancing of the hydrolysis rate (Abelleira-Pereira *et al*., 2015, Hindle, 2013).

The recognition of the sludge hydrolysis stage as being the main rate limiting factor in anaerobic digestion of sewage sludge has led to the development and application of sludge pre-treatment technologies and thus the intensification of the process (Shana *et al*., 2013).

The most widespread pre-treatment for AD used in Europe is the Thermal Hydrolysis Process (THP) where sludge is heated to about 170°C and 7 bar pressure for about 30 min and then anaerobically digested (Shana *et al*., 2013). The aim of the THP is to break the long chain bonds of organic compounds to improve the physical and chemical properties of the sludge to be digested in the AD process (Wang *et al*., 2010). In addition, THP is used to accelerate the hydrolysis step leading to high solubilisation, pathogen reduction, good dewaterability and increase biogas production. The energy input needed for the hydrolysis process is thermal energy and could be satisfied from the energy production of the process, resulting in an energetically self-sufficient process (Abelleira-Pereira *et al.*, 2015, Pérez-Elvira *et al*., 2008).

The study of Cano et al. (2014) determined that a proper energy integration design could lead to important economic savings (5€/ton) and TH can enhance up to 40% the income of the digestion plant, even doubling them when digestate management costs are considered. Moreover, THP increases the methane production up to 50% and makes the sludge digestion process more tolerant to organic matter shock load and improves sludge volatile reduction (VSR) from 30-50% to 50-60% (Cano et al., 2014, Panter, 2008).

Perez-Elvira *et al*. (2010) reported 40% higher yield of biogas form the system TH+AD than from other conventional. Studies by Donoso-Bravo *et al.* (2011) reported 55% higher yield of biogas with TH + AD configuration. Abelleira-Pereira *et al*. (2015) did a study of THP as pre-treatment and reported that THP improval the volatile solids removal (37.6%) and the net electricity production would be over 20% higher than conventional AD.

Other researchers studied THP as an intermediate digestion step concluding there was an enhancement on the already digested sludge organic matter degradation, sludge mass reduction and biogas production (Shana *et al*., 2013). Shana et al. (2011) also showed that the novel intermediate THP configuration produced 20% more biogas compared to THP configuration (MAD + ITHP + MAD) with around 62% methane composition and 66% volatile solid reduction.

One of the most common commercially available thermal processes used is the CAMBI process developed by a Norwegian company, Cambi. This process involves heating sludge to 165 °C for 30 min (see **Figure 2.1**) in which the biogas production increases as a result of 60% VS reduction. Other benefits of this process are the solid dewatering improvement and the increase of the digester capacity as a result of the lower viscosity of processed solids (Panter and Kleiven, 2005). The CAMBI process uses live steam to preheat the sludge to 100 °C minimizing operational and corrosion problems (Elliott and Mahmood, 2007, Weisz and Solheim, 2009).

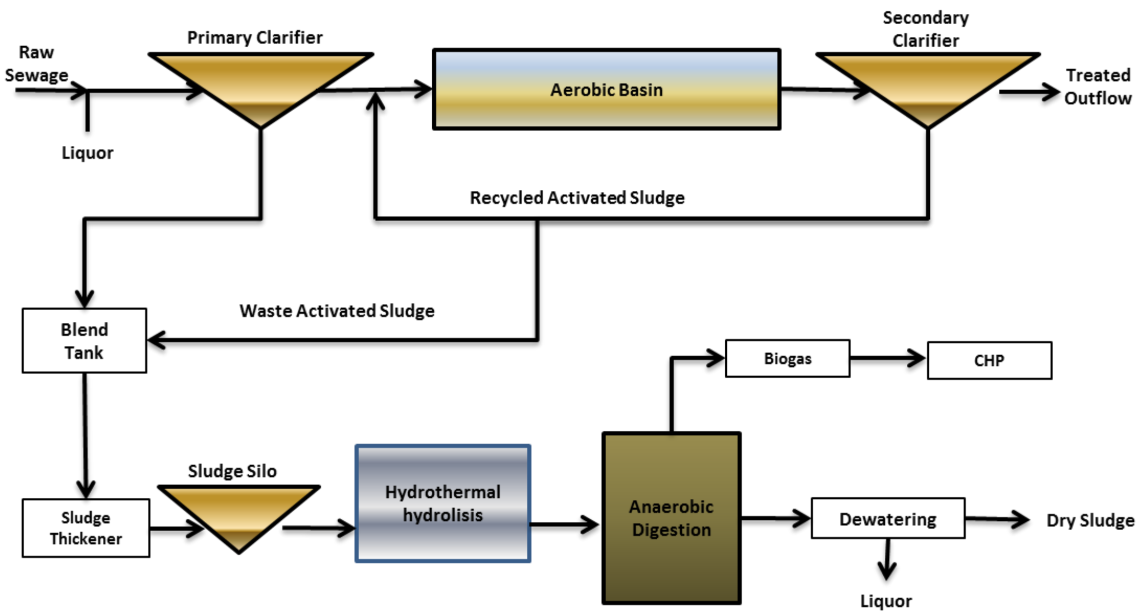


Figure 2.1.- Conventional WWTW with enhanced energy production.

2.6. Hydrothermal processes

Thermal treatments have been used mainly for improving the feedstocks characteristics as they hydrolyse the feedstock to improve the methane generation or increase the energy densification producing chars, bio-oils or syngas.

In **Table 2.3**, different thermal processes are listed with their respected process conditions and main product. Thermal treatments are commonly used to upgrade the characteristics of the biomass converting them into high energy density products. Thermal treatments such as torrefaction and pyrolysis are carried out in free oxygen and water conditions and temperatures ranging from 200 to 300°C and 500 to 1000°C respectively (Chen et al., 2015, Ronsse et al., 2013, Lee et al., 2012, Williams and Besler, 1996).

The hydrothermal treatments are carried out in the presence of water at high pressure and temperatures. The main by-product will depend mostly on the temperature and pressure conditions. Conventional Thermal Hydrolysis (TH) is carried out at 170°C and produces a sludge that is more biodegradable than the raw sludge (Shana et al., 2013). The process refers to hydrothermal carbonization (HTC) when temperatures range from 200°C to 250°C, and predominantly produces a solid biocoal like product called hydrochar; when temperatures range from 250°C to 375°C, the process is known as hydrothermal liquefaction (HTL) producing mainly an oil referred to as biocrude; when temperature range is greater than 375°C, the process is called hydrothermal gasification (HTG) and predominantly produces a gas product containing CO, H_2 and methane called syngas. These by products can be used as fuel sources to produce more energy (Biller and Ross, 2012).

Table 2.3.- Different thermal treatments used for improve the biomass characteristics

Thermal Process	Observations	Process conditions for biomass		Main product	References
		Temperature range	Pressure		
Slow pyrolysis	Limited or free of Oxygen.	500	1 atm	Char	Williams P, 1996 and Ronsse et al 2013
Fast Pyrolysis	Limited or free of Oxygen.	650-1000	1 atm	Bio-oil	Williams P, 1996 and Ronsse et al 2013
Torrefaction	Absence of oxygen.	200-300	1atm	Char	Lee et al, 2012 and Chen et al 2015
HTP	In presence of water.	Up to 180	1atm	Hydrolized sludge	Shana et al., 2013 and Sridhar et al., 2014
HTC	In presence of water.	200-250	10-40bar	Char	Danso Boateng, 2015 and Aragón-Briceño et al., 2017.
HTL	In presence of water.	280-370	10-25Mpa	Bio-crude	Toor et al 2011 and Ekpo et al. (2015)
HTG	In presence of water.	greater than 370	25Mpa	Syngas	Biller and Ross 2014 and Kruse et al 2005

According to Almeida (2010), there is a change in the perception of sewage sludge because researchers consider that sewage sludge has the potential of be an interesting energy resource. It is known that the sewage sludge has great amounts of organic matter. Adopting this fact, that organic matter content in the digestate can be harnessed to produce by-products (hydrochar, bio-oil or syngas) that can be used as fuel sources. Although, the process waters coming from hydrothermal processes are rich in organic compounds and have the potential to be digested in an anaerobic reactor (Aragón-Briceño et al., 2017). Therefore, hydrothermal processes have been considered as alternatives technologies to develop to harness energy from sewage sludge (He *et al*., 2013).

The Thermal pre-treatment know as hydrothermal hydrolysis, has been shown to be a feasible, well established and commercially implemented technology which helps to reduce volatile solids (VS) during AD, improve biodegradability (BD), increase the dewaterability, increases up to 43% methane production and produces a class A biosolid (Pilli et al., 2015). Companies like Veolia and CAMBI have successfully developed the pre-treatment steps for hydrothermal hydrolysis (See **Figure 2.1**) (Aragón-Briceño et al., 2017). Nonetheless Hydrothermal treatment as a post-treatment step after AD is a novel approach that is still under research and development, but preliminary findings have shown that this approach could be even more effective with regard to overall energy production from sewage sludge – i.e., thermal hydrolysis can help to produce as much as 179% more energy when placed as a post-treatment step than when used as a pre-treatment step for AD (See **Figure 2.2**) (Aragón-Briceño et al., 2017).

A range of different solid wastes have been studied by hydrothermal treatments (e.g., municipal solid wastes, agricultural wastes, industrial wastes, etc.), but most of the studies covering hydrothermal treatment of sewage sludge digestate have focused on the characterisation of the resulting products (Berge et al., 2011a, Danso-Boateng et al., 2015, Escala et al., 2013, Kim et al., 2014, Nipattummakul et al., 2010). Less focus has been applied on the anaerobic digestion of the liquid products following hydrothermal treatment (Wirth et al., 2015, Wirth et al., 2012). However, still there is not much information about sewage sludge despite of having the potential to be a feedstock material for thermal treatments for its high hydrocarbons and inorganics compounds contents (Nipattummakul *et al*., 2010).

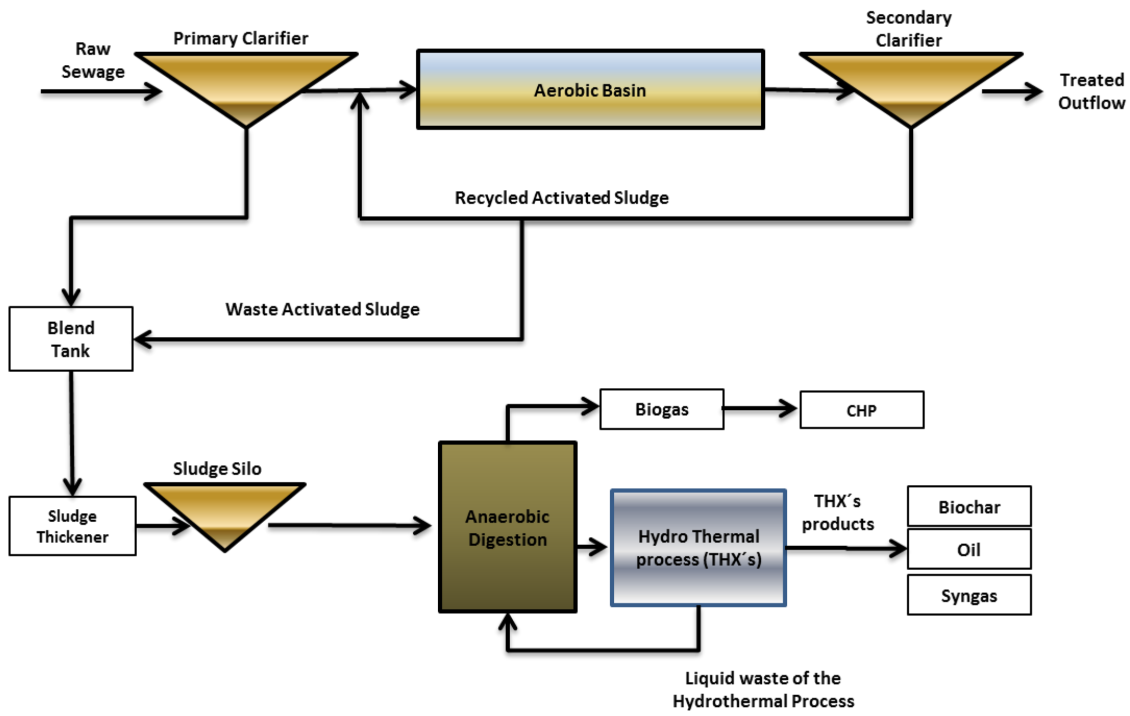


Figure 2.2.- WWTW with hydrothermal treatment after AD.

2.6.1.Hydrothermal Carbonization (HTC)

HTC is carried out at temperatures between 150 to 200 °C and for different retention times. The process consists in concentrate the carbon in a stable and easy handable material. Furthermore upgrade the poor fuels into higher energy density solid fuels. The main product is the hydrochar, and is reported to have good nutrient properties for terrestrial plants and has been proposed as a source for soil amendment and also has the potential to be co-fired with coal. The hydrochar is a novel material that has been probed in many applications as a water purification material, fuel cell catalysis, energy storage, CO2 sequestration, drug delivery and gas sensors (Biller and Ross, 2012, Danso-Boateng *et al*., 2015, He et al., 2013).

The biochar has H/C and O/C ratios comparable to that of low-grade coal but a higher calorific value than such coals and for that reason can be used as a potential fuel source. The aqueous products from HTC contain a lot of organic compounds such as furans, phenols, acetic acid, and other soluble organic compounds (Danso-Boateng *et al*., 2015). Because of that, the aqueous phase rich in organic compounds represents an issue and at the same time a challenge to be solved to avoid harm to the environment.

The advantages of applying HTC to sewage sludge is that it produces an extra value product (biochar) and sanitisation of the sludge (Catallo and Comeaux, 2008, He et al., 2013).

There are some authors that have done studies with higher temperatures than 200 °C and they still call it as HTC (Danso-Boateng et al., 2015, He et al., 2013). In the study carried out by Danso-Boateng *et al*. (2015), the authors concluded that the amount of carbon retained in hydrochars coming from primary sludge decreased as temperature and time increased with carbon retentions of 64–77% at 140 and 160 °C, and 50–62% at 180 and 200 °C. Increasing temperature and treatment time increased the energy content of the biochar from 17 to 19 MJ/kg but reduced its energy yield from 88% to 68%. He *et al*. (2013) recovered in the hydrochar 88% of carbon and removed 60% of nitrogen and sulphur.

2.6.2.Hydrothermal Liquefaction (HTL)

Hydrothermal Liquefaction of biomass consists of the conversion of biomass into liquid fuels and chemical by applying high temperatures and pressures for sufficient time to break down the solid biopolymeric structure of the liquid components (Elliott, 2011). As mentioned previously, the HTL is carried out at intermediate temperatures of approximately 200–375°C, primarily producing oil called biocrude that can be used as a biofuel (Biller and Ross, 2012). That means a good advantage over the conventional incineration because represents it has a solution to the sludge disposal problems, plus an economical benefit (Itoh *et al*., 1994).

However the products of HTL not only are composed by oils, also has a water fraction that is rich in organics, gas fraction and solid fraction which can be used as fuel sources as well.

Actually there are many companies in Europe interested in developing and commercializing the technology of HTL. Nevertheless there are a lot of points to solve before as generate and standardize the process as is the optimal conditions and what to do with the wastes of the process.

HTL in sewage sludge has been studied also in many countries such as USA, UK and Japan because of its environmentally friendly approach. Biocrude can be produced from the dewatered sludge under conditions of 300°C and 10 MPa. However there are no well defined or ideal operational conditions for HTL because the different types of sludge and this affect the biocrude production (Liu *et al*., 2012).

2.6.3.Hydrothermal Gasification (HTG)

HTG is another promising thermal treatment for its viability, efficiency and for its clean conversion of wastes into energy with minimal impact. So mainly the HTG can add value to the wastes by transforming them into a low or medium grade heating fuels (Nipattummakul *et al*., 2010).

HTG is carried out at temperatures greater than 375°C which it predominantly produces synthetic gas (syngas). Syngas is mainly composed of H_2, CO, CO_2, CH_4 and light hydrocarbons, and the variability in composition will depend on the reaction conditions. The H_2 production is favoured at temperatures greater than 500°C and below this temperature CH_4 production is favoured (Biller and Ross, 2012).

That means that the sewage sludge due its high content of organic material and organic compounds, considered a good target to produce a clean fuel with HTG. HTG is a process that can reduce the amount the volume of the solid residue while is producing syngas and oil.

2.7. Nutrients pollution in wastewater

Nutrient pollution is one of the most widespread around the world. The excess of nitrogen and phosphorus cause environmental problems that are hard to deliver and expensive to remedy.

Nitrogen and phosphorus are widespread in nature (air, soil and water) and help to the growth of algae in aquatic life, which provide food and habitat for sea life. However in great amounts, the algae will grow a lot and will be harmful to the environment, reducing the amount of oxygen in the water and sometimes producing toxics that affect directly to the sea life (EPA, 2015).

According to the EPA (2015), the nutrient pollution sources can come from agriculture, storm water, waste water, fossil fuels and at home.

It is known that the waste water, especially the sludge, is rich in nutrients such as nitrogen and phosphorous that are valuable and useful along the organic matter when the soils are depleted or subject to erosion. That means, the sewage sludge has the elements that allow it to be used as a fertiliser or soil improver (European Commission, 2015).

2.7.1.Phosphorus

With the constant growing population the generation of human wastes is alsogrowing up. Waste water is considered one of the main wastes generated from humans and it is known that it is one of the main contaminants of the environment because of its hazardousness (de-Bashan and Bashan, 2004). Due to the large amounts of organic compounds and other minerals many process have been developed to treat the wastewater. However the companies have the need to invest in better process that can be profitable, reliable and comply with the limits imposed by the governments.

One of the most studied processes is related to phosphorus because phosphorus treatment has the potential to be a profitable process.

Phosphorus is one of the most abundant elements on Earth. It is estimated that there are 7000 million tonnes of phosphate rocks as P_2O_5 remaining in reserves that could be economically mined. According to Shu et al. (2006), the human population consumes 40 million tons of P as P_2O_5 each year and it is predicted that P demand will increase by 1.5% each year.

Phosphorus is essential for all living organisms including humans who depend on phosphorous to lead healthy and productive lives and as an essential nutrient for crop production. Phosphorus represents the energy currency for organisms at cell level, and its availability often controls biological productivity; for that reason, in excess quantities, it is the cause of eutrophication (Le Corre et al., 2009, Shu et al., 2006). Eutrophication is the enrichment of nutrients of surfaces waters or other media, leading to excessive production of microbial algae resulting in toxic threat for the animal life and is the responsible for turning water green in water bodies in general.

Human products such as fertilizers, detergents and insecticides contain a lot of amounts of P as phosphates. Essentially the overdose of P in water bodies in European Union (EU) countries comes from human sources in sewage and from livestock (Morse et al., 1993). For that reason the European legislation has regulated the maximun P concentration in effluents depending on the size of discharge (EC Urban Waste Water Treatment Directive 91/271/EEC, UWWTD, 1991).

Nowadays traditional processes of P removal (biological and chemical), based on phosphorus fixation, are not enough, because they are efficient in the sense that they can reduce the P concentration in wastewater effluents to less than 1mg/L but they lead to the accumulation of phosphorus in the sludge which represents one of the main problems for the European Union, for the sludge disposal (Le Corre et al., 2009, Shu et al., 2006).

The pressure of future changes in legislation has encouraged the research community and companies to focus on recovering phosphorus from wastewater in order to comply with the allowed limits and avoid increasing the sludge volume.

2.7.2.Nitrogen

Nitrogen is an essential element that is part of all animals and plants that you can find it in several ways in the nature. It is a very important element for the plant growth; therefore is an essential element for human survival. Despite the fact that there are great amounts of nitrogen surrounding us, the nitrogen is unavailable for plants and animals; the only way that we can obtain our nitrogen is through the food we eat.

However nitrogen in big amounts is considered a pollutant. In water, nitrogen mainly comes from agriculture and sewage and that promotes eutrophication, and in the air the nitrogen mainly comes from combustion (NOx) that contributes to global warming (Lillywhite and Rahn, 2005).

According to the report written by Lillywhite and Rahn (2005), in UK exists around 475 million tonnes of natural nitrogen (nitrogen that already form part of the nature) and 4.7 million tonnes of reactive nitrogen (nitrogen that comes from external sources). Although the reactive nitrogen amount is small compared to the natural nitrogen; its impact is significant and will have consequences later (See **figure 2.3**).

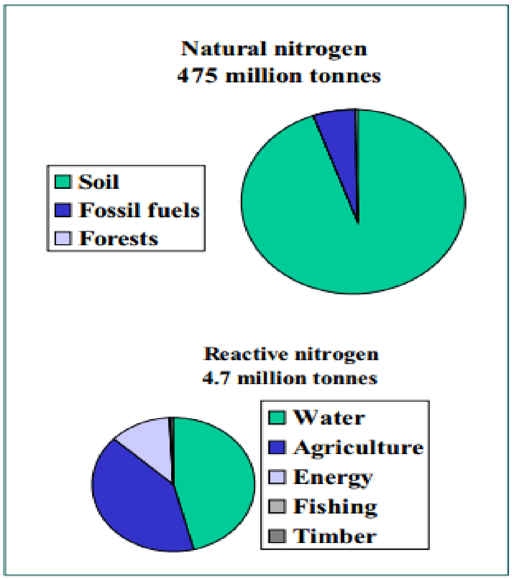


Figure 2.3.- Natural nitrogen versus reactive nitrogen in UK (Lillywhite and Rahn, 2005).

The most common way to introduce nitrogen to the environment is the use of dewatered sewage sludge as a fertilizer. The sewage sludge is considered a good fertilizer for its high content of organic material and nutrients (phosphorus and nitrogen compounds). Nevertheless when the dried sewage sludge is applied to the soil for agriculture, the nitrogen compounds can filter through the ground until they reach the groundwater and enter the aquatic system.

Many researchers have focused on removing the nitrogen in the previous stages before the drying step of the sewage sludge and use it as fertilizer. The nitrogen compound removal is carried out in the aerobic treatment stage by algae during the waste water treatment, but is expensive and the nitrogen is only absorbed and not recovered (or at least seems to be expensive to recover it). Also there are physic-chemical methods to recover nitrogen as struvite crystallization.

For that reason it is important to highlight the importance that nitrogen pollution has and look for new methods or improve the existing ones.

2.7.3.Recovering treatments for phosphorus

The most common method for phosphorus and nitrogen removal (which is one of the nutrients along with nitrogen that are targeted in wastewater discharge) is chemical precipitation and enhanced biological removal. Chemical precipitation increases sludge volume and decreases the biodegradability of the sludge making it an expensive sludge disposal option and non-viable for the future legislation requirements (Shu et al., 2006). Enhanced biological removal is very effective at removing nutrients, however it is the maintenance and energy cost that are expensive and it produces a lot of sludge with biomass.

Another low-cost, low-tech process that control environmental pollution are constructed wetlands. These are a container (as small as a bucket or as big as a very large pond) planted with mainly aquatic, but sometimes with terrestrial plants. Waste water slowly flows either horizontally or vertically from one end to the other and, in the process, the outflow is cleaner. The roots of plants, especially aquatic macrophytes, both emergent and submerged, work as a giant biological filter that removes organic matter of all kinds. At the same time, microorganisms residing in the submerged roots in the wastewater are degrading other pollutants that are later absorbed by the plants. However despite being an economic process, is necessary a large aera of land to construct a wetland and the time of residence usually are long (de-Bashan and Bashan, 2004).

It had to be mentioned that in cases, phosphorous is removed by converting phosphorous ions in wastewater into a solid fraction. This fraction can be an insoluble salt precipitate, a microbial mass in an activated sludge, or a plant biomass in constructed wetlands. These approaches do not recover the phosphorus in a sustainable way because it is removed with various other waste products, some which are toxic (de-Bashan and Bashan, 2004). For that reason the research community have started to look for more selective and high performance processes.

2.7.3.1.Struvite Crystallization

Magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4$ $6H_2O$) commonly known as struvite, in the beginning was considered as one of the main concerns in the pipe line systems in waste water treatment plants due its crystal crusts that affects the efficiency of the treatment (Le Corre et al., 2009, Uysal et al., 2010). However nowadays struvite is seen as one of the most promising compounds for recovery because it has the potential as a fertilizer product that could benefit the waste water companies and other industries (de-Bashan and Bashan, 2004, Le Corre et al., 2009, Shu et al., 2006, Uysal et al., 2010).

Struvite crystallization not only permits the recovery of phosphorus, but also part of the ammonium is recovered as well in a solid form. That is because the Struvite crystallisation occurs when the molar ratio of Mg:N:P is greater than 1:1:1. at alkali pH's (7-11) (Münch and Barr, 2001). Uysal et al. (2010) obtained removal efficiencies of NH_4-N and PO_4-P of 89.35% and 95% (pH 9) from the digestate of a full- scale digester when the molar ratio was 1.5:1:1. Several authors indicate that the optimal pH for struvite crystallisation is around 9 (Münch and Barr, 2001, Uysal et al., 2010).

According to de-Bashan and Bashan (2004) the theoretical potential for struvite recovery approaches to 67,000 tons of P_2O_5 fertilizer per year from the UK alone, and 270,000 tons from Western Europe. Authors as Shu et al. (2006) mentioned that the phosphorus that can be recovered from struvite crystallisation is approximately 1kg of struvite from 100 m^3 of wastewater. Furthermore Crystallisation is profitable compared to chemical and biological removal of phosphorus due to savings from the reduction in chemicals used for precipitation and sludge disposal. This technology provides opportunities to recover phosphorus sustainably from waste streams; even the recovered phosphorus product can be superior in quality to currently available phosphate rock.

According to Le Corre et al. (2009), Japan is the only country where complete P removal and recovery from anaerobically digested sludge liquors as struvite has been implemented and the resulting product is sold to fertilizer companies. The recovery technologies currently tested are based on the crystallization of phosphorus as hydroxylapatite (HAP) or struvite (MAP) using the sludge liquors generated from anaerobic digesters as their influent (See **Figure 2.4**). Suzuki et al. (2007) built a crystallisation reactor and struvite accumulation device for the removal and recovery of phosphorus. The reactor was fed with swine wastewater for 3.5 years with a maximum yield of struvite production of 171g per m^3 of swine wastewater with 95% of purity at a maximum pH of 9. (Suzuki et al., 2007). Münch and Barr (2001) achieved 94% of Ortho-P removal (influent of 64mg/L , effluent with 4mg/L) at pH of 8.5, and they concluded that the use the MAP process (Struvite Crystallisation) is a suitable technology to remove and reuse phosphorus from wastewater treatment sidestreams.

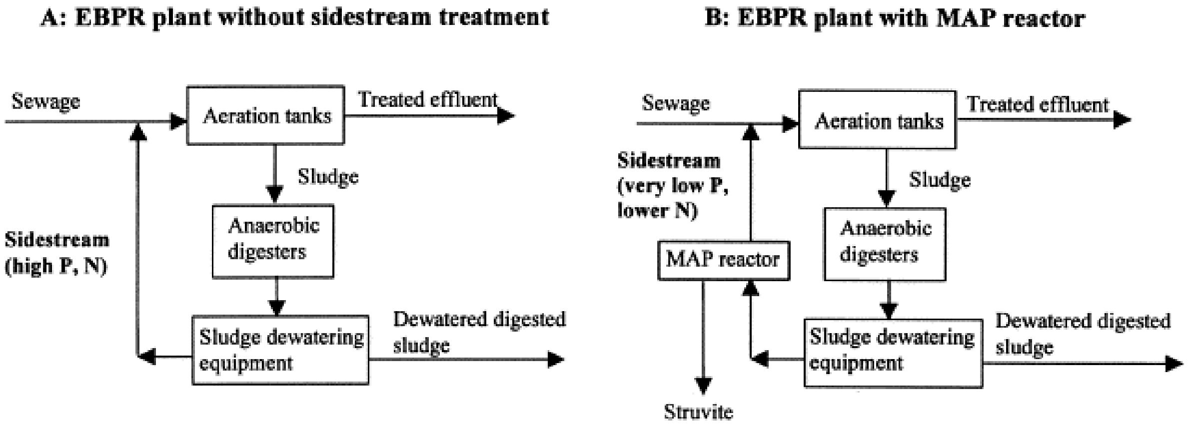


Figure 2.4.- Process flowsheet of Enhanced Biological Phosphorus and Nitrogen Removal (EBPR) wastewater treatment plant without sidestream treatment (A) and with sidestream treatment by MAP process (B) (Münch and Barr, 2001).

2.8. Summary of literature review findings

Having reviewed the relevant literature the key findings are summarised below:

- The EU Directive will set stricter maximum limits for contaminants that would affect the current methods for sewage sludge disposal and the agricultural land disposal will no longer be allowed.
- The most used treatment in the UK for sewage sludge disposal is the anaerobic digestion. This is because the benefits that brigs along use it as the methane production and a pathogen free solid that can be used as fertilizer.

- Thermal hydrolysis is an AD pre-treatment used in a commercial scale in the WWTWs with the aim to enhance the biogas production and reduce the total solids.
- Hydrothermal treatments are good option for harness the properties of the biomass such as sewage sludge. Depending the process temperature, valuable by products can be obtained such as hydrochar, bio-oil and syngas.
- One of the most common process to recover phosphorus and nitrogen is through struvite cristallization. This process consists in form compounds of nitrogen and phosphorus by adding magnesium or calcium salts. The struvite can be used as a material to prepare fertilizers. Therefore, this is the importance of track nutrients such as phosphorus and nitrogen.

2.9. Statement of Research Problem and current Research Gaps

According to the mentioned in the literature review there is an increasing amount of digestate produced in WWTWs and a possibility of a potential ban on the current final disposal route on agricultural land. Therefore, there is a need to look for options aimed at reducing operational costs at WWTW, including digestate stabilisation and disposal, by delivering a sustainable approach. The Hydrothermal processes seemed to be a suitable and profitable alternative to deal with the current sewage sludge management because of the high content of organic matter contented in the sewage sludge can be used in order to obtain fuels as biochar, biofuel and syngas.

There are many studies regarding hydrothermal processes with many feedstocks but there are few studies about the integration of hydrothermal processes with AD.

In this research, a new approach of integrating hydrothermal treatments as AD post-treatment was studied in order to deal with the sewage digestate and harness all the properties from the sewage sludge

Chapter 3. Research Methodology and Analytical Methods

This chapter describes the general the material and methods used in all research phases of the study of hydrothermal procesess as an alternative to conventional sewage sludge management. The methods described in the following sections are arrangend into four main parts, which are in line with the four research objectives proposed in this work: 1) Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatment, 2) Hydrothermal Carbonization of Sewage Digestate: Influence of the solid loading on hydrochar and process water characteristics., 3) Evaluation and comparison of product yields and bio-methane potential from hydrothermally treated sewage sludge., and 4) Mass and Energy Integration Study of Hydrothermal Processing with Anaerobic Digestion of Sewage Sludge.

3.1. Materials

3.1.1.Seed Inoculum

The seed inoculum was collected from Yorkshire Water’s Esholt WWTW in Bradford, UK. Esholt Sewage Treatment Works is the second biggest of the Yorkshire Water’s sewage treatment works serving around 760,000 people in Bradford and Leeds.

The seed inoculum was collected from an anaerobic reactor used for sewage sludge digestion. The seed inoculum was incubated at 37°C in sealed bottles and fed every week with sewage sludge coming from Esholt WWTW to keep it active. The objective to keep it active was for use the same seed inoculum for all the BMP experiments and avoid variations coming from external sources.

3.1.2.Sewage sludge samples

For the first objective, the sewage digestate was collected from Knostrop WWTW in Leeds. This happened because in Esholt WWTW they had a problem to supply sewage digestate.

For the following research stages, the sewage sludge samples were collected at Yorkshire Water’s Esholt WWTW in Bradford, UK. Primary sludge (PS) was collected from primary sedimentation tanks, the secondary sludge (SS) was collected from the secondary sedimentation tank after activated sludge processing and the sewage digestate (SWD) was collected from the meshophilic anaerobic digestion reactor (MAD). All the samples were taken to the laboratory and storen in fridge/freezer at 4-5°C until for no longer than 6 months to prevent any enzymatic or chemical activity.

3.2. Methods

3.2.1.Feedstock characterization

The different sewage sludge (PS,SS and SWD) were characterised according to standard analytical methods for Chemical Oxygen Demand (COD), Total Solids (TS), Suspended Solids (SS), Volatile Solids (VS), Volatile Fatty Acids (VFAs), Phosphorus (Total and Reactive), Total Kjeldahl Nitrogen (TKN), Ammonium and pH (APHA, 2005; He *et al*., 2013) (see **Table 3.1**). The VFAs analysis were performed using a gas cromatograph (Agilent 7890 A) (see **Figure 3.1**).

Table 3.1.- APHA analyses for feedstock characterisation

Analysis	Method
COD	5220-D
TS, SS and VS	2540 B, 2540 E
Phosphorus	4500 P
Total Nitrogen	4500 C
Ammonia	4500 B
Volatile Fatty Acids	5660 D

Figure 3.1.- Gas cromatograph Agilent 7890 A.

Furthermore, elemental analysis for Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) were performed using a CHNS elemental analyser (CE Instruments, Flash EA 1112 Series) for dry sewage sludge (PS, SS and SWD). Proximate analyses were performed in a thermogravimetric analyser (Shimadzu, TGA-50) to determine moisture, ash and volatile matter. Total organic carbon (TOC) analyses were performed in a TOC analyser (HACH Lange, IL550 TOC/TIC Analyser).

3.2.2.Hydrothermal treatments

Thermal experiments were conducted in a non-stirred 500mL stainless steel batch Parr reactor (See **Figure 3.2**). In each batch experiment 220mL of sludge sample were loaded in the reactor and sealed. After treatment, the reactor was cooled down to 25°C.

Solid products and liquid products were separated by filtration using a pre-weighted Whatman filter paper. The liquid products were collected in a separate container and retired for their characterization.

Figure 3.2.- Thermal reactor used for the experiments.

3.2.3.Characterization of the liquid products

The process waters (PW) generated during hydrothermal treatment were processed following standard methods for the characterisation of wastewater samples, for Chemical Oxygen Demand (COD), Total Solids (TS), Suspended Solids (SS), Volatile Fatty Acids (VFAs), Total Phosphorus, Reactive Phosphorus, Total Kjeldahl Nitrogen (TKN), Ammonium and pH. Ultimate analysis was performed using a CHNS analyser (Elemental Analyser, CE Instruments Flash EA 1112 Series) of the totally evaporated process water. Total organic carbon (TOC) analyses were also conducted using a TOC analyser (HACH Lange IL550 TOC/TIC Analyser).

3.2.4.Characterization of the solid products

Solids samples (Hydrochar and sewage solid fraction) were dried overnight at 40°C in an oven and weighted afterwards. A CHNS analyser (Elemental Analyser, CE Instruments Flash EA 1112 Series) was used to perform ultimate analyses of dry hydrochars (see **Figure 3.3**). Proximate analyses were performed in a Thermogravimetric analyser (Shimadzu, TGA-50) to determine moisture, ash content and volatile matter.

Figure 3.3.- Elemental Analyser, CE Instruments Flash EA 1112 Series.

3.2.5.Biochemical methane potential experimental (BMP) tests

The Biochemical Methane Potential (BMP) tests followed the principles and methods described by (Angelidaki et al., 2009) and (Diaz-Baez et al., 2002). BMP tests were carried out for the different sewage sludge, slurries and process waters following hydrothermal treatment. The anaerobic digestion process for each batch was performed in 120mL bottles sealed with a rubber stopper and aluminium cap to avoid biogas leakage and incubated at 37°C (see **Figure 3.4**). All BMP tests were carried out in duplicate and bottles containing only inoculum (blanks) were also incubated. The headspace of each bottle was filled with nitrogen to keep anaerobic conditions and avoid leaching of oxygen into the reactor. Test bottles were kept undisturbed at all time, apart from the periods when mixing occurred during biogas production measurements. Methane production was monitored by using a volumetric method following the absorption of CO_2 in a solution of NaOH (3M) (Herrera and Niño, 2012) (See **Figure 3.5**).

Figure 3.4.- BMP experiments.

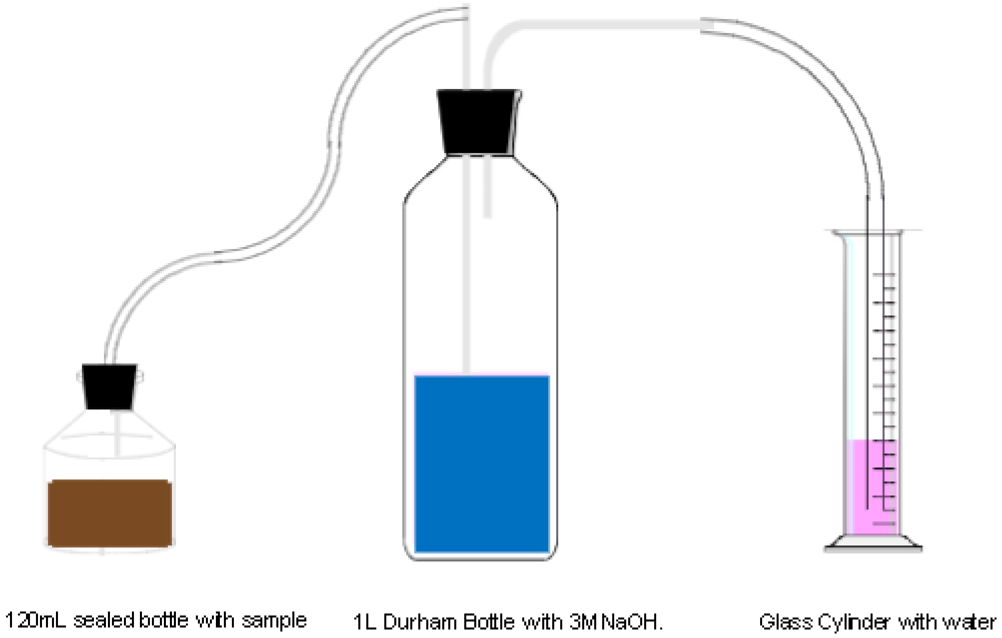


Figure 3.5.- Biogas collection system.

The experimental period for each BMP test lasted for 21 days; monitoring measurements were performed during days 0, 2, 4, 7, 10, 14, 18 and 21 (See **Table 3.2**). For every measurement, a bottle was removed from incubation and sacrificed for the corresponding analyses. During each measurement, the following parameters were monitored: pH, COD and VFAs. TS, VS, TKN, Ammonium and Phosphorus (Total and reactive) were measured from samples collected at day 0 and 21. All the analyses were carried out in duplicate.

Table 3.2.- Gantt chart for the BMP analyses.

Day	**0**	**1**	**2**	**3**	**4**	**7**	**8**	**9**	**10**	**11**	**14**	**15**	**16**	**17**	**18**	**21**
TS	▨															▨
TSS	▨															▨
TKN	▨															▨
Ammonia	▨															▨
T-phosphorus	▨															▨
R-phosphorus	▨															▨
VFAs	▨		▨		▨	▨			▨		▨				▨	▨
Methane	▨		▨		▨	▨			▨		▨				▨	▨
pH	▨		▨		▨	▨			▨		▨				▨	▨
COD	▨		▨		▨	▨			▨		▨				▨	▨

3.2.6.Biogas composition

Methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2) and hydrogen (H_2) were measured in a gas cromatograph (Agilent 7890 A series) coupled with a thermal conductivity detector (TCD) to identify the mentioned gases.

3.3. Data processing and analysis

3.3.1.Biochemical Methane Production (BMP)

In order to assess the performance of methane production by gram of organic matter added (measured as chemical oxygen demand – COD), the following formula was used:

$$BMP = \frac{V_{CH_4} - V_{CH_4,blank}}{(Mass\ of\ substrate\ fed\ in\ biodigester)} \qquad (3.1)$$

where:

BMP = Biochemical Methane Potential (mL of CH_4/ g of COD added)

V_{CH4} = Volume of methane produced in bottle (mL)

$V_{CH4,\ blank}$ = Volume of methane produced in the blanks (mL)

Mass of substrate = Mass of substrate as g of COD

3.3.2. Theoretical BMP (BMP_{th})

The calculation of theoretical BMP values, which are based on the elemental composition (C, H, N and O) of the samples, was made by using stoichiometric equations for maximum biogas production. Both the Buswell's equation and the Boyle's equation were used to calculate the theoretical BMP values for each tested sample (Tarvin and Buswell, 1934, Raposo et al., 2011). The difference between them is that the Boyle's equation does consider the presence of proteins and ammonia in the reaction (Nielfa *et al.*, 2015).

Buswell's equation:

$$\mathrm{BMP}_{thBW} = \frac{22400\left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}\right)}{12n+a+16b} \qquad (3.2)$$

Boyle's equation:

$$\mathrm{BMP}_{thBO} = \frac{22400\left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}-\frac{3c}{8}\right)}{12n+a+16b+14c} \tag{3.3}$$

where *n*, *a*, *b* and *c* represent the molar fraction of C, H, O and N, respectively.

3.3.3.Anaerobic biodegradability (BD)

The anaerobic biodegradability of each sample can be calculated from the values reported from the experimental BMP (BMP_{exp}) and the theoretical BMP (BMP_{Th}), and gives an idea of the level of biodegradability of the feedstock under anaerobic conditions (Raposo *et al*., 2011):

$$BD_{CH4}(\%) = \frac{BMP_{exp}}{BMP_{Th}}\ x\ 100 \tag{3.4}$$

3.3.4.Hydrochar Yield

Hydrochar yield (*Y*), energy densification (E_d) and energy yield (E_y) were determined as follows:

$$Y\ (\%) = \frac{mass\ of\ dry\ hydrochar}{mass\ of\ dry\ Substrate\ feedstock} * 100 \tag{3.5}$$

$$Ed{=}HHVcharHHVfeedstock \tag{3.6}$$

$$(\%){=}Ed \times Y \tag{3.7}$$

where *HHV* is High Heating Value

3.3.5.Carbon recovery in solid and liquid fractions after HT processing

Carbon recovery in hydrochar (Hy_{crec}) and liquid phase (Lq_{crec}) were calculated as follows:

$$(\%)Hy_{crec} = \frac{\frac{\%C_{Hydrochar}}{100}\ x\ char\ mass}{\frac{\%C_{feedstock}}{100}\ x\ mass\ of\ dry\ Digestate\ feedstock} * 100 \tag{3.8}$$

$$(\%)Lq_{crec} = \frac{Total\ organic\ Carbon\ x\ volume\ of\ filtrate}{\frac{\%C_{feedstock}}{100}\ x\ mass\ of\ dry\ Digestate\ feedstock} * 100 \qquad (3.9)$$

3.3.6.High Heating Value

The heating value also called calorific value, defines the energy content of a biomass fuel and it is an important characteristic parameter for designing thermal systems regardless the biomass used. The Heating value can be reported as high heating value (HHV) or low heating value (LHV). The HHV is the heat released from the fuel combustion and their products have returned to the temperature of 25°C and considers latent heat of vaporization of water in the combustion products. On the other hand the LHV does not consider the latent heat vaporisation (Sheng and Azevedo, 2005). For this study the HHV was considered for the design of the thermal systems. In order to know the theoretical calorific value of the hydrochar, the Dulong equation reported by Channiwala and Parikh (2002) was used.

$$HHV\ (MJxKg^{-1}) = 0.336\ (\ \%Carbon) + 1.433\ \left(\%Hydrogen - \left(\frac{\%Oxygen}{8}\right)\right) + 0.0942\ (\%\ Sulphur) \qquad (3.10)$$

3.3.7.Thermal treatment energy calculations

The energy required for the thermal treatments was based on the energy required calculations to heat water in a closed batch system (Berge et al., 2011a). Assuming that the heater has 100% resistance, there is no heating losses in the tank during the thermal treatment and the volume of the water remain constant, the energy required was determined by the followed equation:

$$\Delta E = \Delta T \left(mC_p + \frac{mR}{V}\right) x\ 277x10^3 \qquad (3.11)$$

Where ΔE is the energy required to heat up the water in KWh, ΔT is the change in the temperature in K, m is the mass of the water in Kg, C_p is the heat capacity of the water, R is the constant of the ideal gases and V is the volume of the reactor in m^3

3.4. Objective 1: Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatment

The assessment of the effect of temperature on the characteristics of hydrochars and process waters produced from hydrothermal processing of sewage digestate and the effect of hydrochars was performed. Subsequently, experimental biomethane potential (BMP) tests were conducted using process water on their own and in combination with hydrochars as substrate in order to assess the effect of hydrochars on the AD process. (see **Figure 3.6**).

Due to the increase in energy consumption when increasing the temperature of hydrothermal treatments, hydrothermal carbonization's (HTC) process temperature range (160 to 250°C) was selected to avoid an intensive energy consumption method (Biller and Ross, 2012). To cover this range and to determine which process temperature harness better the properties of the sewage digestate (SWD), in this set of experiments three different process temperatures were assessed, 160, 220 and 250°C with a residence time of 30 minutes. The residence time was selected based on the optimum residence time of the commercialized large scale thermal hydrolysis system for wastewater (Sridhar Pilli et al., 2015).

The characterization of the feedstock, hydrochars and process waters were performed as mentioned in sections 3.2.1, 3.2.3 and 3.2.4. The characterization of the SWD and the thermal by-products were used to calculate high heating value, hydrochar yield, energy densification, energy yield, Carbon recovery in hydrochar and liquid phase and theoretical BMP.

The BMP tests were carried out using SWD, process waters (PW) and slurries (hydrochar + process water). For SWD and slurries, inoculum and slurry were mixed maintaining a ratio of solids of 1:1 with a total VS concentration of 10 gVS/L for the feedstock and 10g/L of VSS for the Inoculum. Process water was used with the same concentration of soluble COD used in the slurries (2g/L of COD), but using the same amount of solids for the inoculum (10g VSS/L). In oder to evaluate the influence of the hydrochar addition in the anaerobic digestion process and biogas production, the analyses mentioned in section 3.2.5 were carried out.

The results from experimental BMP tests were compared to theoretical predictive models in order to determine the best fit and to calculate the biodegradability of the samples.

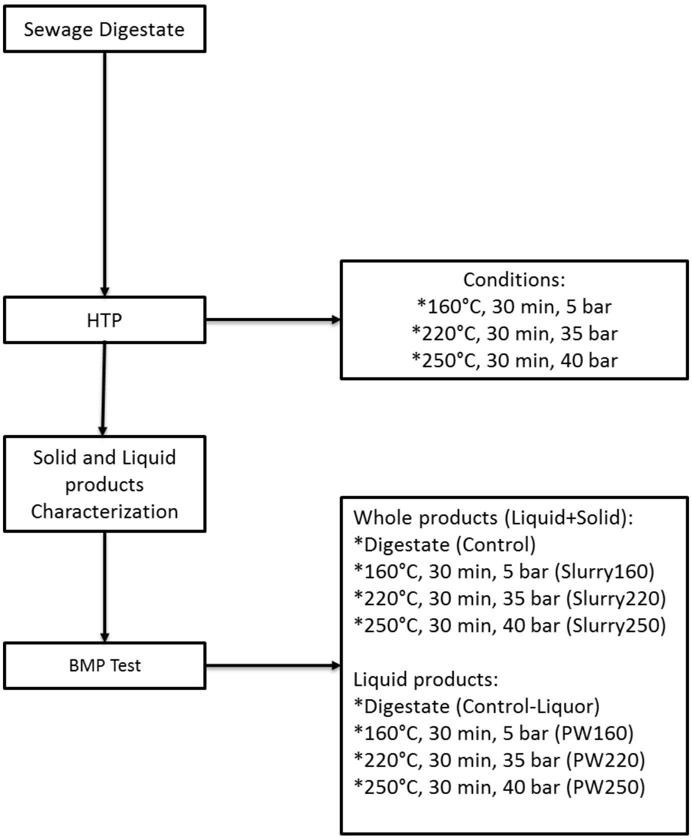


Figure 3.6.- Experimental design for objective 1.

3.5. Objective 2: Hydrothermal Carbonization of Sewage Digestate: Influence of the solid loading on hydrochar and process water characteristics.

In the hydrothermal carbonization, most of the potential energy comes from the solid by-product (Aragón-Briceño et al., 2017). In order to optimize the thermal treatment and harness the most the properties of the anaerobic digested sewage sludge, this objective aimed to investigate the influence of solid loading on hydrochar and process water characteristics from HTC used for processing sewage digestate (see **Figure 3.7**).

Samples of sewage digestate were collected from anaerobic digesters at Yorkshire Water's Esholt WWTW in Bradford, UK. A portion of that sample was stored at 4°C for subsequent characterisation in the laboratory. The remaining sample was centrifuged at 4,000rpm (3220 G) for 30 min and the aqueous fraction (digestate liquor) was separated from the solids and stored at 4°C before sample preparation. The solid fraction (digestate cake) was dried in an oven at 40°C for 7 days. The dry digestate and the liquor were used for the preparation of the actual digestate before undertaking hydrothermal treatment (HTC) at different solid concentrations (solid loadings). The concentrations prepared were 2.5, 5.0, 10.0, 15.0, 17.5, 20.0, 25.0 and 30.0% w/w of solids in digestate samples. Solid loading concentrations were selected based on the maximum solid capacity input reported for biomass for a HTC plant (Child, 2014).

According to the results analisys of the objective 1, the HTC experiments were conducted in a non-stirred 500mL stainless steel Parr batch reactor at 250°C and 40 bar for 30 min, after which the reactor was cooled down to 25°C before collection of the resulting processed samples (HTC slurries). The resulting HTC slurries were collected and prepared for characterization of solid and liquid products (see section 3.2.3 and 3.2.4). Solid (hydrochar) and liquid (process water) products contained in HTC slurries were separated by filtration using pre-weighted 1.2 µm WhatmanTM glass microfiber filter (Grade GF/C). All HTC experiments were conducted in duplicate. Production yields and composition of hydrochars and the levels of solubilisation of organic matter and nutrients in process waters were evaluated.

BMP tests were carried out on process water samples following the method described in section 3.2.5. To avoid inhibition coming from the substrate and to determine the maximum BMP, the inoculum concentration used in each BMP test was 10g/L of Volatile Suspended Solids (VSS) and the process water concentration was 2g/L of COD maintaining a volume ratio of 1:1 (Wirth et al., 2015). Each BMP test was performed at 37°C for 21 days, in a series of 120mL bottles sealed with a rubber stopper and aluminium cap. The experimental biomethane potential (BMP) tests conducted on process waters were used to present an overall energy balance for the proposed AD+HTC process.

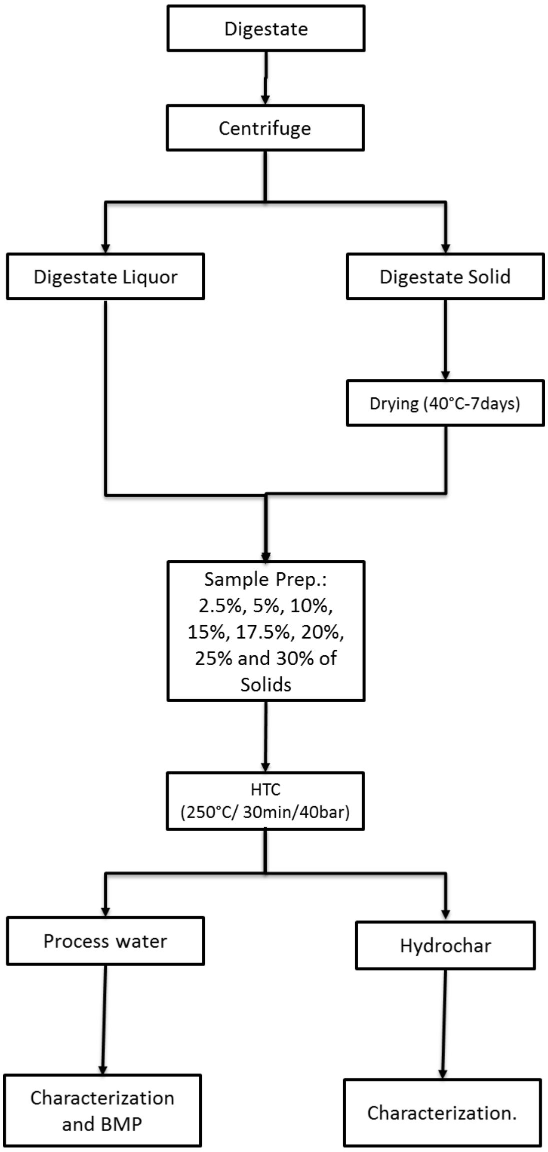


Figure 3.7.- Experimental design for objective 2.

3.5.1.AD-HTC model

A chemical process engineer software (Aspen plus®) was used to analyse in more detail the potential to combined AD and HTC processes; mass and energy balances of the proposed system were made in detail. HTC, AD and CHP (Combined Heat and Power) systems were modelled and interconnected. Aspen Plus V8.8® was used throughout with a 'COMMON' method filter and an 'IDEAL' base method.

3.6. Objective 3: Evaluation and comparison of product yields and bio-methane potential from hydrothermally treated sewage sludge.

To propose new process configurations for WWTWs in order to integrate HTPs as part of a comprehensive sewage sludge management strategy, it is importat to investigate the changes to sewage sludge samples collected along treatment process units in a conventional WWTW, when subjected to hydrothermal processes at different temperatures.

The methodology was conducted according to **Figure 3.8**. Sludge samples were collected from primary sedimentation tanks (primary sludge - PS) and secondary sedimentation tank (secondary sludge - SS) at Esholt WWTW. All sludge samples were stored at 4°C after collection and then used for the hydrothermal treatments (HTT) prior to characterisation. In addition, primary (PS), secondary (SS) and a mix of 1:1 TS ratio of PS-SS sludge (MIX) were processed by anaerobic treatment for 30 days in the lab, before further hydrothermal processing. Resulting samples were named as follows: digested primary sludge (ADPS); digested secondary sludge (ADSS); and digested mix of PS and SS (ADMIX).

Thermal experiments were conducted as described in section 3.2.2 at 160°C for 30 min at 5 bar and at 250°C for 30 min at 40 bar.

BMP tests were carried out with process water samples following the method described in section 3.2.5 using different sewage sludge and process water separated from HTC experiments.

The characterization of the different sewage sludge, digestates, hydrochars and process waters were used to calculated the mass and energy balance of the process.

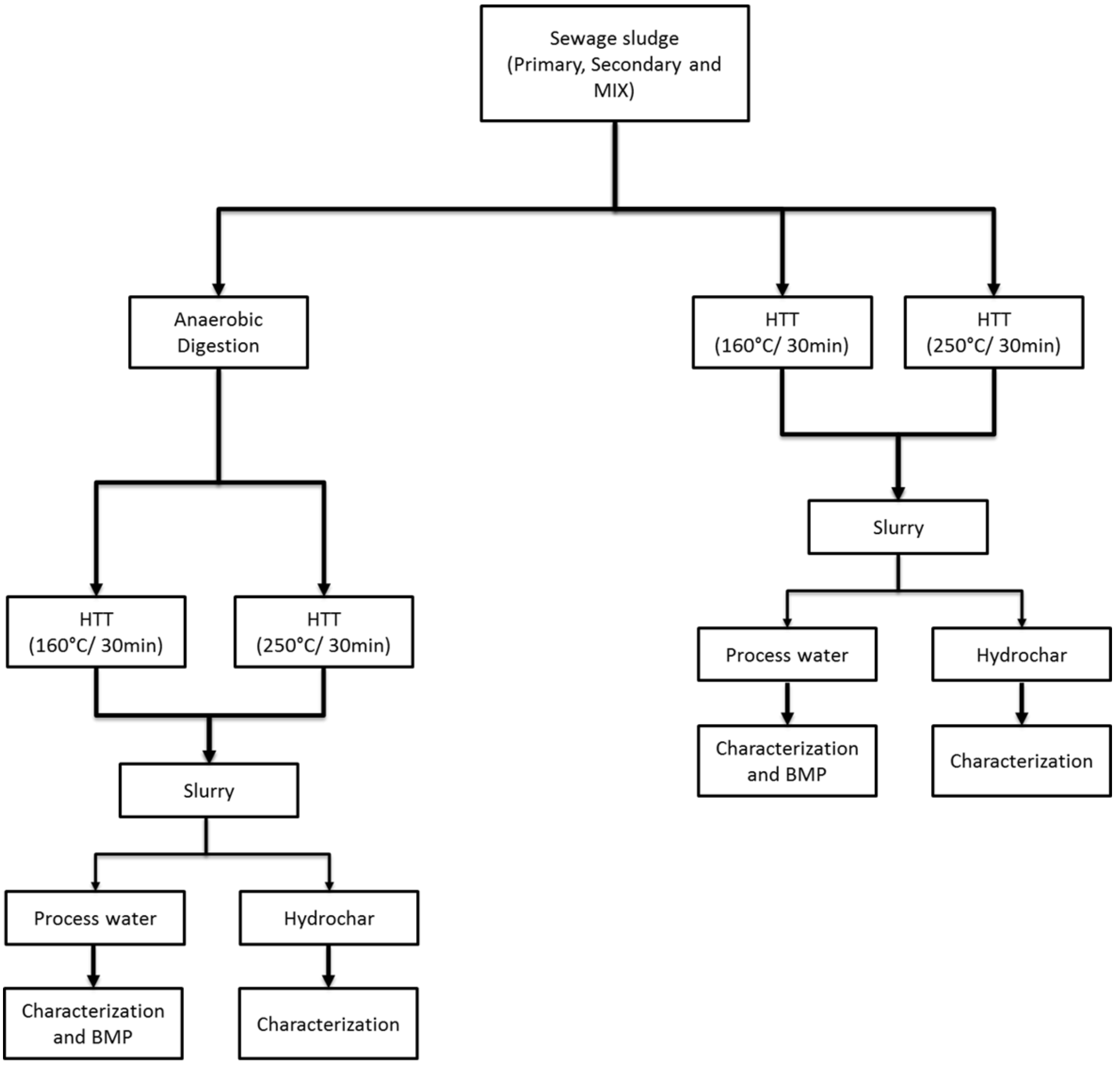


Figure 3.8.- Experimental design for objective 3.

3.7. Objective 4: Mass and Energy Integration Study of Hydrothermal Processing with Anaerobic Digestion of Sewage Sludge

This objective assesses the integration of HTPs with AD as a post-treatment to the AD of sewage sludge through mass and energy balances from proposed process configurations from different sewage sludge based on the results obtained from experimental analyses.

Different sewage digestate were used to compare the energy production between them since the primary sludge have high organic content. Therefore, as stated by Pérez-Elvira and Fdz-Polanco (2012), the best option will be to segregate primary and secondary sludge in order to produce more energy in the overall system.

Six proposed scenarios were evaluated from the different sewage sludge and their digestates (PS, SS, MIX, ADPS, ADSS and ADMIX). The calculation of each scenario required a combination of real data from the experiments in this study, data from literature and reasonable assumption with regards to specific decision criteria. The calculations and scenarios from this study are not intended to be an accurate guide but rather to provide indicative effort for evaluation of the process. As part of a comprehensive sewage sludge management strategy, this study included an integral evaluation of the products yields, waste generation, energy implications and potential economic benefits.

The overall process of integrating hydrothermal processing with anaerobic digestion of sewage sludge is divided in four main processing areas. Firstly, the feed (PS, SS or MIX sludge) undergoes mesophilic anaerobic digestion processing (37°C) producing digestate (ADPS, ADSS or ADMIX) and biogas. The next process is compound by a thickener which concentrates the digestate to 15% of solids. Next, the thickened digestate is submitted to thermal processing (160 or 250°C) converting it to process water and hydrochar. The thermal recovery efficiency from the heat exchanger is considered in this stage. Then, a centrifuge is used to separate the hydrochar (solid fraction) from the process water (liquid fraction). The hydrochar is considered as a potential fuel source based on its high heating values (HHV) but non-energy recovery process is considered. On the other hand the process water is anaerobically treated at mesophilic conditions in a second reactor producing biogas as well. The biogas produced by the first and second reactors are mixed and combusted in a combine heat power (CHP) unit to produce the energy for the system. The energy produced from the biogas is used to cover the energy requirements of the hydrothermal system and the exceeding energy is used for other equipment (see **Figure 3.9**)

The assumptions adopted as a basis for the mass and energy balance of the different scenarios build in this study are presented in the methodology section of chapter 7.

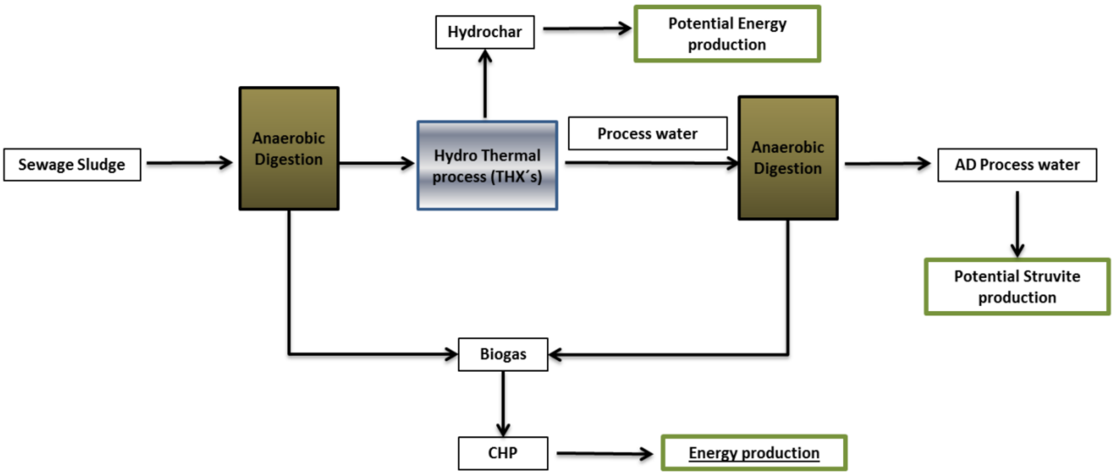


Figure 3.9.- General process diagram for experimental design of objective 4.

Chapter 4. Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatment

4.1. Introduction

Over the past decade, sludge management at Waste Water Treatment Works (WWTWs) has been considered one of the biggest concerns for water companies and environment protection agencies. In the UK, over 16 billion litres of waste water per day are collected and treated in 9,000 WWTWs before they are discharged to inland waters, estuaries or the sea. As a result of that, around 1.4 million tonnes (dry weight) of sewage sludge are produced annually in the UK (DEFRA, 2012b).

Sewage sludge can be used for the production of bioenergy due to its large organic matter content; in fact, nearly one half of the organic matter in sewage sludge is susceptible to anaerobic biodegradation, resulting in the formation of biogas (Abelleira-Pereira et al., 2015, Hindle, 2013) (Kim et al., 2014). In the UK for instance, the anaerobic digestion (AD) process has become the most common alternative for SS treatment with the added benefit of energy generation from methane, which has helped to reduce the net energy consumption from the national grid for sewage treatment. Despite the progress made with regard to the development and implementation of pre-treatment processes aimed at increasing the anaerobic biodegradability of sewage sludge (mainly for secondary sludge), the resulting digested sludge (digestate) still contains large amounts of non-biodegradable organic matter that can be harnessed for additional energy production, which makes it an interesting feedstock for thermochemical conversion (Mumme et al., 2015, Kim et al., 2014). Current practices for digestate disposal in the UK and across Europe include agricultural application, but upcoming changes in EU legislation would make digestate no longer suitable for this practice (Dichtl et al. (2007). As a consequence, WWTWs will have to face the very difficult task of finding alternatives to current sewage sludge treatment and final disposal routes.

Hydrothermal treatments (HT) are considered an alternative technology to harness energy from SS in the presence of water and avoid the energy-intensive drying step required for other thermal processes (He *et al.*, 2013). The main aim of the hydrothermal processing routes is energy densification via hydrochar production, which is produced largely by the removal of oxygen. After HT, the resulting hydrochars show moderate calorific value and are biologically inert, so they can be co-fired with coal or safely disposed in agricultural land as soil amendment (Bargmann et al., 2014, He et al., 2013, Biller and Ross, 2012). Hydrothermal processing also generates a by-product or “process water" rich in organic compounds that cannot be directly disposed into the environment, but has been proved to be suitable for methane production via anaerobic digestion (Almeida, 2010, Becker et al., 2014, Kim et al., 2014, Stemann et al., 2013, Wirth et al., 2015, Zhao et al., 2014).

The integration of a hydrothermal treatment step into waste water systems has been suggested to be energy positive (Mumme et al., 2015, Sridhar Pilli et al., 2015). In fact, commercial high-temperature processes like CAMBI® and BIOTHELYS® have been successfully developed as pre-treatment steps for hydrothermal hydrolysis of SS, which has resulted in improving methane production to up to 43%, when compared with conventional AD processes without pre-treatment (Sridhar Pilli *et al.*, 2015). Hydrothermal treatment as a post-treatment step after AD are still under research and development, but preliminary findings have shown that this approach could be even more effective with regard to overall biogas production from sewage sludge – i.e., thermal hydrolysis can help to produce as much as 36% more biogas when placed as a post-treatment step than when used as a pre-treatment step for AD (Shana et al. (2011). Therefore, further research on process conditions and overall benefits from hydrothermal processes as a post-treatment step after AD is still needed.

A range of different solid wastes have been studied for hydrothermal processing, including microalgae and manures (Ekpo *et al.*, 2015), municipal solid wastes (Berge et al., 2011a), sewage sludge (Danso-Boateng *et al.*, 2015), digestate (Kim *et al.*, 2014), and wood chips (Stemann et al., 2013).

Most of the studies regarding hydrothermal treatment of sewage digestate have focused either on the characterisation of the resulting products (Berge et al., 2011a, Danso-Boateng et al., 2015, Escala et al., 2013, Kim et al., 2014, Nipattummakul et al., 2010) or on the anaerobic digestion of the liquid products following hydrothermal treatment (Wirth et al., 2015, Hübner and Mumme, 2015, Wirth et al., 2012, Mumme et al., 2014). Kim *et al*. (2014) demonstrated that hydrothermal carbonisation can be used to convert sewage digestate into a solid fuel by increasing the high heating value and carbon content in the resulting hydrochar. Danso-Boateng *et al*. (2015) reported the effect of process conditions in hydrochars and process waters characteristics and included data for theoretical biomethane potential in process waters from treated primary sewage sludge. Hübner and Mumme (2015) showed that process waters from the pyrolysis of farm digestate can be converted into biogas without any additives or inoculum acclimation – i.e., COD removal rates of 63% and methane yields of up to 220 Lg^{-1}_{CODs}. Mumme *et al.* (2014) showed the behaviour and biodegradability of biochars in anaerobic digestion and concluded that the addition of biochar to anaerobic digesters may contribute to reduce ammonia inhibition. However, there are no studies that integrate the influence of process conditions during hydrothermal treatments of sewage digestate on the characteristics of hydrochars and process waters, and the fate of nutrients like nitrogen and phosphorus.

This objective is aimed at making a contribution in that regard and hence, investigates the effect of process temperature on the characteristics of hydrochars and process waters from hydrothermal processing of sewage digestate and compares the yields and characteristics of the different products including the fate of nitrogen and phosphorus species. In addition, experimental biomethane potential (BMP) tests were conducted on process waters on their own and in combination with hydrochars to assesses the effect that hydrochars may have on AD processes. The results from experimental BMP tests were compared to theoretical predictive models.

4.2. Results and discussions

4.2.1.Chemical Oxygen Demand and nutrient balance of thermal products

The COD, nitrogen and phosphorus content of the feedstock (Control) and their fate after hydrothermal processing are shown in **Figure 4.1**. The contribution of the gas was not considered because in all the cases the gas fraction was lower than 0.5%.

The fate of phosphorous following hydrothermal treatment is shown in **Figure 4.1a**. The results indicate that the organic phosphorus fraction in the aqueous phase, initially reported as 64.4% of the total P present in the digestate, increases after hydrothermal treatment at 160°C and 250°C to 79.7% and 86.6%, respectively. This is accompanied by a reduction in P content in the solid fraction from 21.7% in the raw feedstock (Control) to 19.4 and 11% in the hydrochar after treatment at 160 and 250°C, respectively.

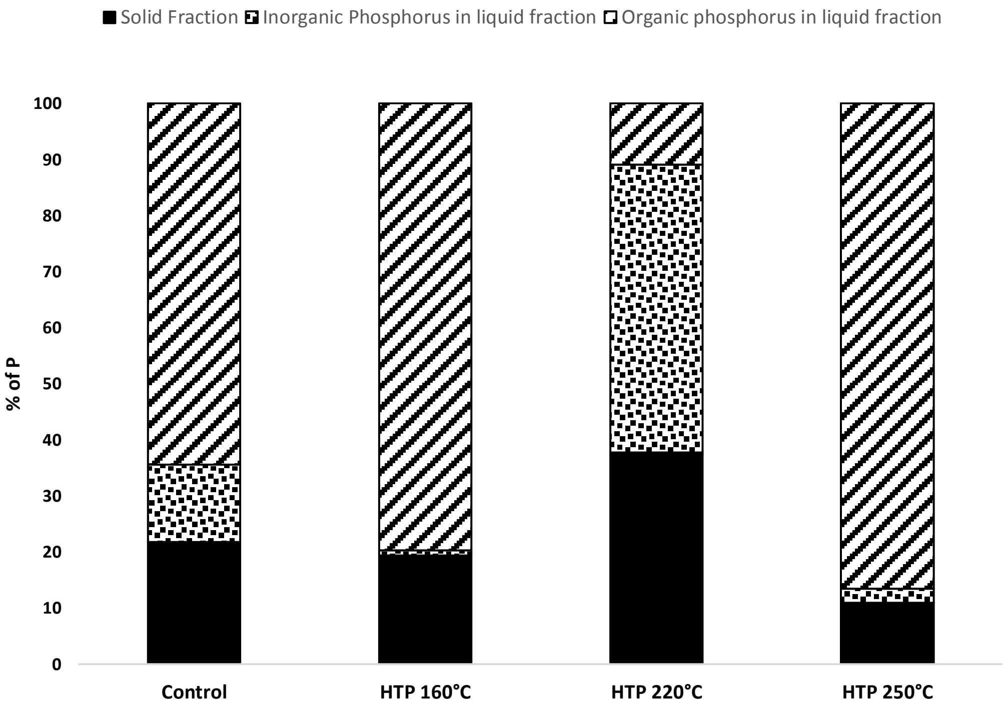
Hydrothermal treatment at 220°C results in a decrease of organic P to 10.9%. On the other hand, the inorganic phosphorous content (PO_4^{3-}) initially at 13.9%, increased at 220°C to 51.3% whereas treatment at 160 and 250°C resulted in a decrease to less than 2.5%. Hydrothermal treatment at lower temperatures favours the extraction of organic P, which then releases inorganic P. As the temperature increases, further additional organic P can be released as more complex molecules start to hydrolyse. The fate of P during hydrothermal treatment is highly feedstock dependent and is linked to the levels of other metals present in the feedstock (Ekpo *et al*., 2015). The P associated with the hydrochar at 220°C is increased once more to 37%, maybe due to precipitation of some of the inorganic P with metals such as Al, Ca and Mg present in the hydrochar. The solubilisation of phosphorus by thermal treatments is important as it means that the phosphorus can be recovered by struvite precipitation and gives extra value to the process water.

The fate of nitrogen following hydrothermal treatment is shown in **Figure 4.1b**. The solubilisation of nitrogen is increased at higher temperature. The initial levels of nitrogen in the solid fraction decreased from 58.3% to 42.4%, 38.9% and 34.3% for the treatments at 160, 220 and 250°C, respectively. As it is shown in **Figure 4.1b**, after the thermal treatment, the nitrogen solubilized mostly in ammonia form (Inorganic nitrogen). The importance of solubilizing inorganic nitrogen and phosphorus is because the inorganic fraction is more susceptible to be up taken by the microorganisms or recovered by physic-chemical analyses (Le Corre et al., 2009, Jackson and Williams, 1985).

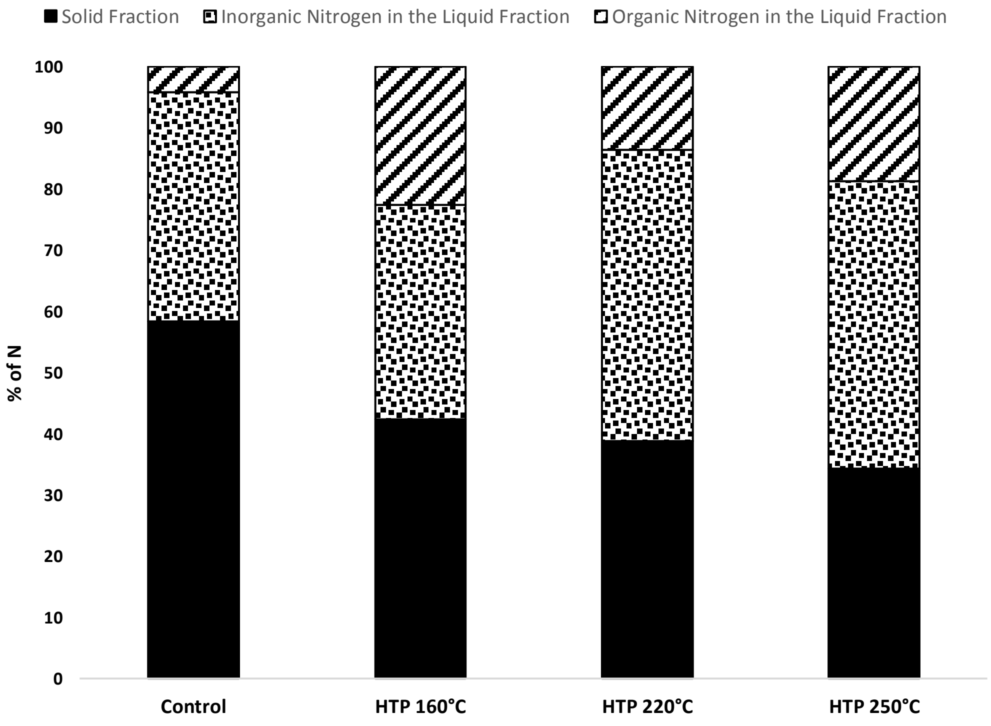
Hydrothermal treatment results in the solubilisation of organic matter from the digestate (**Figure 4.1c**). The raw digestate (Control) initially contained 4.6 wt% of solubilised COD in the liquid phase and this was increased to 31.7 wt%, 32.6 wt% and 30.5 wt% after hydrothermal treatment at 160, 220 and 250°C, respectively. The solubilisation of the organic matter into the aqueous phase is a result of hydrolysis releasing inorganic and organic compounds from carbohydrates, proteins and lipids (Danso-Boateng *et al*., 2015).

The composition of carbon and the nutrient species in hydrothermal products will depend mainly on the nature of the feedstock and process temperature (Ekpo et al., 2015, Toor et al., 2011). During hydrothermal treatment, the levels of water soluble products generally increase with reaction severity due to the combination of solubilisation of inorganics and increase in production of soluble organics hydrocarbons (Ekpo et al., 2015, Keymer et al., 2013, Qiao et al., 2011).

a)


■ Solid Fraction
▨ Inorganic Phosphorus in liquid fraction
▨ Organic phosphorus in liquid fraction
% of P
100
90
80
70
60
50
40
30
20
10
0
Control
HTP 160°C
HTP 220°C
HTP 250°C

b)


■ Solid Fraction
▨ Inorganic Nitrogen in the Liquid Fraction
▨ Organic Nitrogen in the Liquid Fraction
% of N
100
90
80
70
60
50
40
30
20
10
0
Control
HTP 160°C
HTP 220°C
HTP 250°C

c)

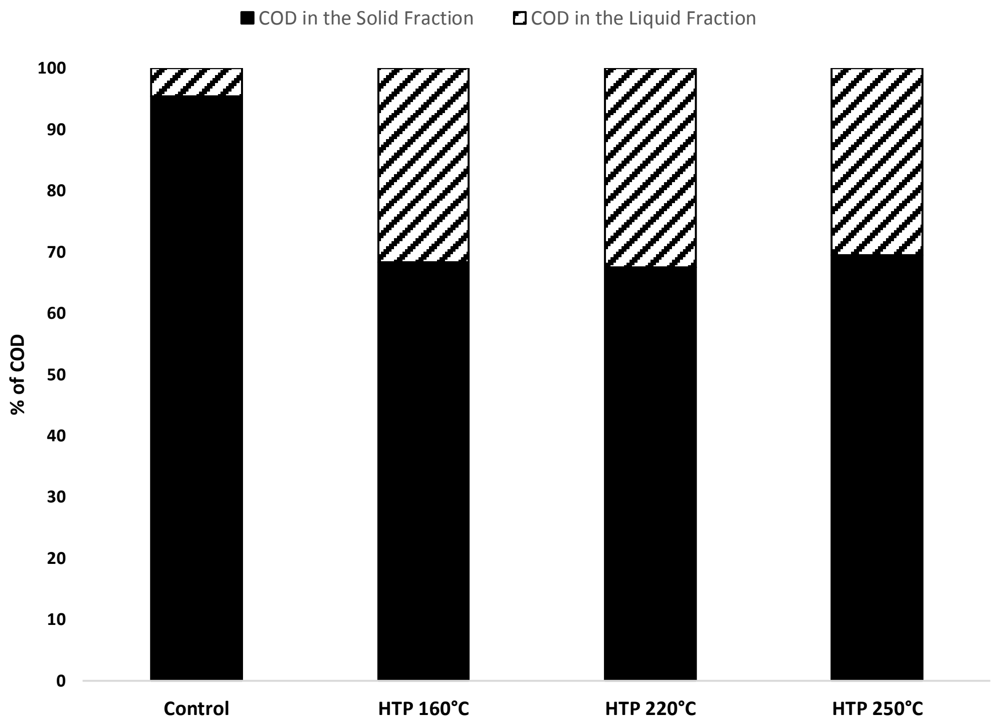


Figure 4.1. Fate of Phosphorus (a), Nitrogen (b) and organic matter (c) after hydrothermal processing of digestate samples (Control) for 30 min and at 160°C (5bar), 220°C (35bar) and 250°C (40bar).

4.2.2.Hydrochar Characteristics

According to Berge et al. (2011a) hydrochar characteristics depend primarily on their feedstock composition. The volatiles, ash content, elemental composition and yields of the hydrochars are presented in **Table 4.1**. According to Danso-Boateng *et al*. (2015) and Ekpo *et al*. (2015), hydrochar yields are influenced by reaction temperature and time. Hydrochar yields decrease with increasing temperature and reaction time. In the work reported herein, the highest yield of hydrochar was obtained at 220°C (73.4%), followed by the yields reported at 160°C (68.8%) and at 250°C (56.8%) (**Table 4.1**). These results match those reported by Danso-Boateng et al. (2015) and Ekpo et al. (2015) in primary sludge and sewage digestate.

The ash content increases after hydrothermal carbonisation as shown in **Table 4.1**, from 31.77% in the feedstock to 45.11%. These levels of ash content from anaerobically digested sewage sludge were similar to the results that Ekpo *et al*. (2015), Danso-Boateng *et al*. (2015) and Berge et al. (2011a) reported (33.03 - 38.94%; 78.3 - 81.4%; and 58.8% dry basis, respectively) at process temperatures of 160 -200°C, 250°C and 250°C respectively..

The volatile matter content of the hydrochar decreases after thermal treatment, having the lowest value at 220°C (43.82%) followed by the results found at 160°C (49.65%) and at 250°C (51.11%); our figures are below the reported values by Danso-Boateng *et al.* (2015) for anaerobically digested sewage sludge after carbonisation (55.33 - 66.17%). The reduction of volatile matter is due to chemical dehydration and decarboxylation and the increase in fixed carbon (FC).

4.2.2.1.Elemental composition in Hydrochar

The nitrogen content in the original digestate samples (5.04 wt%) is higher than the figures found in the hydrochar after hydrothermal treatment at 160, 220 and 250°C (i.e., 4.19, 2.01 and 4.23 wt%, respectively). This suggests there is a 'sweet spot' where the nitrogen content is minimised. Reincorporation of nitrogen into the hydrochar may occur at higher temperatures as carbonisation reactions proceed more rapidly. A reduction in nitrogen content in the hydrochar corresponds to an increase in solubilised nitrogen. The oxygen content of the hydrochars is lower to the initial digestate. The initial oxygen content was 20.32 wt% and after hydrothermal treatment at 220°C and 160°C is observed to decrease slightly to 14.66 and 15.46 wt% respectively; oxygen then reduces slightly to 14.78 wt% at 250°C. The hydrogen content of the hydrochar increases after treatment at 160°C and 250°C from 3.93% to 4.19 and 4.89% respectively, but reduces after 220°C treatment to 3.91 wt%.

Table 4.1.- Proximate and ultimate analyses of the feedstock (digestate) and hydrochar.

Sample	Proximate Analyses				Ultimate analysis					Yield (%)
	Moisture (%)	Ash (% dry base -db)	Volatile matter (%db)	Fixed carbon[a] (%db)	C (%)	H (%)	N (%)	O[b] (%)	S (%)	
Digestate (Control)	4.66	31.77	55.81	7.76	34.78	3.93	5.04	20.32	1.15	
Hydrochar										
160 °C - 30 min	2.56	38.63	49.65	9.16	35.53	4.19	5.11	15.46	1.07	68.8
220 °C - 30 min	2.02	45.11	43.82	9.05	33.21	3.91	2.01	14.66	1.09	73.4
250 °C - 30 min	2.81	36.88	51.11	9.21	38.03	4.89	4.23	14.78	1.19	56.8

[a] 100 - (moisture + ash + volatile matter).
[b] Calculated as difference between sum of C,H,N,S, ash.

4.2.2.2.Energy characteristics of Hydrochar

High heating values (HHV) of the hydrochars produced at different process temperatures are presented in **Table 4.2**. Temperature is reported to have a major influence on heating values improving HHV with increasing temperature (Danso-Boateng *et al*., 2015); however, this is feedstock dependent and not true for all feedstocks (Smith *et al*., 2016). Many authors have shown a reduced heating value for hydrochars produced from certain feedstocks compared to the original feedstocks (Berge *et al*., 2011a; Zhang *et al*., 2014). In this case, the HHV of the hydrochars generally increase but only slightly. The HHV of the original digestate is increased from 16.61 Mj kg^{-1} to a maximum of 17.80 Mj kg^{-1} representing only a marginal energy densification. Assessment of the combustion behaviour of this fuel has not been performed. The hydrochar contains 36.88% ash and 4.2 wt% N and so it would still be classified as a low-quality fuel because of its low heating value and high ash content. Despite that, the HHV of the hydrochars produced are within a similar range to those reported by Danso-Boateng et al. (2015) for primary sludge (17.2 - 18.4 Mj kg^{-1}) at process temperatures of 160-200°C and retention times from 30 to 240min. This indicates that for sewage derived solids and digestates, the energy densification is quite low compared to other feedstocks and indicates that a significant amount of the energy in the original feedstock is in the soluble water fraction (process waters), which may be recovered via anaerobic digestion.

The calculation of energy yield provides a means of quantifying the energy remaining within the hydrochars from the original feedstock (Digestate), and is defined as the energy densification ratio multiplied by the mass yield of the hydrochar (Danso-Boateng *et al.*, 2013). The energy yield depends a lot on the type of feedstock and decreases with increasing temperature agreeing with the results from Danso-Boateng et al. (2015). The energy yields in our hydrochars ranged from 61.22% at 250°C to 70.05% at 160°C, but these values are significantly higher than the energy yield obtained by Berge et al. (2011a) for digestate (41.5%) and more similar to the results by (Danso-Boateng et al., 2015) for sewage sludge (68 - 89%). Energy densification takes place when the solid mass decreases as a result of dehydration and decarboxylation reactions; that means the carbon content increases and the hydrogen and oxygen content decrease. Therefore, temperature and reaction time have significant influence on the energy densification of the hydrochar (Danso-Boateng et al., 2015, Danso-Boateng et al., 2013). The energy densification values for the hydrochars obtained herein were 1.02 (for carbonisation at 160°C), 0.96 (for carbonisation at 220°C) and 1.08 (for carbonisation at 250°C). The values in our study were lower when compared with values obtained from primary sewage sludge by Danso-Boateng *et al.* (2015), which ranged from 1.02 to 1.28 at temperatures between 140 and 200°C and reaction times between 15 - 240min. However, it has to be taken into account that digestates have a lower carbon content compared with primary sewage sludge due to anaerobic digestion in which organic carbon is released during its conversion into biogas (CH_4 and CO_2).

Table 4.2.- Energy characteristics of hydrochar.

Hydrochar	HHV (Mj/Kg)	Energy densification (Mj/Kg)	Energy Yield (%)	H_{yCrec} (%)	L_{yCrec} (%)	CSF
Digestate (Control)	16.61	-	-	-	-	-
160 °C - 30 min	16.97	1.02	70.05	70.28	32.65	0.26
220 °C - 30 min	14.33	0.96	70.62	70.11	31.93	0.26
250 °C - 30 min	17.80	1.08	61.22	62.04	33.99	0.23

HHV: High heating value
L_{yCrec}: Carbon recovered in the liquid fraction
H_{yCrec}: Carbon recovered in the solid fraction
CSF: Carbon Storage Factor

4.2.2.3.Carbon balance in the Hydrochar

The carbon content of the hydrochars obtained after hydrothermal treatment are similar to those reported by Danso-Boateng et al. (2015) (36.63-39.24%) and Berge et al. (2011a) (32.6%). It is important to highlight that it is sometimes challenging to make direct comparisons between hydrothermal treatments conducted by different reserchers due to differences in reactor configurations, reaction conditions and solid loadings, all of which have a large influence on the characteristics of the products during carbonisation (Berge et al., 2011a).

The carbon balance across solid and liquid products is presented in **Table 4.2**. The fraction of carbon recovered in the biochar (H_{yCrec}) as a percentage of initial feedstock carbon, indicates that the carbon in the solid fraction gradually reduces with increasing temperature. The lower value of the carbon recovery in the carbonisation at 250°C (62.04%) was due to a lower hydrochar yield. Nevertheless, the carbon recovery in the hydrochar increased to more than 70% after treatment at 220°C. The carbon recovery in the liquid fraction (L_{yCrec}) is related to the Total Organic Carbon (TOC) obtained in the liquid fraction after carbonisation (see **Table 4.3**). **Table 4.2** also indicates that a similar fraction of Carbon in the liquid was recovered after hydrothermal treatment at each temperature. The carbon fraction that was transferred from the feedstock into the liquid phase ranged from 32.7% at 160°C to 31.9% at 220°C and 34.0% at 250°C, indicating that there was carbon solubilisation after hydrothermal treatment in agreement with (Danso-Boateng et al., 2015).

The carbon storage factor (CSF) is the mass of carbon remaining (stored) in the solid following the biological decomposition in a dry mass of feedstock (Barlaz, 1998) and a similar approach can be applied to the remaining carbon in hydrochars after HT processes. Berge et al. (2011a) have shown some evidence that after the HTC process (of municipal solids wastes) more carbon is stored within the hydrochar than if the waste material had been disposed uncarbonised. The CSFs of the digestate following hydrothermal treatment were 0.26, 0.26 and 0.23 for the treatments at 160°C, 220°C and 250°C respectively. Therefore, CSF values decreased as the carbonisation temperature increased, in agreement with the results reported by (Danso-Boateng et al., 2015). Indeed, higher levels of CSF were obtained in our study at lower temperatures from sewage sludge digestate ranging from 0.30 (at 140°C) to 0.28-0.33 (at 160°C) and slightly lower values of CSF (0.26 to 0.28) at the highest temperature tested (200°C). (Berge et al., 2011a) obtained lower values of CSF (0.14) from digestate after carbonisation at 250°C. This assessment is potentially useful in understanding the behaviour of hydrochars if used as a carbon source for soil amendment.

4.2.3.Characteristics of process waters

The characterisation of the feedstock's liquid fraction (Control liquor) and the process waters after hydrothermal treatment is shown in **Table 4.3**. The results show that the pH in the aqueous phase is influenced by temperature and is generally alkaline. The highest pH of 9.15 was observed after treatment at 160°C, this reduces to 7.14 as the temperature increases to 220°C but then increases to 8.08 as the temperature increases to 250°C. The changes in pH are related to the presence of VFAs, amino acids and ammonia nitrogen that are generated during hydrothermal treatment (Qiao *et al.*, 2011). The hydrolysis of organic material results in a significant increase in soluble carbon (Wirth *et al*., 2015). In this case, the concentration of soluble Chemical Oxygen Demand (COD) increases 7-fold after hydrothermal treatment, increasing from 1,843 mg/L in the initial digestate, to 12,992 mg/L after 220°C treatment; 12,642 mg/L after 160°C treatment; and 12,164 mg/L after 250°C treatment. The same trend is observed for Total Organic Carbon (TOC) concentrations which shows a 10-fold increase from 461 to 4,879 mg of TOC per litre.

Table 4.3.- Characterization of filtered digestate (Control liquor) and process waters after HTP.

Parameter	Control liquor	160°C, 5bar, 30min	220°C, 35bar, 30min	250°C, 40bar, 30min
Soluble COD (mg/L)	1,843	12,642	12,992	12,164
pH	7.78	9.15	7.14	8.08
TKN (mg N/L)	1,493	2,066	2,191	2,354
Ammonium (mg-N/L)	1,344	1,258	1,704	1,685
Total Soluble Phosphorus (mg-P/L)	91.27	94.03	72.60	103.83
Reactive Phosphorus (mg-P/L)	80.12	53.88	59.84	56.84
VFAs (mg COD/L)	4.8	191.1	406.0	715.7
TOC (mg-C/L)	461.56	4,686.77	4,583.71	4,879.33
C (%)	30.53	45.77	49.21	67.97
H (%)	4.44	6.77	6.32	6.56
N (%)	10.19	11.11	12.31	6.56
S (%)	0.74	1.85	2.41	1.82
O (%)[a]	54.11	34.50	29.75	10.92

[a] Calculated as a difference from the sum of C, H, N and S.

The total soluble phosphorus concentration increases after 160°C and 250°C treatments (3% and 13.8% of P concentration, respectively) and decreases after 220°C treatment (21.5% of P). The concentration of reactive phosphorus decreased with respect of the feedstock between 32.7 and 25.3% after hydrothermal treatment.

There are many proteins in the digestate because of the large amount of organic matter from bacterial biomass. During hydrothermal treatment, the proteins hydrolyse and ammonium is released increasing the nitrogen concentration in the process waters (Keymer et al., 2013, Wilson and Novak, 2009). The soluble nitrogen concentration increased with temperature from an initial concentration of 1,493 mgN/l to 2,066, 2,191 and 2,354 mgN/L for the treatments at 160°C, 220°C and 250°C, respectively. The concentration of ammonium nitrogen was lower although gradually increased with temperature.

The concentration of Volatile Fatty Acids (VFAs) increased with temperature and corresponded to 191, 406 and 715 mg/L of COD for 160°C, 220°C and

250°C treatments respectively (see **Table 4.3**). Acetic acid makes the highest contribution to VFAs produced in all the treatments.

Following hydrothermal treatment, the level of carbon in the aqueous phase is higher than in the hydrochars for all treatments, as shown in **Tables 4.2** and **4.3**. The carbon composition in the hydrochar ranges between 33 and 38%, whereas in evaporated residues of process waters, the carbon content ranges from 30 to 68%. The carbon content increases at higher temperature agreeing with the results obtained from TOC analysis. This demonstrates that for this type of feedstock, a large degree of solubilisation occurs following hydrothermal treatment, in agreement with previous reports from similar treatments (Ekpo et al., 2015, López Barreiro et al., 2015).

In addition to carbon, the levels of hydrogen and nitrogen increase after hydrothermal treatment. Moreover, the sulphur content in the liquid fractions increased from 0.74% up to 2.81% after hydrothermal treatment; that may have implications on increasing the levels of H_2S in the final biogas (or precipitation of metal sulphides), if process waters are recycled back into anaerobic digesters.

4.2.4.Anaerobic digestion of HT Slurries and Process waters

The experimental determination of Biomethane Potential was performed for a period of 21 days and deemed to have completed once the daily production of biogas was less than 1% (Nielfa *et al.*, 2015). During all the assays, soluble COD, VFAs, methane potential (BMP), and phosphorus and nitrogen species were measured. The organic composition of the substrates has a big impact on the performance of anaerobic digestion (AD) processes with regard to methane production and stabilisation of organic matter (Nielfa *et al.*, 2015). **Figure 4.2** presents the changes in soluble COD concentration during anaerobic digestion of the different substrates. The results indicate that the soluble COD was consumed by the consortium of anaerobic bacteria in most of the resulting slurries and their process waters to produce biogas. For the 250°C slurry, from the 4th to the 10th day there was a COD solubilisation that may have come from the hydrochar (see **Figure 4.2a**). The presence of hydrochar seems to affect the consumption of organic matter by anaerobic bacteria.

The raw digestate (Control Slurry) and filtered digestate (Control Liquor) did not produce big changes in soluble COD consumption. That may be because the digestate and its filtered fraction has previously been treated by anaerobic digestion and only a small amount of organic matter is available for further biodegradation; however, that still represents a matter of concern for fugitive methane emissions if untreated digestate is disposed on land.

The COD degradation efficiency of the Slurries and Process Waters within 21 days were 56.6% for the raw digestate, 66.9% for the 160°C slurry, 84.6% for the 220°C slurry and 63.6% for the 250°C slurry. Process waters had similar degradation efficiency as the slurries where the filtered digestate had 59.4%, and 69.1%, 79.6% and 63.8% for the 160°C, 220°C and 250°C process waters respectively. These figures are lower than the results obtained by Wirth *et al*. (2015), who reported COD degradation efficiencies between 84 and 107% in process waters from anaerobically digested sewage sludge after HTC at 200°C for 6 hours.

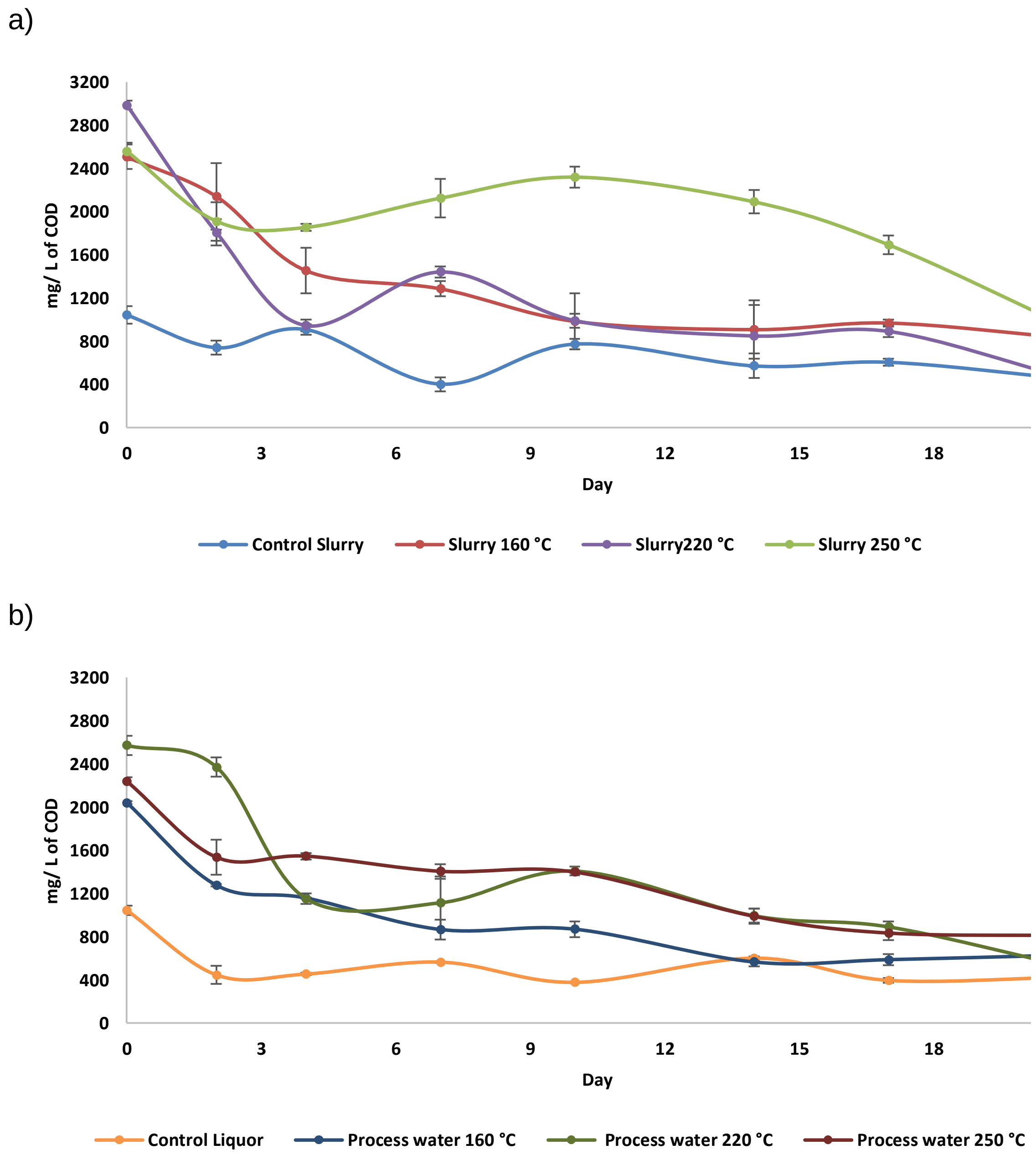


Figure 4.2.- Changes in soluble COD of Slurries (a) and Process Waters (b) during BMP tests.

During the anaerobic digestion process, substrate constituents are hydrolysed by bacterial action into soluble COD. The soluble COD is fermented and turned into VFAs and eventually converted into biogas by methanogenic bacteria. Yields of VFAs produced per mg soluble COD added (mg of VFAs/ mg of COD_{sol} added) during the anaerobic digestion process of Slurries and Process Waters are shown in **Figure 4.3**. The 160°C HTP treatment did not improve the contribution to VFA formation from the hydrochar as the maximum VFA/COD concentration found from the slurry sample (0.15 mg of VFAs/ mg of COD_{sol} added, at day 2) was lower than the corresponding figures found in its process water (0.22 at day 2 and a maximum of 0.24 mg of VFAs/ mg of COD_{sol} added, at day 4). That may suggest potential inhibitory effects on VFA production caused by the actual nature of the hydrochar produced at 160°C. For the HTP treatments at 220°C and 250°C, the resulting hydrochar made a substantial net contribution towards VFA formation with an increment of 13.3% at 220°C and 16.1% at 250°C, with regard to the highest figures found from process waters. For the 220°C slurry, the maximum yield found was 0.17 mg of VFAs/ mg of COD_{sol} added at day 2 and the corresponding figure found in its process water was 0.15 mg of VFAs/ mg of COD_{sol} added, also at day 2. The 250°C slurry produced 0.30 mg of VFAs/ mg of COD_{sol} added after 7 days, while the corresponding process water reported a maximum of 0.31 mg of VFAs/ mg of COD_{sol} added within the same period; the maximum yield of VFA production was found from the slurry at day 14 (0.36 mg of VFAs/ mg of COD_{sol} added).

After reaching their maxima, VFA concentrations would decrease until they will be totally consumed by methanogenic bacteria; therefore, biogas production rates (see **Figures 4.4a and 4.4b**) are intrinsically related to VFA concentrations and based on our findings, it seems that HTC treatments at 220°C and 250°C produce a hydrochar that enhance VFA production and hence, they would potentially contribute to higher methane yields. However, it seems that the net accumulation of VFAs reported from products obtained at 250°C (**Figure 4.3**) is the result of less VFA transformation into methane (**Figure 4.4**), which raises questions over the inhibitory effect that the hydrochar and the process water at 250°C may have over methanogenic bacteria.

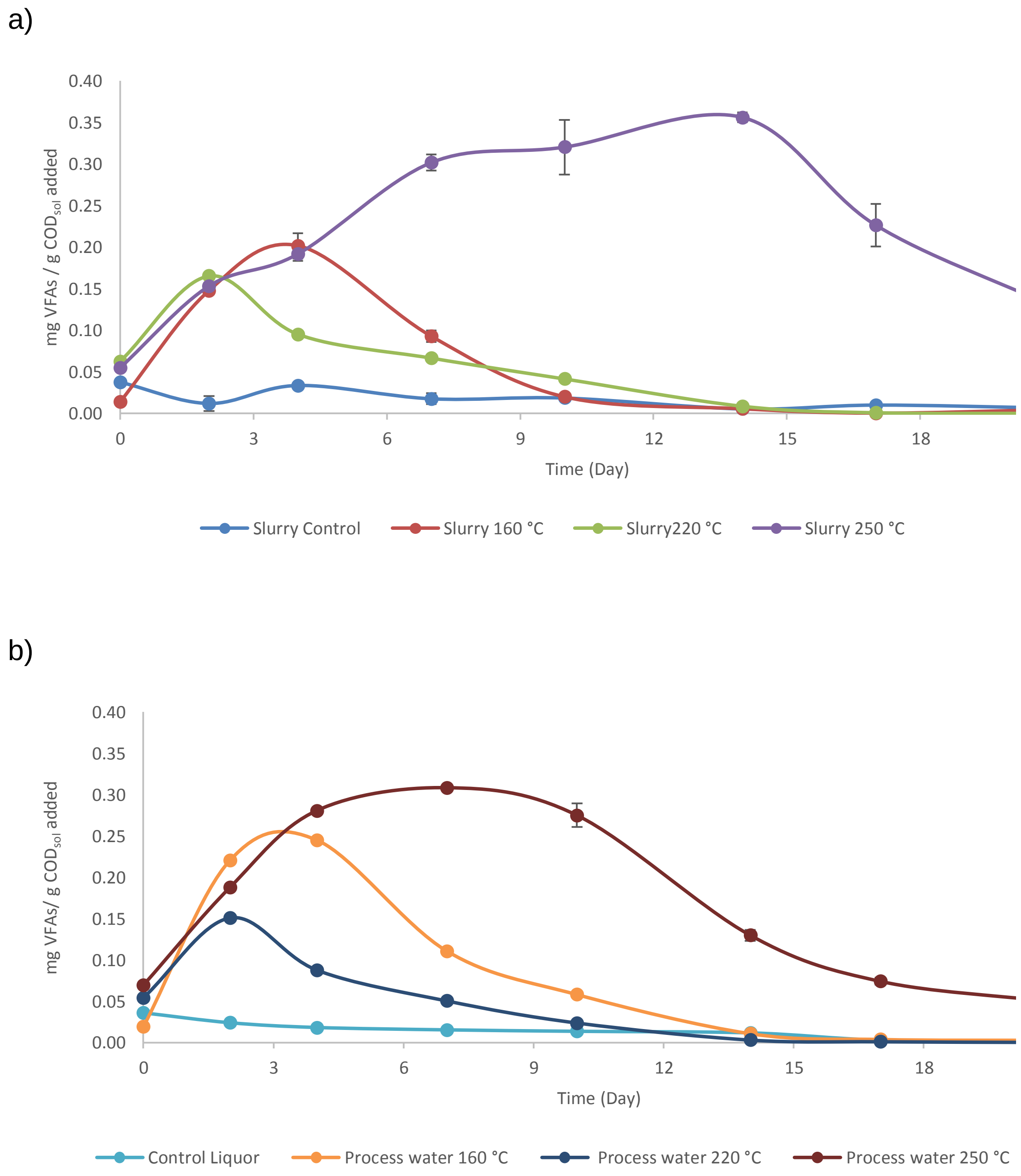


Figure 4.3.- Normalised VFA production from Slurries (a) and Process Waters (b) during BMP tests.

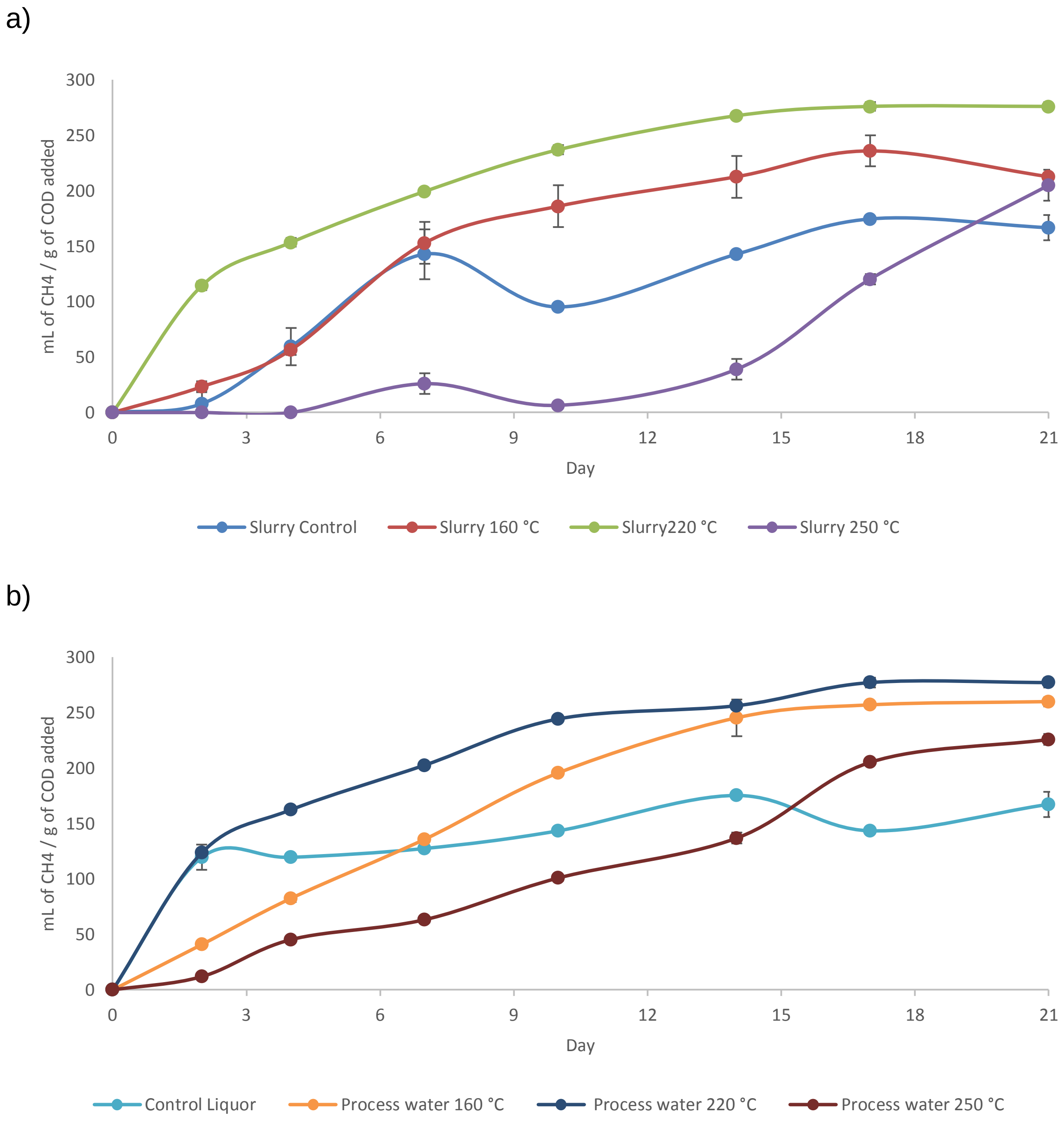


Figure 4.4.- Cumulative methane production from Slurries (a) and Process Waters (b) during BMP tests.

Previous studies using hydrothermal processes as a pre-treatment for anaerobic digestion have shown an increase in methane yields in BMP tests, due to the additional solubilisation of organic matter achieved via thermal hydrolysis (Keymer *et al.*, 2013). After hydrothermal treatment, the BMP increases between 17% and 58% compared with the control (175 mL of CH_4/ g of COD). It is shown in **Figure 4.4** that the BMP values for the slurries following hydrothermal treatment were 236 at 160°C, 276 at 220°C and 205 at 250°C, all reported in mL of CH_4/ g of COD. Nevertheless, it is worth to provide further discussion to the results from the BMP test of the digestate treated at 250°C, as it seems that the methane production could have continued after the 21 days of the BMP test, considering the remaining VFA concentration (**Figure 4.3**). Therefore, the methane potential of the digestate treated at 250°C has been underestimated and it is inferred that the net methane production should have been higher than the results obtained at 220°C after 21 days. The presence of hydrochar affects the production of biogas which is reflected in the delay of VFA production (Figure 3) and the subsequent delay in the production of methane (Figure 4). Also it was observed that an additional solubilisation of COD (**Figure 4.2a**) occurs after the VFAs reached the highest concentration. Although other factor that might influence is the presence of less digestible higher molecular weight organic compounds formed during the thermal process at that temperature (Danso-Boateng et al., 2015), or other compounds that could delay methane production.

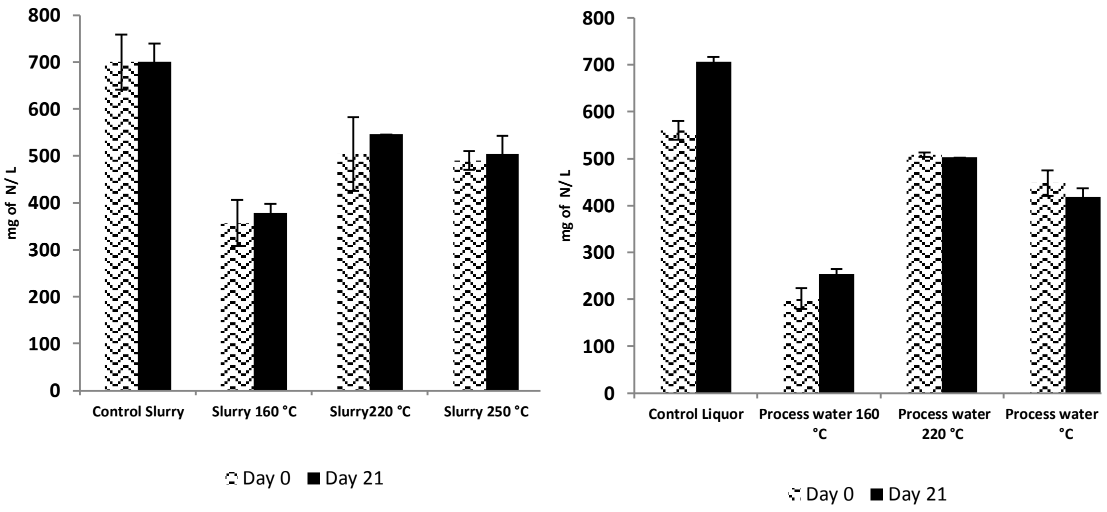
The BMP values for process waters following hydrothermal treatment increased between 29% and 58% compared with the control sample (175 mL of CH_4/ g of COD). The highest value was for the processed water of 220°C treatment (277 mL of CH_4/ g of COD) followed by 160°C treatment (260 mL of CH_4/ g of COD) and 250°C treatment (225.8 mL of CH_4/ g of COD). The BMP values of process waters were similar to the slurries of the digestate after hydrothermal treatment for the treatments at 160 and 220°C and the hydrochars did not affect the anaerobic process unlike the 250°C slurry and its process water.

A similar study was carried out by (Qiao et al., 2011) in which they use sewage sludge treated at 170°C for 1 hour; they also performed BMP tests on the slurry and the processed water. The results showed an improvement of 65.5% in methane production from the slurry (257 mL of CH_4/ g of VS) and 147.5% (385 mL of CH_4/ g of VS) of methane production of the process water with respect the raw sewage sludge (155 mL of CH_4/ g of VS).

4.2.4.1.Nutrient solubilisation during the BMP test

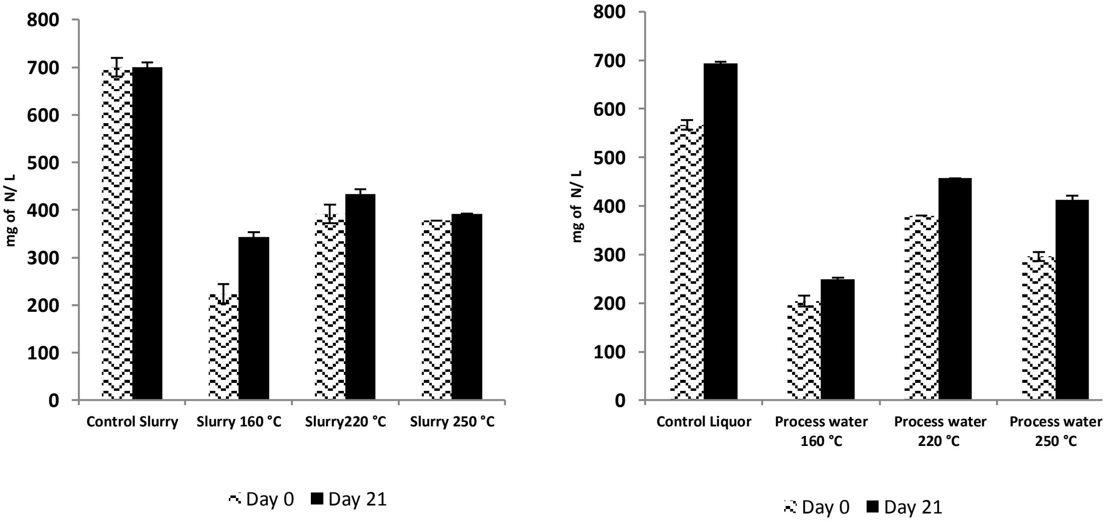
Figure 4.5 shows the soluble nitrogen fraction (soluble TKN and ammonium) before and after anaerobic digestion (i.e., at Day 0 and Day 21 of the BMP tests). It can be seen that after anaerobic digestion, with the exception of the slurry control and the processed water at 220 and 250°C treatment, the soluble TKN concentration increased from 3 to 26% in all the other substrates. However, these increases are within the error bars range and can be considered null.

It is necessary to track the ammonia concentration because it is thought that concentrations above 1.1g of N per litre can cause inhibition of the methanogens (Hansen et al., 1998). The ammonium concentration increases in all substrates after the anaerobic digestion between 4 and 39%. As a result, the nitrogen solubilised during the anaerobic digestion was mostly ammonium coming from the hydrolysis step of proteins and bacterial biomass. As a consequence, an increase in the nitrogen concentration, especially in ammonium is observed (Münch and Barr, 2001, Wilson and Novak, 2009). These findings match with previous studies of substrates such as algae after hydrothermal and anaerobic treatments, in which the soluble nitrogen concentration increased after anaerobic digestion (Keymer et al., 2013, Ras et al., 2011).



a) Soluble TKN in slurries

b) Soluble TKN in process waters



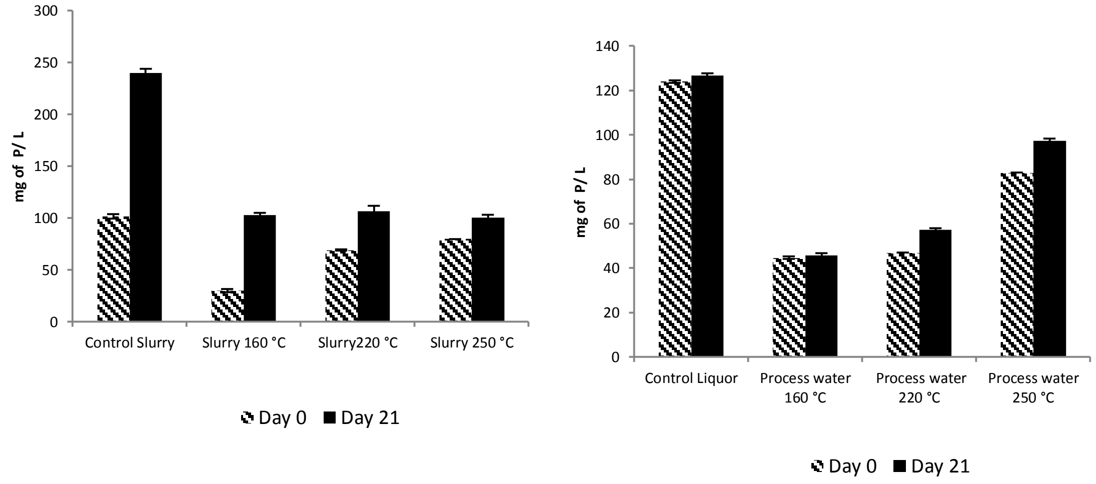
c) Ammonium in slurry

d) Ammonium in process waters

Figure 4.5. Changes in the concentrations of soluble TKN and ammonium in slurries (a and c) and process waters (b and d) before (Day 0) and after (Day 21) BMP tests.

The total soluble phosphorus concentration after anaerobic digestion tends to increase. **Figure 4.6** indicates that there is a solubilisation of phosphorus for all the substrates after anaerobic digestion ranging between 2 to 242% over the starting concentration, which is in agreement with the work conducted by (Münch and Barr, 2001). Most of the phosphorus solubilised was reactive phosphorus as shown in **Figures 4.6c and 4.6d**, where the concentration increased after anaerobic digestion. All the slurries had good solubilisation of reactive phosphorous. The highest solubilisation was for the 160°C slurry with almost a 9-fold increase over the starting concentration. The level of P solubilisation from the slurry produced at 160°C (242%) is comparable with that for the control slurry (236%); whereas for the slurries produced at higher temperature, the solubilisation of P is much lower (26-54%), which may be due to interaction with the hydrochar.

Those results represent an improvement in nutrient retention when compared with figures found in digestate cake (sewage sludge digestate after dewatering); that characteristic may also improve the release rate of P in the hydrochar when spread on land. Hydrothermal treatment of the process waters alone results in significantly less solubilisation of phosphorous (2 - 33%), with the majority of P coming from the biomass in the inoculum. The process waters did not experience major changes with regard to the concentration of reactive phosphorus probably due to the small amount of solids presented in the mixtures, which may indicate a high adsorption capacity of the hydrochar for phosphate species.


a) Total soluble phosporus in slurries

b) Total soluble phosphorus in process waters


c) Reactive phosphorus in slurries

d) Reactive phosphorus in process waters

Figure 4.6. Changes in Total Soluble Phosphorus and Reactive Phosphorus concentrations in slurries (a and c) and in process waters (b and d) before (Day 0) and after (Day 21) BMP tests.

4.2.5.Theoretical BMP v. Experimental BMP

The use of empirical formulas to predict the potential production of methane is widely accepted, due largely in part to being relatively fast, reliable and economical. Nevertheless these equations do not differentiate between biodegradable and non-biodegradable organic matter (Lesteur et al., 2010, Nielfa et al., 2015). According to Labatut *et al.* (2011) the values of the theoretical formulas are always higher than the experimental ones because they do not account for the substrate biodegradability or metabolic processes. For example, the Buswell’s equation does not count the carbon that is locked in the cell protoplasm of new anaerobic bacteria (nearly 12%) (Labatut *et al.*, 2011). Therefore, not all the biodegradable organic matter used by the bacteria contributes to the production of methane.

To define how accurate Buswell’s and Boyle’s equations are in order to determine the methane yields in the hydrothermally treated substrates, a comparison between the experimental and theoretical BMP was carried out as shown in **Table 4.4**. The values of theoretical BMPs (BMPth) were calculated based on the elemental composition of the process waters with and without the presence of hydrochars. Previously, authors have reported that the theoretical productivity decreases in substrates containing higher nitrogen, hydrogen and sulphur content, which can produce toxic concentration of ammonia and hydrogen sulphide (Denis and Burke, 2001).

The Buswell’s equation predicts higher values than the Boyle’s equation. However, the BMPth values in both cases are higher than the experimental values. The Boyle’s equation has the closest match to the experimental values and that may be due to the fact that the model considers the presence of proteins and ammonia whereas the Buswell’s equation does not consider the presence of nitrogen (Nielfa *et al.*, 2015).

Some researchers have proposed that the theoretical methane yields are affected by reaction temperature and time during hydrothermal treatment (Danso-Boateng *et al*., 2015). The predictive equations both show similar trends, with the highest temperature for hydrothermal processing resulting in the highest BMPth. As the predictive calculations are based on elemental content, the control samples have a higher predicted BMPth than the hydrothermally treated samples. The biodegradability and methane yields of the substrates can also be determined by using values of BMPexp and BMPth (Raposo *et al.*, 2011). The biodegradability represents the amount of organic material that is degraded during the anaerobic process. Table 4 presents the biodegradability of the substrates based on both the Boyle’s and Buswell’s equations.

The experimental BMP tests show that the lower temperature hydrothermal treatments produce higher BMP than the higher temperature processing.

This is probably due to inhibitory effects related to increasing process temperatures because of the formation of inhibitory compounds such as phenols, furans, etc (Biller and Ross, 2012, Danso-Boateng et al., 2015). The control shows the lowest BMP as expected. Comparison between the theoretical prediction and experimental figures generally indicates that for lower temperature processing (160 - 220°C), the equations provide a reasonable match. The experimental BMP is 96% of the theoretical BMPth determined by the Boyle equation and 70% of the BMPth determined by the Buswell equation. As the temperature rises to 250°C, the experimental BMP drops significantly to 44% of BMPth, however this still represents a significant enhanced biogas formation. The value of biodegradability in the digestate treated at 250°C does not represent the complete potential as this test was still generating methane after 21 days so this result may underestimate the true BMP. The biodegradability values provide more robust data for predicting overall enhanced energy recovery, which can be used to better calculate and assess energy balances for integrating AD and HTC at WWTWs. Based on the results in this study, it is likely that lower temperature hydrothermal treatment is more advantageous than higher temperature for processing sewage sludge digestate.

For lower temperature hydrothermal treatment, slurry samples had similar biodegradability as process waters and the presence of hydrochars did not affect the biodegradation of the organic matter present in process waters. Biodegradability dropped for both process water and slurry following higher temperature processing indicating that inhibitory effects may occur.

Table 4.4.- Comparisons between experimental BMP and theoretical BMP.

Sample	BMPexp (mL of CH_4 /g of COD added)	BMPth Boyle's Equation (mL CH_4 / g COD)	BMP Buswell's eq. (mL CH_4 / g COD)	BD Boyle's Equation	BD Buswell's Equation
Control Slurry	174.6	251.0	303.7	70%	57%
160° Slurry	235.9	271.6	353.9	87%	67%
220° Slurry	276.1	289.3	384.4	95%	72%
250° Slurry	205.0	403.0	513.2	51%	40%
Control Liquor	175.4	251.0	303.7	70%	58%
160°C Process Water	260.0	271.6	353.9	96%	73%
220°C Process Water	277.2	289.3	384.4	96%	72%
250°C Process Water	225.8	403.0	513.2	56%	44%

BD: Biodegradability; DT: Digestate treated;
BMP_{exp}: Experimental Biomethane Potential; BMPth: Theoretical Biomethane Potential.

4.2.6.Energy production of the hydrothermal treatments.

The energy production of the conventional AD is limited by the production of methane from sewage sludge in which 35 to 45% of the organic fraction is biodegradable (Shana *et al.*, 2011). Thermal hydrolysis as a pre-treatment helps to improve biogas production up to 43% and COD removal up to 75% (Sridhar Pilli *et al.*, 2015). However, the integration of thermal treatments following anaerobic digestion, not only improves digestate dewaterability by reducing moisture in the solid fraction, but also it was found that the solid fraction has the potential to be used either as a solid fuel or as a carbon source for soil amendment.

Table 4.5 shows the energy production per kg of sewage sludge from different process configurations including conventional AD, thermal hydrolysis (TH) as a pre-treatment of AD processing (TH + AD) and different hydrothermal treatments as post-treatment steps following AD.

The biogas production following thermal hydrolysis as pretreatment is better than the conventional AD and the hydrothermal treatments. However, the use of hydrochars as an energy source gives an added value to the hydrothermal treatments favouring the energy production. The additional energy that can be obtained from hydrothermal treatments comes from the hydrochar that can be used as a solid fuel and ranges from 153 to 179% in comparison with the thermal hydrolysis that is just 43%. The results suggest a better use of the sewage sludge when hydrothermal treatment is used after AD.

Table 4.5.- Energy production of different thermal treatment configurations for a 15% solids sewage sludge.

	Energy produced from CH_4 per kg of feedstock (Mj)	**Energy produced in char per kg of feedstock (Mj)**	**Overall energy produced per Kg of feedstock (Mj)**
Conventional AD	7.08	-	7.08
*TH + AD	10.13	-	10.13
AD + 160T + AD	8.09	11.68	19.77
AD + 220T + AD	8.36	10.52	18.88
AD + 250T + AD	7.86	10.10	17.96

BMP of Mix sludge = 226 of CH4 /g of COD added (experimental value)
*BMP of THP Mix sludge = 323.2 of CH4 /g of COD added (assuming 43% additional production) (Sridhar Pilli et al., 2015)
HHV of methane, 1m3 = 35.8Mj

4.3. Conclusions

Hydrothermal treatments improved the characteristics of the sewage digestate producing hydrochars and process waters rich in organic matter and nutrients. Anaerobic digestion was demonstrated to be a suitable option to treat process waters from hydrothermal treatments for further biomethane production. Processing of digestate at 250°C resulted in a hydrochar that enhanced the net production of VFAs, although delayed methane production (longer lag phase) and hence, higher methane production would be expected. The addition of hydrochar (250°C) to the process water delayed VFA production during anaerobic digestion. Hydrothermal processing of process water and slurries at lower temperature (160-220°C) produced high levels of biogas, with no detrimental effect due to the presence of hydrochar. The Boyle's equation had a closer match to the values provided by experimental biomethane potential (BMP) tests at lower temperature. Further studies are needed to understand the influence of adding hydrochar on the quality and safety of the digestate for final disposal, as well as the impacts on AD processes due to process water recycling.

4.4. Summary

In this chapter, the potential of hydrothermal processing as a novel alternative to treat the digestate has been be evaluated. The effect of temperatures is evaluated with respect to product yields, biomethane potential and solubilisation of organic carbon. Three different temperatures were evaluated: 160, 220 and 250°C at 30 minutes reaction time. The hydrochar yields obtained were 73.42% at 220°C, 68.79% at 250 °C and 56.75% at 160°C treatment. It was found that the 250 °C treatment lead to the production of the hydrochar with the best characteristics for energy production. The solubilisation of carbon was increased from 4.62% in the raw feedstock to 31.68%, 32.56% and 30.48% after thermal treatments at 160, 220 and 250°C, respectively. The thermal treatment enhanced the potential methane production in all products up to 58% for both, the whole fraction (hydrochar + processed water) and processed waters. However the BMP of the process water coming from the 250 °C treatment was sub-estimated. The Boyle's and Buswell's equation were used to calculate theoretical methane yields for all hydrothermal products. Theoretical methane yields were compare with experimental data from biomethane potential (BMP) tests and it was found that the Boyle's equation had closer agreement to BMP values.

4.5. Publications and awards derived from this chapter

- ***Aragón C.**, Ross A. and Camargo-Valero M. (2017). "Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatment.". Applied Energy, Volume 208, 15 December 2017, Pages 1357-1369 . https://doi.org/10.1016/j.apenergy.2017.09.019
- ***Aragón C.**, Camargo-Valero M. and Ross A. (2017). Integration of hydrothermal carbonisation in the waste water treatment. In proceedings of the 1st International Symposium on Hydrothermal Carbonisation. Queen Mary, University of London, London, United Kingdom.
- ***Aragón C.**, Camargo-Valero M. and Ross A. (2016). Potential of sewage sludge digestate for energy and nutrient recovery. In proceedings of the

Resource Recovery from Waste (RRFW) Annual Conference 2016. Leeds, United Kingdom.

- ***Aragón C.**, Camargo-Valero M. and Ross A. (2016). Hydrothermal Processes as an Alternative to Conventional Sewage Sludge Management. In proceedings of the 2nd AD Network (a BBSRC NIBB) Early Career Researcher conference (Poster presentation). University of Birmingham, Birmingham, United Kingdom.

Chapter 5. Hydrothermal Carnonization of Sewage Digestate: Influence of the solid loading on hydrochar and process water characteristics.

5.1. Introduction

Sewage sludge (SS) is produced as part of routine operations at wastewater treatment works (WWTWs) and its management is still an important global issue due to the large amounts generated on a daily basis (He et al., 2013). In the UK, 1.4 million tonnes of sewage sludge (dry weight) are produced annually and around 75% of that undergoes anaerobic digestion (AD) (DEFRA, 2012b). Despite anaerobic treatment, the resulting sewage digestate is still rich in organic matter and hence, it has the potential to be used as a feedstock for the production of solid energy carriers (Almeida, 2010, Danso-Boateng et al., 2015, He et al., 2013, Kim et al., 2014, Mumme et al., 2011, Yoshida and Antal, 2009).

Hydrothermal carbonization (HTC) is considered an alternative technology to harness energy from sewage digestate, as wet feedstocks are perfectly suitable for this process – i.e., no need for energy intensive dewatering units, as it is the case in digestate pyrolysis. HTC is conducted at temperatures ranging from 200 to 250°C and pressures ranging from 10 to 40 bar (Biller and Ross, 2012, Hübner and Mumme, 2015, Mumme et al., 2011, He et al., 2013). HTC products include process waters rich in organic compounds suitable for anaerobic digestion and a charcoal like material (hydrochar) that can be used either as a solid fuel or as a soil amender (Biller and Ross, 2012, Wirth et al., 2015, Danso-Boateng et al., 2015). Hydrochars often have a higher energy density than the feedstock due to deoxygenation (Biller and Ross, 2012) and process waters tend to concentrate soluble organic matter and nutrients like nitrogen and phosphorus compounds (Aragón-Briceño et al., 2017). The specific hydrochar and process water characteristics however are highly dependent on the choice of feedstock and process conditions (Zabaleta et al., 2017, Wirth et al., 2015).

The integration of HTC into wastewater systems as a post-treatment step after AD is still under development, but commercial HTC processes are already available – i.e., The Terranova® Ultra-Process (© TerraNova Energy GmbH, 2018). That offers potential energetic and economic benefits from the stabilisation of sewage digestate while producing not only a solid fuel product that can be used in a coal fired power plant, but also carbon-rich process water for enhanced biomethane production in existing AD units at WWTWs (Aragón-Briceño et al., 2017). The majority of studies reported in published literature on the use of HTC for sewage digestate processing, have been conducted in batch reactors at laboratory scale. Common findings lead to conclude that feedstock characteristics, as well as temperature and reaction time are the main operating conditions influencing hydrochar characteristics; in general, the higher the process temperature and the longer the carbonization time, the higher the carbon content and energy density of the resulting hydrochar (Aragón-Briceño et al., 2017, Zabaleta et al., 2017, Danso-Boateng et al., 2015, Ekpo et al., 2015, Wirth et al., 2015, Wirth and Mumme, 2013, Mumme et al., 2014, Escala et al., 2013, He et al., 2013, Berge et al., 2011a). For sewage digestate in particular, HTC processing at high temperatures and short reaction times however (250°C, 30min), can still produce a hydrochar with High Heating Values (HHV) in a range suitable to be used as solid energy carriers (Aragón-Briceño et al., 2017).

On the other hand, the influence of solid loading on the characteristics of the resulting hydrochar and process water has received less attention. The only few examples reported in the literature using food waste as feedstock have concluded that higher solid loading contributes to higher hydrochar yields, carbon efficiencies and energy ratios(Zabaleta et al., 2017). Therefore, the influence of solid loading on HTC used for sewage digestate processing and its effect on the characteristics of the resulting hydrochar and process water have not been reported. Most importantly, there are no previous research works studying the influence of solid loading on the anaerobic biodegradability of the process water or its total bio-methane potential; scientific evidence is desperately needed in order to fill this gap and contribute to the better understanding of the overall energy production in an integrated AD+HTC system at sewage treatment works.

Therefore, the main objective of this study is to investigate the influence of solid loading on hydrochar and process water characteristics from HTC used for processing sewage digestate. Production yields and composition of hydrochars and the levels of solubilisation of organic matter and nutrients in process waters are presented. Results from experimental biomethane potential (BMP) tests conducted on process waters are used to present an overall energy balance for the proposed AD+HTC process. The results reported in this work would inform the potential for implementing a comprehensive treatment process that integrates AD and HTC for sewage sludge management at WWTWs.

5.2. Methods

5.2.1.1.Mass and energy balance

Aspen plus was used to analyse in more detail the potential to combined AD and HTC processes; mass and energy balances of the proposed system were made in more detail. HTC, AD and CHP (Combined Heat and Power) systems were modelled and interconnected. Aspen Plus V8.8 was used throughout with a 'COMMON' method filter and an 'IDEAL' base method. The following assumptions were made: ambient conditions of 1 bar and 23°C and molar air composition assumed as 79:21 split of N_2:O2 only.

Experimental ultimate and proximate results of digestate sludge and associated hydrochar after HTC at 250°C and 40 bar were used to create 'nonconventional solid' components for their representation in the model. Acetic acid was used as a model representation of COD for the liquid fraction of the digestate liquor and HTC process water, where there is 0.938g of acetic acid for 1.0g of COD.

The HTC system begins with sludge contained in the stream labelled 'INLET', which is pumped to a pressure of 40 bar and contains a flow of 100 kg per hour. The pressurised sludge then exchanges heat with the HTC outlet in the heat exchange 'HX'. The sludge is then heated to the desired HTC temperature of 250°C. The HTC reactor has been represented by a 'RYield' block which allows the user to specify desired yields of components at a specific temperature and pressure. Experimental data has been used accordingly so the reactor outlet's holds hydrochar and process water in the quantity and composition found under lab under conditions (40 bar, 250°C).

A separator block was used as representation of a centrifuge which splits the solid and liquid fractions. A heater block has been used before the AD unit to represent the thermal energy requirements of heating the process liquid to 35°C. The process water is sent to an anaerobic digester that has been simulated in another RYield block at 35°C and 1 bar. Here, BMP lab results have been used to determine its outlet yield composition. A Separator block has been used to represent the extraction of biogas from the head space of the digester.

After that, the biogas is then ready for processing in the combined cycle gas turbine system. It is first compressed to 8 bar before meeting compressed air (also at 8 bar) in the combustion furnace. The furnace has been simulated with an adiabatic 'RGibbs' block. Excess air was used to maintain a temperature that was below 1,100°C, generally used as the upper-limit operating temperature of furnace materials.

The hot exhaust gas is passed through a turbine which recovers energy as electrical power based on the decompression from 8 bar to 1 bar. The decompressed exhaust gas, still carrying an abundance of thermal energy exchanges heat with compressed water (20 bar) to generate high pressure steam. The high pressure steam, passes through a turbine, decompressing to 1 bar and generating further electrical power. The remaining steam is cooled to 23°C in a 'Heater' block in order to determine the thermal power output of the system.

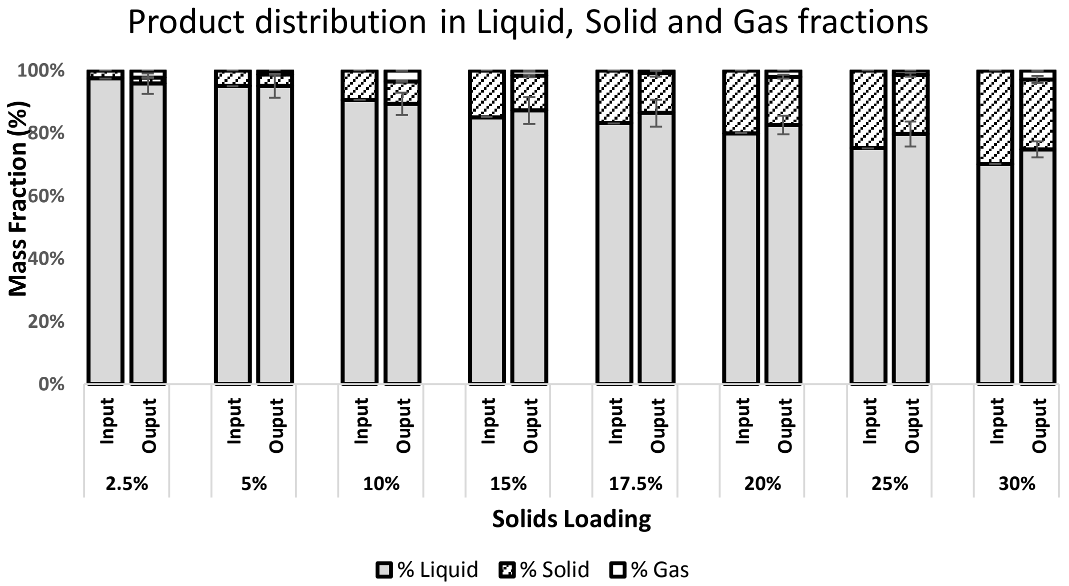
The electrical power balance has been created using a 'Mixer' block that quantifies the net electrical power production via the summation of consumption from pumps and compressors with production from turbines. The power consumption for centrifuge has been set at 35 kWh/t as stated in Huber Technology (2018). The thermal power balance has been created using another 'Mixer' block that quantifies the net thermal power production/consumption based on the heat duties of heater blocks 'HTC-HEAT', 'AD-HEAT' and 'HEAT-EX'. The CHP efficiencies calculate the power balances from blocks used only in energy recovery, whereas system efficiencies account for the pumps and heaters used during the HTC process.

5.3. Results and discussions

5.3.1.Mass balance

The distribution of products from sewage digestate before and after HTC at different solid loadings is presented in **Figure 5.1.** The output mass of combined solid and liquid fractions was reduced after HTC treatment by 1.4 to 3.5%. These values were slightly lower compared with the study carried out by Zabaleta et al. (2017), who reported mass losses between 2.3 and 7.1% when food waste was under HTC processing at different solid loadings and different temperatures (180-200°C). The mass losses were attributed to the transfer of the initial carbon (2-11%) to the gas phase, mainly CO_2, derived from the decarboxylation reactions (Berge et al., 2011a, Zabaleta et al., 2017).

The solid fraction of the feedstock was reduced between 24 to 37% following HTC. That is due to solubilisation of some of the original biomass into the liquid phase during HTC, which includes both soluble inorganic and organic material (Aragón-Briceño et al., 2017, Ekpo et al., 2015). Nevertheless, as the solid loading increases, there is a slight increase in the yield of solid product following HTC (**see Figure 5.1b**).



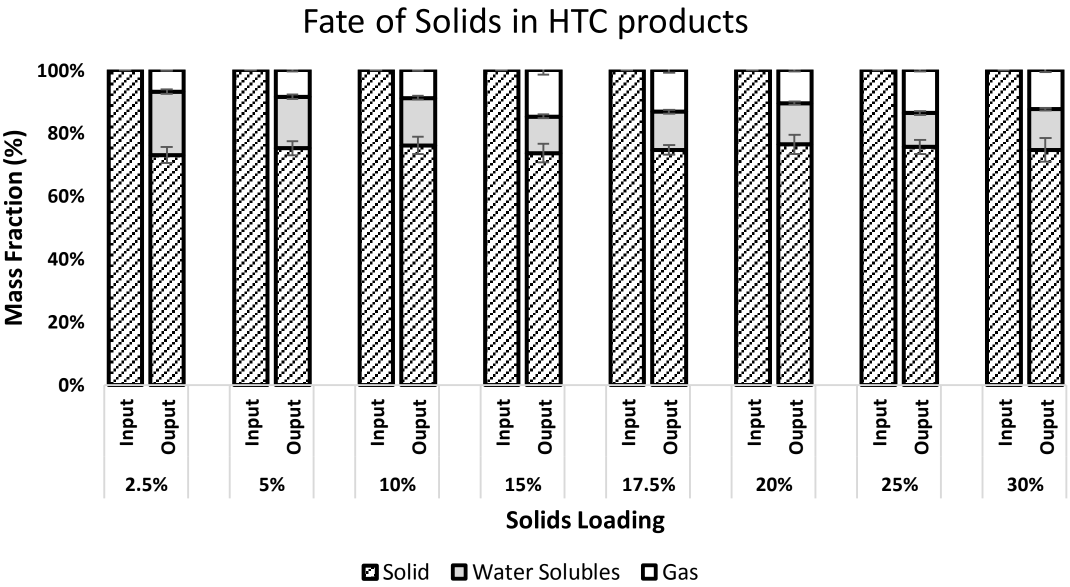


Figure 5.1.- Changes in the feedstock after HTC at different solid loadings. a) Product distribution in Liquid, Solid and Gas fractions and b) Fate of solids from the feedstock

5.3.2.Hydrochar characteristics

5.3.2.1.Physical characteristics

The yield of hydrochar generally increases with increasing solid loading in agreement with the results reported from food waste by Zabaleta et al. (2017). Hydrochar yields range from 67.9% at 2.5 wt% loading to 75.6% at 25.0% loading (**Table 5.1**). The yields obtained in this study are similar to the values reported by Danso-Boateng et al. (2015) from primary sewage sludge

(60.5 to 81.1% at 4.5% solid loading) and slightly higher than the findings reported by Aragón-Briceño et al. (2017) from sewage digestate (56.8% at 4.5% solid loading).

The ash content of the resulting hydrochar reduces as the solid loading increases from 51.2% at 2.5% loading to 48.5% at 30% loading (**Table 5.1)**. This suggests that less carbon is solubilised as the solid loading increases and correlates with a slight increase in hydrochar yield. The ash content of hydrochars are similar to those reported for hydrochar produced from sewage sludge (Aragón-Briceño et al., 2017, Ekpo et al., 2015, Danso-Boateng et al., 2015, Berge et al., 2011b).

The volatile matter content of the resulting hydrochars is similar at all solid loadings and ranges between 40.4 and 42.4%; however, the volatile matter content of the hydrochars is lower than the feedstock – i.e., 51.8% for the feedstock, while hydrochars had a minimum of 40.3% after HTC.

Table 5.1.- Proximate and ultimate analyses of the feedstock (digestate cake) and hydrochar.

Sample	Proximate Analyses				Ultimate analysis					Yield (%)
	Moisture (%)	Ash (%db)	Volatile matter (%db)	Fixed carbon [a] (% db)	C (%)	H (%)	N (%)	O^b (%)	S (%)	
Feedstock	2.1	36.7	51.8	9.3	33.3	4.61	4.0	20.3	1.2	
Hydrochar										
2.5%Hy	2.0	51.2	41.9	4.9	32.1	4.2	1.9	9.4	1.2	68%
5%Hy	1.7	50.0	41.7	6.5	32.3	4.2	2.1	10.3	0.8	72%
10%Hy	0.9	48.4	42.4	8.4	33.1	4.4	2.3	10.5	1.2	75%
15%Hy	1.7	49.4	40.4	8.5	33.0	4.3	2.3	9.8	1.3	74%
17.5%Hy	1.7	49.7	40.7	7.9	33.1	4.2	2.3	9.4	1.3	75%
20%Hy	1.6	48.6	41.5	8.4	33.8	4.3	2.4	9.7	1.3	76%
25%Hy	1.7	48.0	41.7	8.5	33.8	4.3	2.6	9.9	1.3	76%
30%Hy	1.9	48.5	41.2	8.4	34.4	4.4	2.8	8.7	1.2	75%

[a] 100 - (moisture + ash + volatile matter).

[b] Calculated as difference between sum of C,H,N,S.

5.3.2.2.Elemental composition of the hydrochar

The elemental composition of hydrochars following HTC are shown in **Table 5.1**. The carbon content of the hydrochars increases with increasing solid loading (from 32.1% at 2.5% solid loading to 34.4% at 30.0 solid loading), but there only a slight increase in carbon content compared to the original feedstock was achieved at the highest solid loading tested (≥ 20% solid loading). Levels of oxygen are reduced significantly following HTC due to the occurrence of dehydration and decarboxylation reactions. **Figure 5.2** shows Hydrogen-to-Carbon (H/C) and Oxygen-to-Carbon (O/C) ratios of the feedstock and hydrochars. The slight reduction of the H/C ratio in the hydrochars provides evidence for dehydration and decarboxylation during hydrothermal carbonisation (Danso-Boateng et al., 2015). Nevertheless, changes in solid loading did not provide a clear correlation with regard to its influence on dehydration and decarboxylation reactions, in agreement with the findings reported by Zabaleta et al. (2017). Nitrogen content in the hydrochar increases along with increments in solid loading (see **Table 5.1**); however, all hydrochars have a much lower N content (1.9 - 2.8%) when compared with the original feedstock (4.0%) as the hydrolysis of N-rich compounds during HTC promotes the accumulation of ammonium in process waters (Aragón-Briceño et al., 2017).

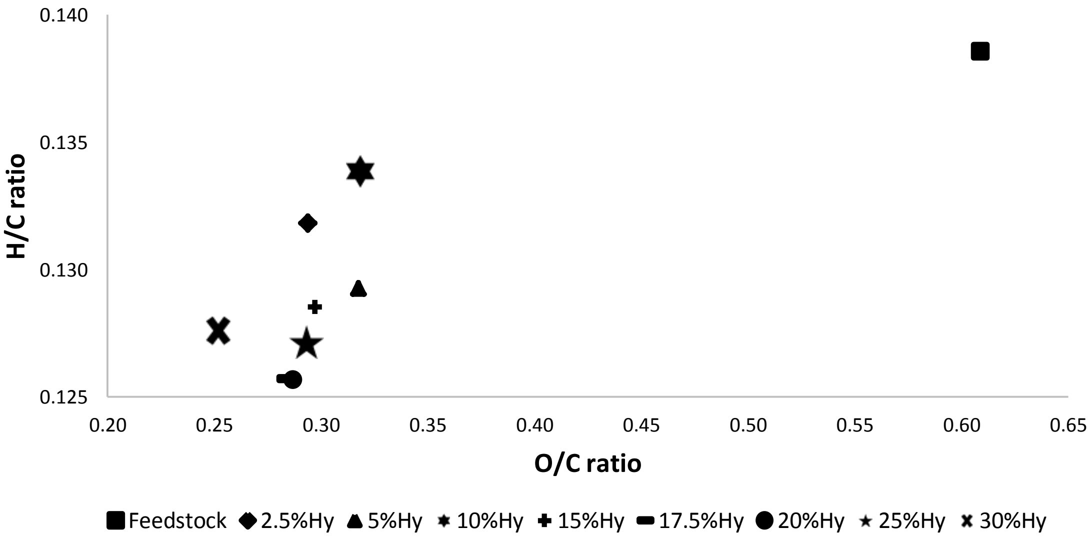


Figure 5.2.- Atomic H/C and O/C ratios of feedstock and hydrochars following HTC (250°C and 30min retention time) at different solid loadings.

5.3.2.3. Energy characteristics of the hydrochar

The energy density of hydrochars and feedstock are listed in **Table 5.2**. The Higher Heating Value (HHV) of the hydrochars are only slightly higher than the original feedstock (14.4 MJ kg^{-1}), with a maximum value of 16.5 MJ kg-1 at 30 wt% solid loading. This low level of energy densification is typical for wet feedstocks such as sewage digestates, which tend to result in larger levels of solubilisation of the organic carbon during HTC processing. There is a slight increase in HHV as solid loading increases and this corresponds to a higher carbon content in the resulting hydrochar. The energy densification values obtained for hydrochars ranged from 0.97 to 1.03 MJ Kg^{-1}. The HHVs of the hydrochars produced were higher compared with the values reported by Berge et al. (2011a) for digestate (13.7 MJ Kg^{-1}) and lower than those reported by Danso-Boateng et al. (2015) (17.2 – 18.4 MJ Kg^{-1}) and Aragón-Briceño et al. (2017) (17.8 MJ Kg^{-1}) for primary sludge and digestate, respectively. The energy densification recovered within the hydrochar is considerably lower compared with other feedstocks, but indicates that a significant amount of the energy is present in the liquid fraction and potentially available for recovery via anaerobic digestion (Aragón-Briceño et al., 2017).

The energy yield provides useful information about the amount of energy remaining within the hydrochar from the original feedstock. The energy yield showed a similar trend as HHV with ranges from 65.9 to 76.7% but it seems from 20% solid loading in HTC the energy yield are similar.

Table 5.2.- Energy characteristics of the feedstock and hydrochars.

Hydrochar	HHV (Mj/Kg)	Energy densification (Mj/Kg)	Energy Yield (%)	HyCrec (%)	LyCrec (%)
Feedstock	14.4	-	-	-	-
2.5%Hy	15.4	0.97	65.9	65.5	33.4
5%Hy	15.3	0.97	69.8	69.9	35.8
10%Hy	15.8	1.00	74.4	74.3	27.1
15%Hy	15.7	0.99	73.1	73.0	16.9
17.5%Hy	15.6	0.97	72.5	74.3	19.4
20%Hy	15.9	1.00	76.2	77.6	18.6
25%Hy	16.0	1.01	76.6	76.8	17.5
30%Hy	16.5	1.03	76.7	77.1	20.5

HHV: High heating value

H_{yCrec}: Carbon recovered in the solid fraction

L_{yCrec}: Carbon recovered in the liquid fraction

5.3.2.4. Carbon Balance

Previous reports have observed that the carbon content in hydrochars produced from sewage digestate via HTC processing range from 10 to 39% (Aragón-Briceño et al., 2017, Danso-Boateng et al., 2015, Ekpo et al., 2015, Berge et al., 2011a). However, carbon yields are highly dependent upon feedstock composition and process conditions (i.e., temperature, pressure, solid loading, etc.) (Funke and Ziegler, 2010). The carbon content of the hydrochars is reduced after HTC compared to the feedstock (see **Table 5.1**), which is unusual and only observed for certain feedstocks such as sewage digestate.

The carbon balance across the solid and liquid products is presented in **Table 5.2**. The carbon recovery in the hydrochar (Hy_{Crec}) increases as the solid loading increases. On the other hand, the carbon recovered in the liquid fraction (Ly_{Crec}) reduces as the solids loading increases. Funke and Ziegler (2010) reported that wet biomass can be almost completely dissolved into the liquid fraction at low solid loading. This suggests that there is a saturation point in which solubility becomes important. The recovery of carbon in the hydrochar is likely to be influenced by the degree of polymerization occurring during HTC and the solubility restrains in the water. In this study, the HyCrec ranged from 65.5 to 77.6% and LyCrec ranged from 16.9 to 35.8%. The values obtained are similar to those obtained by Aragón-Briceño et al. (2017).

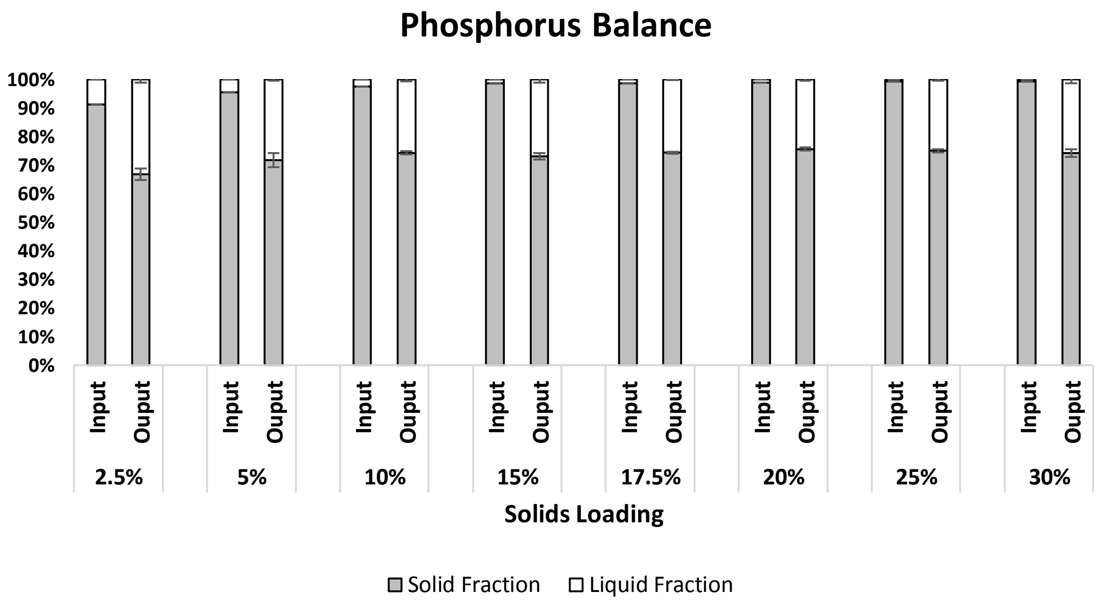
5.3.2.5.Nutrient balance

The fate of phosphorus and nitrogen after HTC is shown in **Figure 5.3a** and **Figure 5.3b**. **Figure 5.3a** indicates that there is solubilisation of phosphorus into the liquid fraction (up to 25%) as reported by Aragón-Briceño et al. (2017). The solids loading showed an influence on the solubilization of the phosphorus, as the solids loading increased, the phosphorus solubilization decreased. However, in all the cases the majority of the phosphorus remained in the hydrochar (66.8 to 75.7%).

Figure 5.3b shows that a significant proportion of nitrogen from the feedstock is solubilised into the liquid fraction after HTC treatment. The amount of nitrogen transferred from the feedstock into the water increased up to 48% of the total nitrogen contented into the liquid, leaving the nitrogen content in the hydrochar ranging between 15 to 50%. Solid loading, as observed for phosphorus, also significantly influences the level of nitrogen solubilisation in the process water following HTC. The levels of soluble N decrease as the solid loading increases. The change in feedstock N is due to the liquor containing much higher levels of soluble N than the press cake.

The importance of tracking the fate of the phosphorus and nitrogen is that this will provideinformation about the final disposal or use of hydrochar (fertilizer) or process water (struvite precipitation).

a)



b)

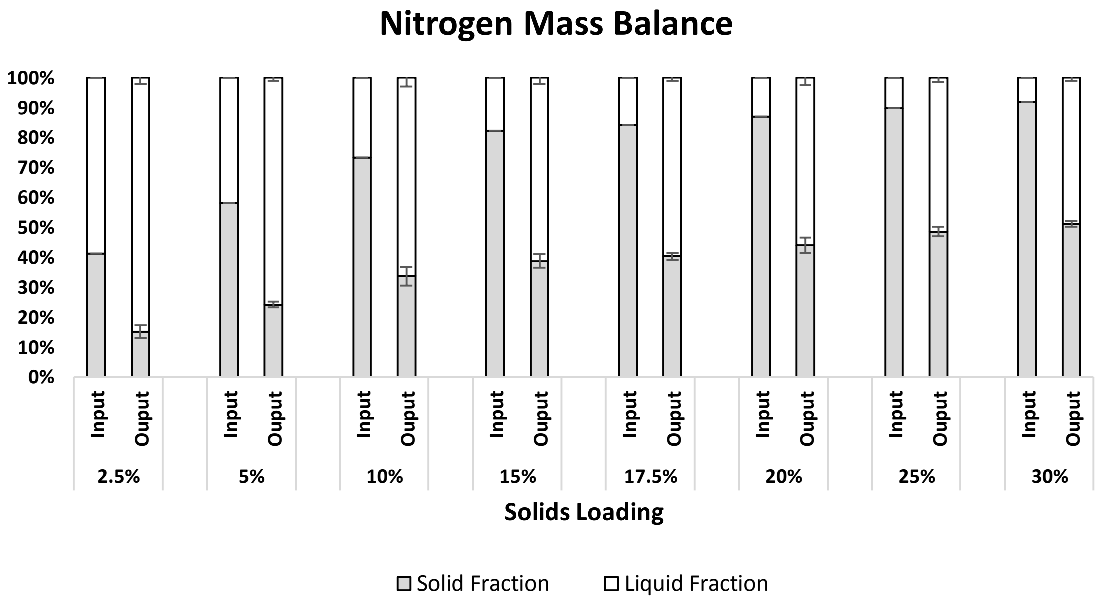


Figure 5.3.- Mas balance distribution of Phosphorus (a) and Nitrogen (b) before and after HTC treatment at different solid loadings.

5.3.3.Characteristics of the process waters

The composition of the process waters following HTC at different solid loadings are listed in **Table 5.3**. Properties such as pH and soluble hydrocarbons are measured by total organic carbon (TOC) and chemical oxygen demand (COD). The level of soluble inorganic species containing nitrogen are measured by total Kjeldahl nitrogen (TKN) and soluble ammonia, total and reactive phosphorus (TP and RP), and total solids (TS) and total volatile solids (TVS) are also measured. The levels of volatile fatty acids (VFA) and the elemental composition of the process waters (CHNOS) are also measured on the evaporated process waters. All of these properties are shown to change with solid loading.

Table 5.3.- Characteristics of the control and process waters from different solids loading.

		Process waters of different loadings							
Parameter	**Liquor**	**2.5%**	**5%**	**10%**	**15%**	**17.5%**	**20%**	**25%**	**30%**
pH	7.7	7.9	7.84	8.11	8.11	8.09	8.17	8.28	8.29
CODsol (mg/L)	2103	9575	14894	24114	33333	35461	44326	53192	72340
TOC (mg/L)	657	3623	6953	10016	12277	13737	16215	19922	29778
TKNsol (mg/L)	1463.0	2114	2716	4172	4634	4886	5726	6594	8064
Ammonia (mg/L)	1316	1652	2016	2744	3080	3173	3733	4368	5264
TP[b]sol(mg/L)	48.4	66.1	90.3	129.2	136.6	123.2	137.7	141.3	167.6
RP[c] (mg/L)	38.1	59.5	81.4	106.4	117.0	100.5	110.8	106.4	114.7
TS (g/L)	2.4	5.0	8.2	15.1	17.6	21.3	26.2	26.9	39.0
TVS (g/L)	1.7	4.6	7.6	14.4	16.5	19.8	24.5	25.4	36.8
VFAs (mg of COD/L)	350	909	1265	2009	2317	2587	2814	3705	4606
C (%)	43.9	44.1	48.0	52.2	51.9	51.8	52.7	53.1	53.1
H (%)	5.4	4.8	5.6	6.8	6.4	6.5	7.0	6.8	6.4
N (%)	3.5	5.6	6.8	7.8	7.5	7.5	6.7	7.5	6.9
O[a] (%)	47.1	44.1	38.2	32.0	33.0	32.9	32.7	31.4	32.4
S (%)	0.1	1.4	1.4	1.2	1.3	1.3	1.0	1.2	1.1

[a] Calculated as difference between sum of C,H,N,S.

[b] Total Phosphorus

[c] Reactive Phosphorus

5.3.3.1.pH

The pH values of process waters are listed in **Table 5.3**. The results indicate that the pH of the process waters after HTC treatment increases with solid loadings for all sewage digestate samples from 7.7 to 8.3. Changes in pH are mainly related to the presence of organic and inorganic compounds (Qiao et al., 2011). The increasing pH is linked to the formation and solubilisation of ammonium and solubilisation of alkaline salts (Aragón-Briceño et al., 2017, Ekpo et al., 2015, Mumme et al., 2011). Furthermore, according to Berge et al. (2011a), the pH of an anaerobically treated waste can remain basic depending on its buffering capacity, which may hinder the initial hydrolysis step during the thermal process.

5.3.3.2.Total Solids and Total Volatile Solids

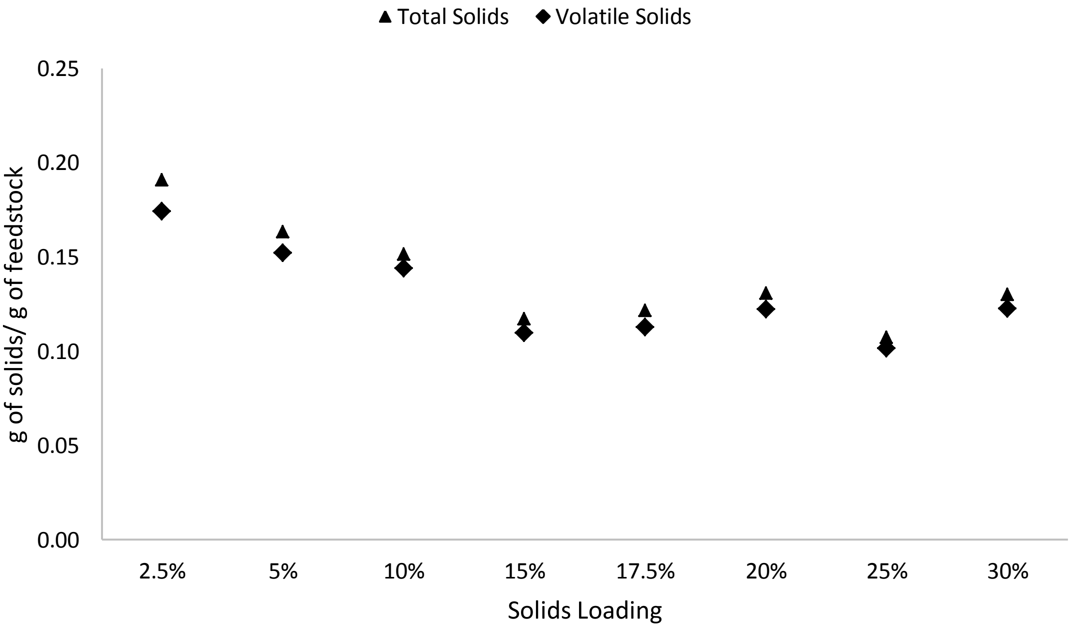
Table 5.3 lists the total solid (TS) and total volatile solid (TVS) concentration of process waters at different solid loadings. As expected, the TS concentration is directly related to the amount of solid loading. HTC results in the solubilisation of organic material following hydrolysis (Ekpo et al., 2015, López Barreiro et al., 2015). TS concentration in process waters increases from 2.4 g/L initially present in the digestate liquor to a maximum of 39 g/L in the process water at 30% solids loading.

The solubilisation of total and volatile solids (TS and VS) into the process waters at different solid loadings are reported in **Figure 5.4a** and demonstrates a significant effect of the solid loading on the solubilisation of organic compounds. At high solid loadings, the concentration of TS and TVS are higher, but the solubilisation is lower due to saturation in the liquid fraction. The highest solubilisation was observed at 2.5% solid loading, which corresponded to 0.17g of TVS solubilised per gram of feedstock processed. As the solid loadings increases beyond 15.0%, the solubilisation became constant having values between 0.10 and 0.12g of TVS solubilised per gram of feedstock processed.

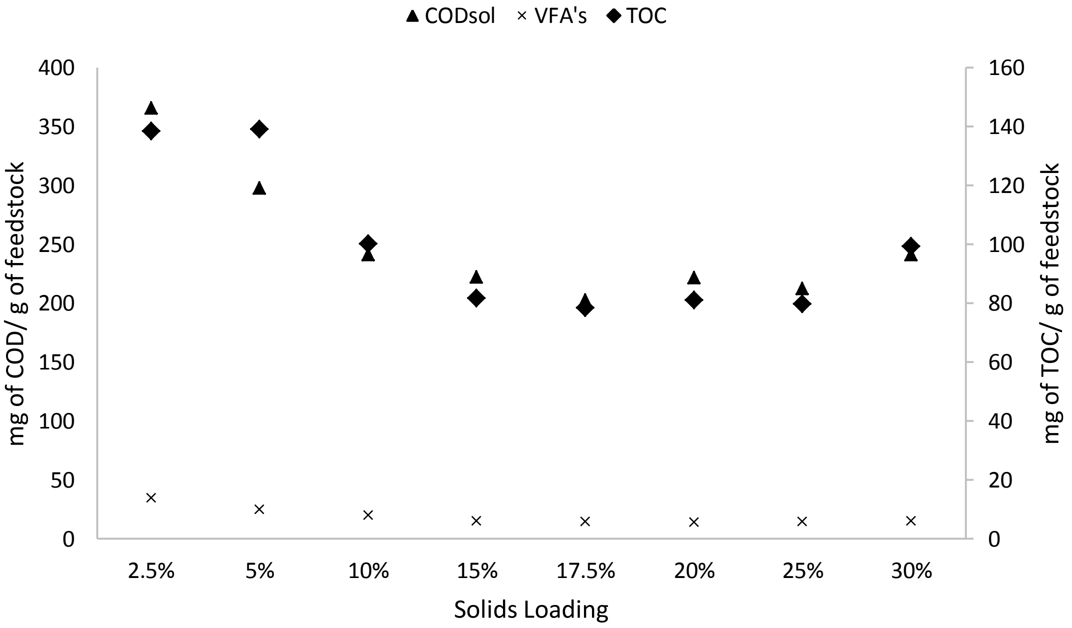
5.3.3.3.Chemical oxygen demand and Total Organic carbon

The levels of water soluble products generally increase with reaction severity due to the solubilisation of inorganics and the increased production of soluble organics from hydrolysis (Ekpo et al., 2015, Keymer et al., 2013, Qiao et al., 2011). However, the composition of carbon and nutrient rich compounds will depend mainly on the nature of the feedstock being treated and process temperature (Ekpo et al., 2015, Toor et al., 2011).

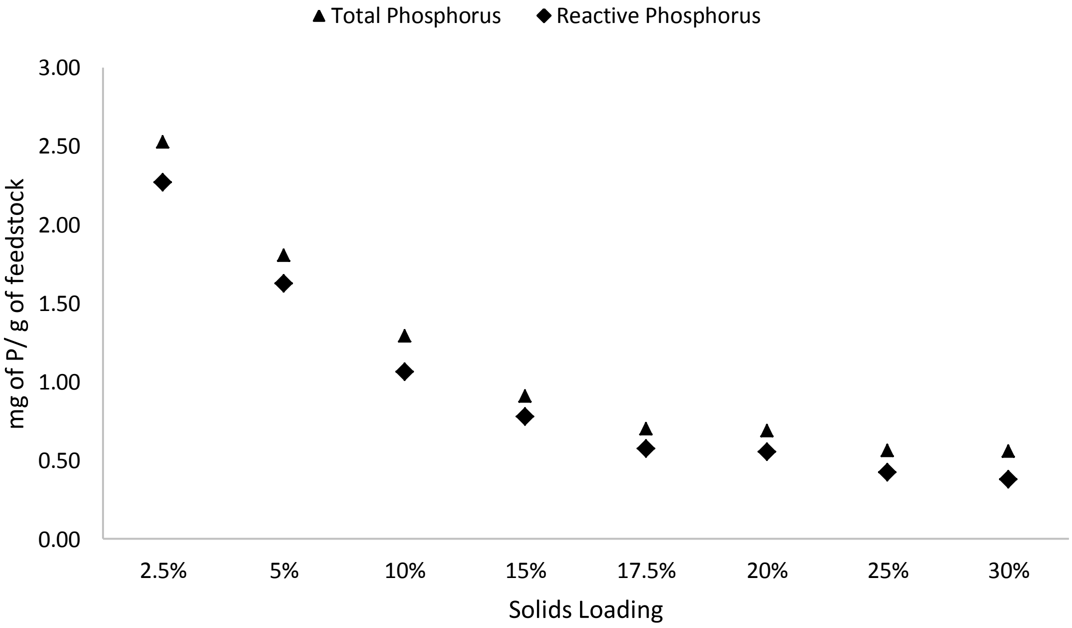
a)



b)


▲ CODsol
× VFA's
◆ TOC
400
350
300
250
200
150
100
50
0
160
140
120
100
80
60
40
20
0
mg of COD/ g of feedstock
mg of TOC/ g of feedstock
2.5%
5%
10%
15%
17.5%
20%
25%
30%
Solids Loading

c)


▲ Total Phosphorus
◆ Reactive Phosphorus
3.00
2.50
2.00
1.50
1.00
0.50
0.00
mg of P/ g of feedstock
2.5%
5%
10%
15%
17.5%
20%
25%
30%
Solids Loading

d)

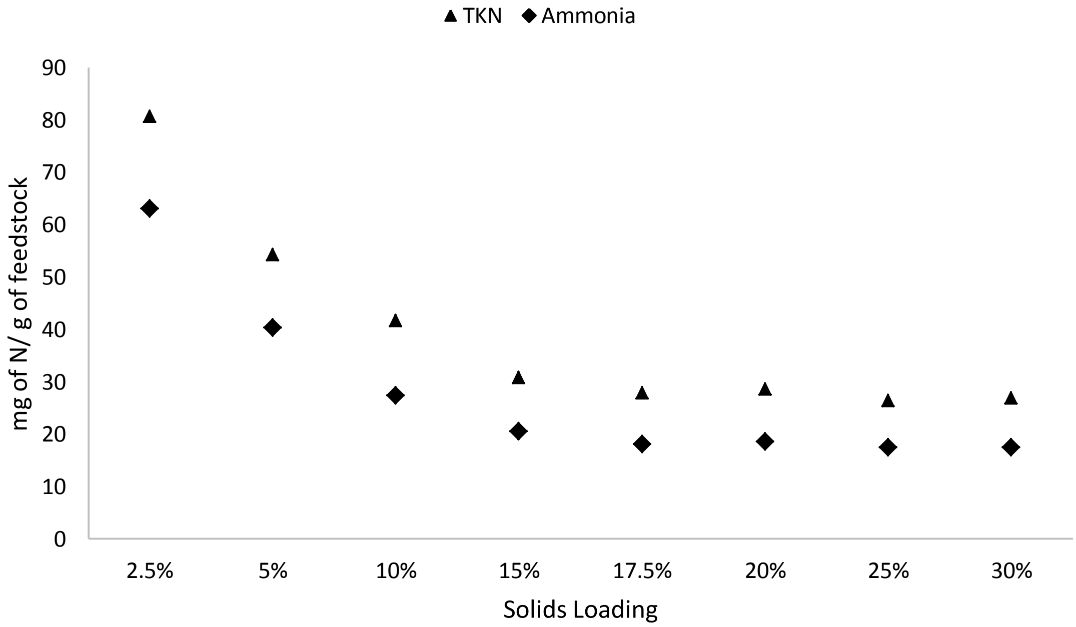


Figure 5.4.- Solubilisation of (a) carbon rich compounds (Chemical Oxygen Demand (COD), VFAs (Volatile Fatty Acids) and Total organic carbon (TOC)); (b) nitrogen rich compounds (Total Kjeldahl Nitrogen (TKN) and Ammonium; (c) phosphorus rich compounds (Total Phosphorus (TP) and Reactive Phosphorus (RP)); and (d) solids (Total Solids (TS) and Volatile Solids (VS).

The solubilisation of carbon compounds is due to hydrolysis, which releases organic compounds such as acetic acid, butanoic acid, alkenes, phenols, etc. (Danso-Boateng et al., 2015). Therefore, it is reflected in the increasing amount of COD and TOC measured in process waters.

The COD concentration of the filtered sewage digestate (liquor) was 2,100mg of COD/ L. After the HTC process, the COD concentration increased significantly between 9,500 and 72,300mg of COD/L depending on the solid loading during HTC processing. The solubilisation of organic compounds into process waters bring the possibility to recycle some of the carbon embedded in sewage digestate back into the anaerobic digester to boost methane yields, and to reduce fugitive emissions of methane from the digestate cake when dispose on arable land. However, process waters need to be carefully added to anaerobic digesters as operational organic loading rates should not exceed design criteria as higher concentrations of COD may affect the balance between hydrolysis, acetogenesis and methanogenesis in anaerobic digestors. According to the study carried out by Hübner and Mumme (2015), concentrations of organic matter in the feedstock exceeding 30g of COD per L can permanently inhibit methanogenesis due to over-acidification. Therefore, the right recirculation rate of process waters is a factor that must be considered when enhance methane production in anaerobic digesters is selected as the preferred route for the valorisation of process waters.

TOC concentration in process waters follows the similar trend found for COD. The concentration of TCO in the digestate liquor was 800mg of Carbon/L but after HTC, TOC concentration in process waters increased to a maximum of 27,900mg of Carbon/L at the highest solid loading tested. Both COD and TOC concentrations, increased with respect to the amount of solids in the mix (see **Table 5.3**). In the study performed by Stemann et al. (2013), COD and TOC concentrations increased similarly. An increase in the percentage of elemental carbon in the evaporated process waters was observed and ranged from 43.9 to 54.0%. Comparable results were reported by Aragón-Briceño et al. (2017) who used a similar sewage derived digestate and reported elemental carbon content in process waters ranging from 46 to 68%.

The solubilisation of organic matter in process waters was found to range between 240 and 360mg of COD solubilised per gram of feedstock processed (**Figure 5.4b**) and between 100 and 140mg of Carbon per gram of feedstock processed. That corresponds to an increased solubilisation 3 to 4.5 times higher compared with the digestate liquor based on COD and between 4 and 6 times higher based on TOC (80mg of COD per gram of feedstock and 20mg of Carbon per gram of feedstock). The solubilisation of organic matter from the feedstock's solid fraction increased until a maximum was found at 15% solid loading; however, carbon solubilisation becomes constant beyond this threshold (See **Figure 5.4b**), as the aqueous phase seems to be saturated and any excess hydrolysed material could be concentrated on the hydrochar. The saturation concentration of hydrolysed organic compounds is important to consider as it is possible that additional washing of hydrochars may liberate additional soluble organic compounds, this in turn may improve the properties of the hydrochars for further applications.

5.3.3.4.Volatile Fatty Acids (VFA's)

Table 5.3 presents the concentration of VFAs in process waters, which indicates an increase in VFAs with increasing solid loading. In this context, VFA analysis refers to the presence of C1-C6 organic acids and includes acetic acid, propanoic acid, isobutyric acid, butyric acid, isovaleric acid and valeric acid. VFAs concentration ranges from 909 to 4,606 mg of COD/ L (2.5 and 30% solids concentration, respectively). VFAs can be considered to appear from the decomposition of hydrolysis products during the HTC process (Berge et al., 2011a). Berge et al. (2011a) and Danso-Boateng et al. (2015) detected acetic, propanoic, and butanoic acids together with many other organic and inorganic compounds like aromatics, aldehydes and alkenes. The solubilisation of VFAs (**Figure 5.4b**) follows the same trend as the other parameters measured where higher levels of solubilisation were achieved for the lower solid loadings (2.5, 5.0 and 10%) and became constant beyond 15% of solids loading.

5.3.3.5.Phosphorus

The solubilisation of phosphorus in process waters following HTC is due to decomposition of complex organic phosphorus containing compounds (e.g., phospholipids, DNA and phosphates monoesters), which results in a combination of reactive (PO_4^{3-}) and organic phosphorus compounds in solution(Dai et al., 2015, Ekpo et al., 2015). **Table 5.1** shows the total and reactive phosphorus concentrations in the digestate liquor and process waters at different solid loadings. The results indicate that the concentration of phosphorus (total and reactive) increase as the solid loading increases. The concentration of total phosphorus ranged from 66 to 167mg P/L and for reactive phosphorus from 59 to 114mg P/L for process waters derived from mixes containing 2.5wt% to 30wt% solid loading (i.e., the difference between total and reactive phosphorus gives an estimate of the concentration of organic phosphorus compounds in solution). The results indicate that the total and reactive phosphorus concentrations increase with increasing solid loading. However, once again, a saturation point is reached with the reactive phosphorus remaining relatively constant beyond a solid loading of 15%. Despite the increase of TP and RP in process waters, that only represents a small proportion of the total phosphorus originally present in the feedstock. The solubilisation of phosphorus in mg/g of feedstock (TP and RP) is shown in **Figure 5.4c**. The overall phosphorus solubilisation from the feedstock decreases as the solid loading increases. This is typical of HTC feedstocks containing counter ions such as Mg^{2+} and Ca^{2+} that are capable of promoting P precipitation as PO_4^{3-} on the hydrochar surface.

In **Figure 5.5a** it is possible to observe that the percentage of phosphorus solubilised from the solid fraction ranged from 24 to 27%. This shows that the phosphorus transferred from the solid fraction to the liquid fraction remain constant independently of the solid loading.

5.3.3.6.Nitrogen

Sewage sludge contains large concentrations of organic matter from faecal material (primary sludge) and bacterial biomass (surplus activate sludge), that largely contributes to the presence of nitrogen compounds in anaerobic digesters processing sewage sludge. During anaerobic digestion, nitrogen compounds are taken up by anaerobic bacteria that mainly constitute the solid fraction of the digestate. For that reason, when hydrothermal treatment is performed, proteins are hydrolysed resulting in the release of soluble ammonium in process waters (Keymer et al., 2013, Wilson and Novak, 2009).

Table 5.3 shows the concentration of TKN and ammonium in process waters from HTC. As expected, there is an increase in TKN and ammonium concentrations as the solid loading increases, with figures ranging from 2,114 to 8,064mg N/L of TKN and from 1,652 to 5,264mg N/L of ammonium, at 2.5wt% and 30wt% solid loading respectively.

The effect of solid loading on the solubilisation of nitrogen compounds follows a similar trend found with other organic and inorganic species (phosphorus and carbon containing compounds – i.e., TP, RP, COD, TOC, TS, VS, etc.), and results in an increase in the concentration of nitrogen in process waters (soluble TKN and ammonium). The solubilisation of nitrogen compounds in mg of N/g feedstock (N reported herein using soluble TKN and ammonium analysis) is shown in **Figure 5.4d**. Nitrogen solubilisation ranged from 80.72 to 26.38 mg of N-TKN/g feedstock and from 63.8 to 17.47 mg of N-Ammonium/g feedstock within the solid loading tested (2.5 - 30 wt%); however, it seems that N solubilisation reaches a maximum at 15 wt% solid loading, which then becomes relatively constant at higher solid loadings.

In **Figure 5.5b** shows the percentage of nitrogen extracted from the solid fraction exclusively into the process water. Nitrogen compounds present in the solid fraction of the anaerobic digestate were hydrolysed and solubilised into process water with efficiencies ranging between 43 and 66%. However, it was observed that the percentage of nitrogen solubilised into the process waters was higher at low solid loadings, which could infer some dependency on process conditions (temperature, pressure, contact time, etc.).

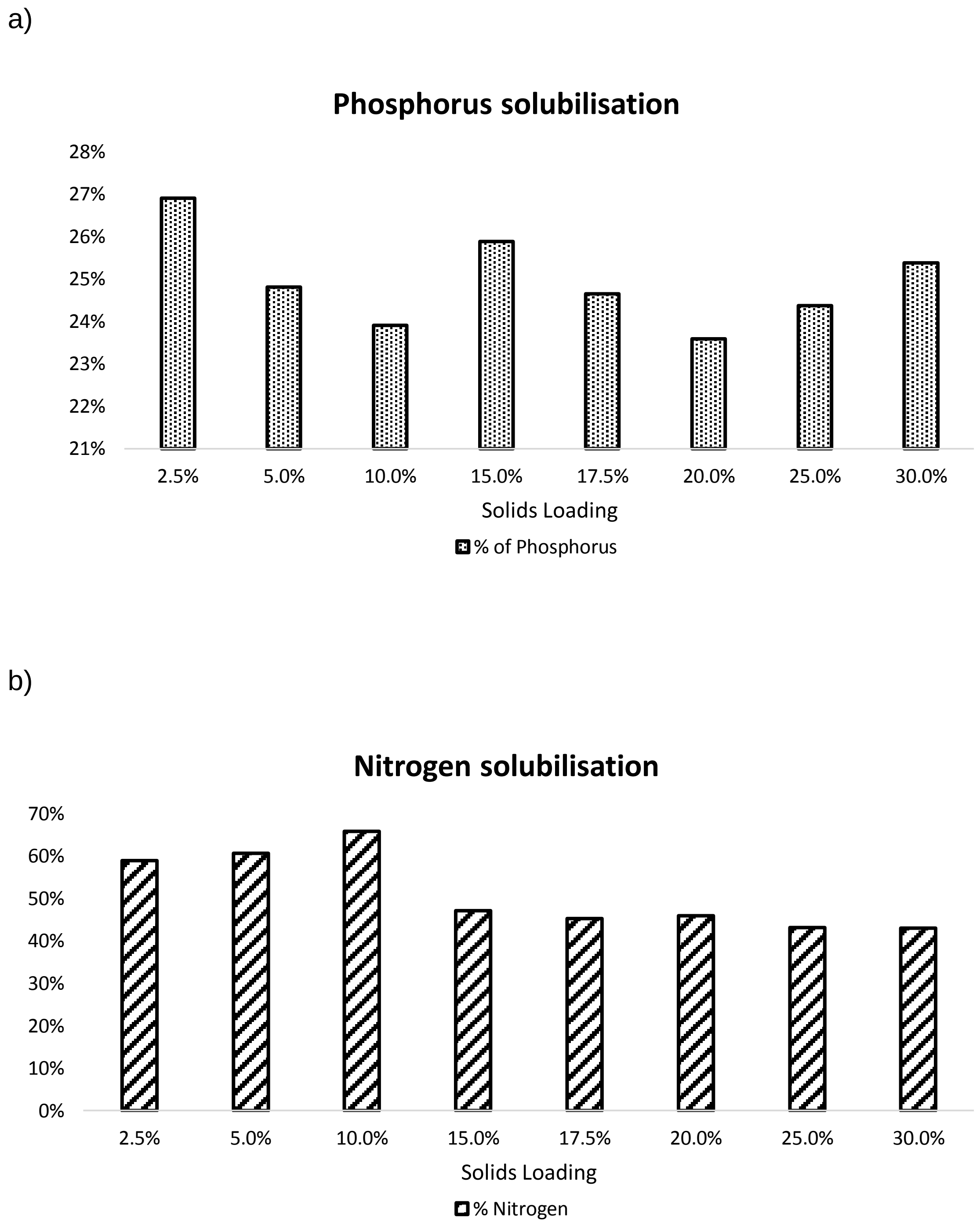


Figure 5.5.- Percentage of Nitrogen (a) and Phosphorus (b) extracted from the original solids into process waters after HTC processing.

5.3.4. Anaerobic digestion and biomethane potential of process waters (BMP)

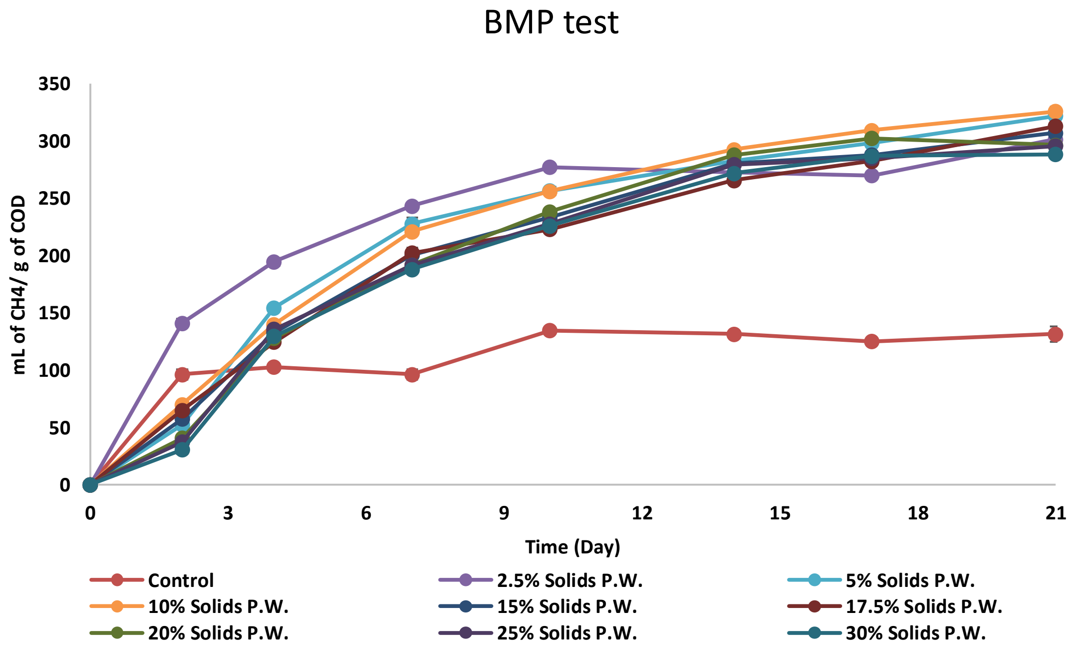
The importance of measuring the methane production in process waters is because the potential positive energy implications in the HTC-AD system. According to Aragón-Briceño et al. (2017), process waters derived from sewage digestate are proven to be a suitable substrate for biomethane production via anaerobic digestion. Anaerobic biodegradability of HTC process waters should not be limited by hydrolysis as most of the complex organic matter has been already hydrolysed during thermal processing (Wirth and Mumme, 2013), however there are some organic inhibitors (e.g., phenols and PAHs) that can affect the anaerobic digestion process as a whole but mainly the methanogenesis step (Hübner and Mumme, 2015).

Figure 5.6a shows the results from BMP tests for process waters generated at the different solid loading rates tested. A significant increment in methane yields was observed when digestate liquor used as a control (131 mL CH_4/g COD on average) was compared with process waters (228 – 301 mL CH_4/g COD). It is worth mentioning that methane yields increased with solid loadings until a maximum was reached at 10% before decreasing. This may be due to process waters generated from higher solid loadings having higher levels of phenols as found by Berge et al. (2011a). Previous studies investigating the anaerobic digestion of HTC and pyrolysis derived process waters from digestate report methane yields ranging from 220 to 227mL of CH_4 per g of COD (Aragón-Briceño et al., 2017, Wirth and Mumme, 2013).

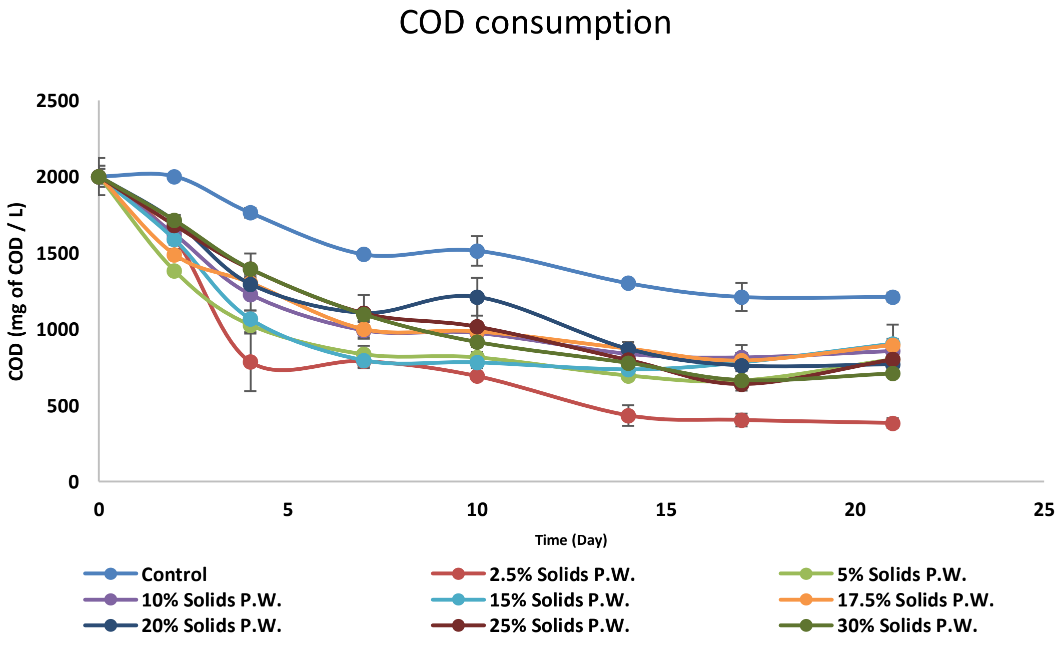
COD consumption during anaerobic processing is presented in **Figure 5.6b**. According to Becker et al. (2013), the anaerobic degradation of HTC process waters should not be limited by hydrolysis as only limited concentrations of complex organic matter are in the aqueous phase following thermal treatment and hence, organic matter removal is expected to be higher from process waters. COD removal was found to range from 55 to 81%, being the process water coming from 2.5% of solid loading with the higher COD removal and the lowest from process water coming from 15% of solid loading. VFAs were totally consumed with the exception of the control (Digestate Liquor) that showed no additional biogas production after day 9th (see **Figure 5.6c**). These results are similar to the values of COD removal (63.8%) reported at similar thermal conditions (250°C, 30min and 40bar) with sewage digestate (Aragón-Briceño et al., 2017) and match reported data from other studies with HTC and Pyrolysis process waters treated anaerobically (32 to 75% COD removal) (Hübner and Mumme, 2015, Wirth and Mumme, 2013)

Regarding to the biogas composition (**Table 5.4**), methane concentration ranged between 74 to 80% showing a good quality biogas coming from process waters at different solids loading, which was slightly higher than the figures obtained by Wirth and Mumme (2013) in HTC liquor from corn silage (70% methane). Therefore, net methane production seems to be slightly favoured by the increase in solid loading.

a)


BMP test
mL of CH4/ g of COD
0
50
100
150
200
250
300
350
0
3
6
9
12
15
18
21
Time (Day)
Control
2.5% Solids P.W.
5% Solids P.W.
10% Solids P.W.
15% Solids P.W.
17.5% Solids P.W.
20% Solids P.W.
25% Solids P.W.
30% Solids P.W.

b)


COD consumption
COD (mg of COD / L)
0
500
1000
1500
2000
2500
0
5
10
15
20
25
Time (Day)
Control
2.5% Solids P.W.
5% Solids P.W.
10% Solids P.W.
15% Solids P.W.
17.5% Solids P.W.
20% Solids P.W.
25% Solids P.W.
30% Solids P.W.

c)

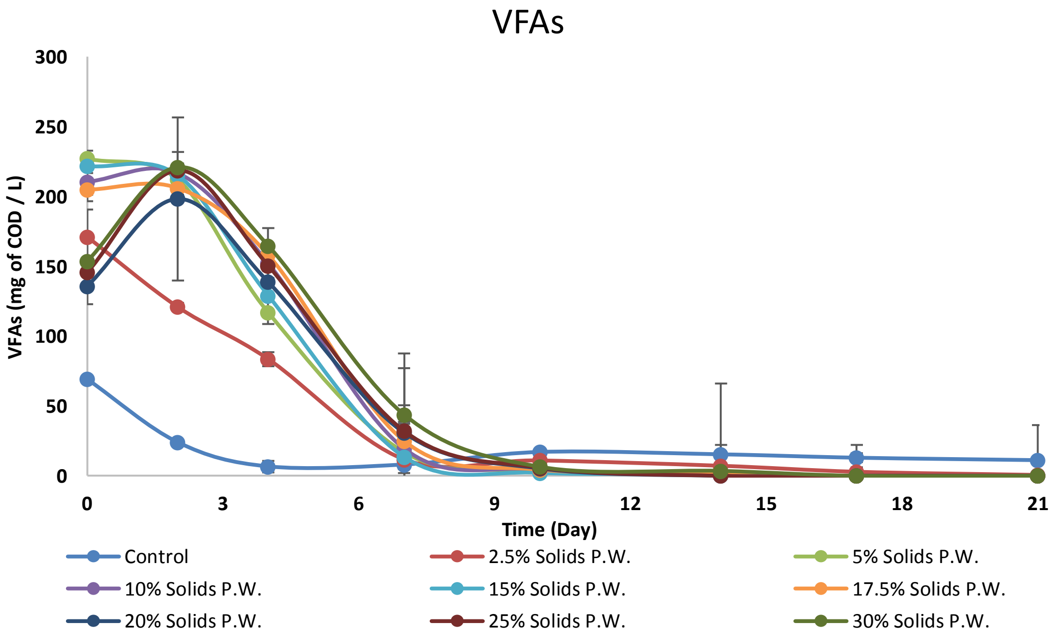


Figure 5.6.- BMP test results (a) from process waters - PW at different solid loadings and changes in COD (b) and VFA (c) concentration during BMP tests.

5.3.5.Maximum potential methane yields

Table 5.4 shows the results from using the Boyle's equation to predict theoretical BMP values from the control samples and process waters and to compare them with corresponding experimental BMP values.

According to Raposo et al. (2011), anaerobic biodegradability of feedstocks can be determined from BMP_{exp} and BMP_{th} values. The anaerobic biodegradability is defined as the amount of organic matter that can be degraded during the anaerobic process. The biodegradability (BD) of process waters is lists in **Table 5.4** and ranged from 75 to 89%. It is known that the predictive values should be higher than the experimental ones as the calculations are based on elemental content (Aragón-Briceño et al., 2017).

The biodegradability of the process waters increased from 36 to 89% compared with the digestate liquor (control). This demonstrates that the digestate still have some organic compounds that can be used to produce methane and can be solubilised through HTC. The biodegradability in the process water decreases as the solid loading increases.

Table 5.4.- Comparison of the Experimental BMP v. theoretical BMP.

Sample	BMPexp (mL of CH_4 /g of COD added)	BMPth Boyle's Eq. (mL of CH_4 /g of COD)	*BD Boyle's eq	COD removal	Methane content in Biogas
Control	134.6	431.5	36%	40%	63%
Processed Water					
2.5% P.W.	301.5	337.5	89%	81%	74%
5% P.W	321.7	370.3	87%	60%	77%
10% P.W.	325.6	435.4	75%	57%	79%
15% P.W.	306.8	360.4	85%	55%	78%
17.5% P.W.	312.7	400.9	78%	55%	79%
20% P.W.	302.1	403.1	75%	62%	80%
25% P.W.	295.4	351.5	84%	60%	80%
30% P.W.	288.2	368.2	78%	62%	80%

*BD: Biodegradability

5.3.6.AD+HTC system analysis

Previous studies have shown that the use of hydrothermal treatments as post-treatment rather than pretreatment has better benefits in terms of energy production (Aragón-Briceño et al., 2017). **Table 5.5** shows the energy potentially produced by hydrochars and process waters estimated from HHV and experimental BMP values, as well as the net energy production from the methane produce by the anaerobic digestion of the sewage sludge. The amount of energy consumed was calculated based on the energy required to heat process waters from 25 to 250°C considering the corresponding solid loading in the 500mL HTC reactor. According to Berge et al. (2011a), the energy required to heat water in a closed system is small in comparison to that required to evaporate water in traditional dry thermochemical conversion processes.

The results show that the potential energy embedded in the hydrochar increases as the amount of solids increase from 10.4 to 12.3Mj per kg of hydrochar. Although, the energy consumption is smaller in those experiments with higher solid loadings (Zabaleta et al., 2017).

On the other hand, the potential energy obtained from biogas coming from the process waters reduces as the amount of solid loading increases from 3.9 to 1.3Mj per kg of hydrochar. This is because the methane potential in process waters is similar no matter the amount of solids is loaded in the HTC reactor. Therefore, overall potential energy produced did not show significant differences.

The net energy balance showed to be a positive from 5% of solid loading in the HTC reactor and increase as the solids loading increases. Some authors found that solid loadings at and over 15% have showed a positive energy balance (Zabaleta et al., 2017). However, it has to be considered that sludge beyond 25% of solids, might not be suitable for a continuous flow system due to the problems of managing a highly viscous fluid. The sludge of 20% of solids seems to be the best option for HTC in order to harness all the properties of the sewage digestate.

The hydrochars contribute with up to 50% of the overall energy produced when they are used as a solid fuel source. However, when they are disposed as soil amenders and not used as fuel source, the net energy produced drops. Despite of that, when the solid loading is over 15%, the net energy produced still produce a positive energy balance showing an increment in the energy production per kilogram of feedstock as the solid loading increases.

Table 5.5.- Energy production and consumption per kg of feedstock.

Reaction	[a]Energy produced in char per kg of feedstock (Mj)	[b]Energy produced by AD of P.W. per kg of feedstock (Mj)	[d]Energy produced by the AD of the sewage sludge per kg of feedstock (Mj)	Overall Energy produced by AD per kg of feedstock (Mj)	Overall energy produced per Kg of feedstock (Mj)	[c]Energy consumed per Kg of feedstock (Mj)	Overall Net Energy Balance (Mj)	Net Energy Balance (Mj) (not considering hydrochar)
2.5% Solids	10.4	3.9	7.08	10.9	21.4	40.7	-19.4	-29.8
5% Solids	10.8	3.1	7.08	10.2	21.0	19.8	1.1	-9.7
10% Solids	11.8	2.3	7.08	9.3	21.2	9.4	11.8	-0.1
15% Solids	11.5	1.8	7.08	8.9	19.0	5.9	13.1	2.9
17.5% Solids	11.1	1.6	7.08	8.7	18.7	4.9	13.8	3.8
20% Solids	11.9	1.6	7.08	8.7	20.5	4.2	16.3	4.5
25% Solids	12.1	1.3	7.08	8.4	20.5	3.1	17.4	5.3
30% Solids	12.3	1.3	7.08	8.4	20.7	2.4	18.3	5.9

[a] Values were determined according to the HHV of the hydrochars. [b] Values were obtained from the experimental BMP potential of the process waters and the relationship $1m^3$ = 35.8Mj (Passos and Ferrer, 2014). [c] Energy consumed were determined based in energy required to heat water from 25°C to 250°C in 500mL reactor. [d] Energy produced from the anaerobic digestion of sewage sludge reported by (Aragón-Briceño et al., 2017).

Figure 5.7 shows the AD+HTC integration scenario built in Aspen. The scenario considers an inlet of 1 Ton of digestate sludge with 20% of solids. The mass balance showed a production of 13.92 kg of biogas and 153 kg of hydrochar per ton of sludge. Most of the nitrogen is solubilised within the liquid fraction (65%) after the HTC, which can used as a liquid fertiliser or for irrigation. On the other hand, despite of the solubilisation process during the HTC, the phosphorus that stays mostly into the solid fraction (96%). So it is important to consider the fate of nitrogen and phosphorus before use the hydrochars as a solid fuel source.

The electrical and thermal power produced by the methane of the process water in the CHP unit (23.1 and 37.0 KWh respectively) covers nearly the electrical and thermal power consumption (-37.8 and -98.9 KWh respectively). However, the net energy and thermal power production of the system are negative (-14.7 and -61.9 KWh) when only the process water is considered as the energy source (See **Table 5.6**). Furthermore, the computer simulation showed an electrical efficiency of 37% and a thermal efficiency of 59%.

The inclusion of the hydrochar as a fuel source to the system, maximises the energy production turning positive the electrical and thermal production (99.6 and 199.5 KWh) making the AD+HTC system self-sufficient. Moreover, the application of the HTC improves the dewaterability of the solid up to 70% making more efficient the centrifugation (Escala et al., 2013).

Table 5.6.- Energy balance of the HTC-AD integration scenario for 20% solids of digestate sludge.

Concept	Electrical power production (KWh)	Thermal power production (KWh)
HTC-AD scenario (P.W. as only energy source)	-14.7	-61.9
Hydrochar potential energy	114.3	261.4
Total	99.6	199.5

[a] Electrical power efficiency of 35% for hydrochar slurry (Kempegowda et al., 2017)

[b] Thermal efficiency of 80% for heating biomass in fast pyrolysis (Shemfe et al., 2015)

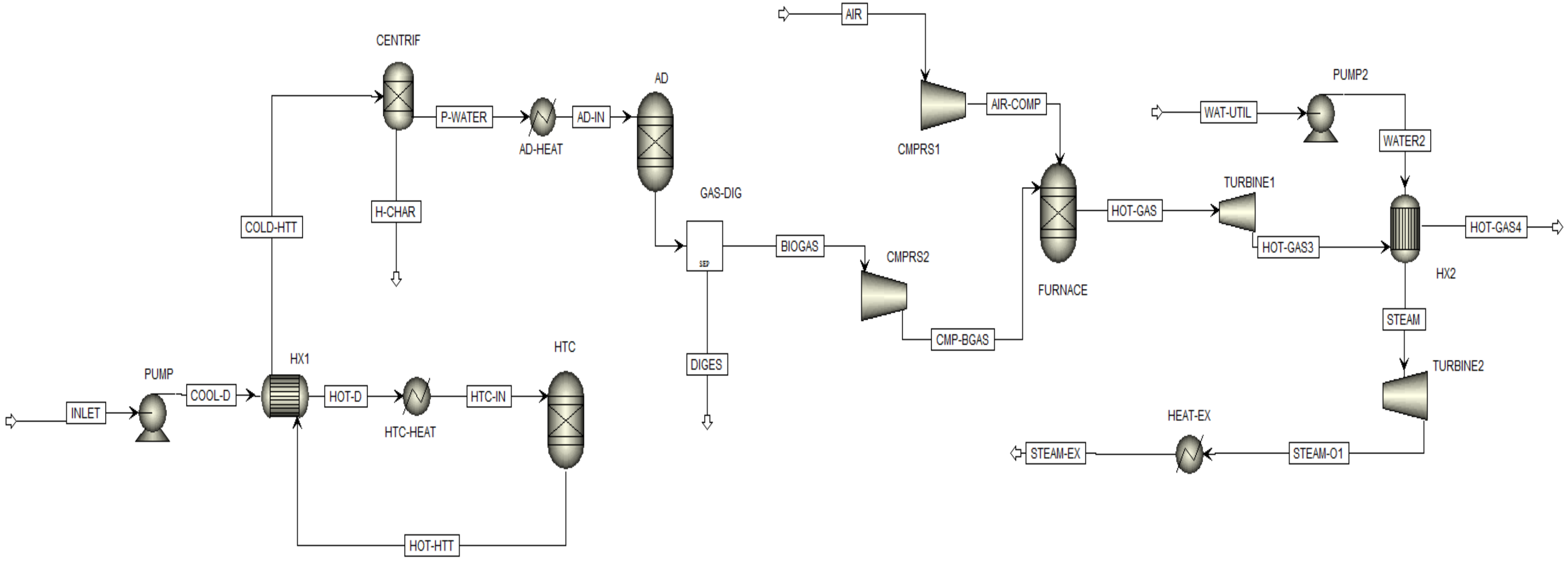


Figure 5.7.- Aspen diagram for the integration of the HTC process at the end of a WWTW with a sludge of 20% of solids.

5.4. Conclusions

Solid loadings had a direct influence on hydrochar composition and its energetic properties. The carbon and nitrogen content in hydrochar increased as the solids loading increased. Similar trend occurred with the HHV and hydrochar yield. The process waters were also influenced by the solid loading increasing the concentration of carbon, nitrogen and phosphorus compounds, which increases the potential for resource recovery from sewage digestate. With regard to the accumulation of soluble organic matter in the process waters, a significant increment in methane yields was observed when digestate liquor used as a control for BMP tests (131 mL CH_4/g COD on average) was compared with process waters anaerobically digested (228 – 301 mL CH_4/g COD). The energy balance of the proposed AD+HTC process is positive beyond 5% of solid loading when the hydrochars are considered as a fuel source and when they are not, the energy balance is positive beyond 15% of solid loading. The sewage digestate of 20% solids seems to be the best option for carbonisation in terms management and energy. The AD+HTC scenario showed a significant positive energy balance when process water and hydrochar are considered as fuel sources. Although further studies are needed in order to better understand the influencing factors controlling process conditions that lead to improvements in the hydrothermal carbonisation of sewage digestate, this research work demonstrates the great potential from combining AD and HTC as an alternative to conventional sludge management systems in wastewater treatment works.

5.5. Summary

In this chapter, the influence of solid loading on the composition of the resulting hydrochar and process water is presented. An evaluation of product yields, solubilisation of organic carbon and biomethane potential of the process water is compared for 2.5-30% solid loadings at a HTC temperature of 250°C with a 30-minute reaction time. Hydrochar yields ranged from 68 to $75\%_{wt}$. The concentration of organic carbon increased from 2.6g/L in the raw digestate to 72.3g/L in the process water following HTC at the highest solid loading. Recycling process water from the HTC unit into the AD unit can enhance the energy production by bio-methane up to 54% when compared with the conventional AD. Calculations of energy balances indicate that high solid loading favours energy production.

5.6. Publications and awards derived from this chapter

- “Best platform presentation in session 2: Process Integration.” at The 3rd AD Network: Early Career Researcher (ECR) conference (2017). Birmingham, UK.
- “Anaerobic Digestion Network: travel Bursary for Early Career Researcher – UK to Overseas (1500£)” to attend to the 15th IWA World Conference on Anaerobic Digestion (2017). Beijing, China.
- ***Aragón C.**, Camargo-Valero M. and Ross A. (2017). “Hydrothermal Carbonisation of Sewage Digestate: Influence of solid loading on hydrochar and process water characteristics.” In proceedings of the 15th IWA World Conference on Anaerobic Digestion. Beijing, China.
- ***Aragón C.**, Camargo-Valero M. and Ross A. (2017). “Hydrothermal Carbonisation of Sewage Digestate: Influence of solid loading on hydrochar and process water characteristics”. In proceedings of the 3rd AD Network (a BBSRC NIBB) Early Career Researcher conference. University of Birmingham, Birmingham, United Kingdom.
- ***Aragón C.**, Camargo-Valero M. and Ross A. (2019). “Hydrothermal Carbonisation of Sewage Digestate: Influence of solid loading on hydrochar and process water characteristics.” Submitted to Water Research journal on the 24/01/2019.

Chapter 6. Evaluation and comparison of product yields and bio-methane potential from hydrothermally treated sewage sludge.

6.1. Introduction

In recent years the use of biomass as a renewable resource for energy has gained more attention. In UK it’s produced annually around 1.4 million tonnes (dry weight) of sewage sludge. Anaerobic digestion is the most common option for sewage sludge (SS) treatment due the energy generation from methane (Aragón-Briceño et al., 2017). Nevertheless, one half of the SS is susceptible to anaerobic biodegradation resulting in biogas.

One of the main limiting steps of the AD process is the solubilisation of the organics through hydrolysis. For that reason, the resulting digested sludge (digestate) from the anaerobic digestion still contains large amounts of non-easy biodegradable organic matter that can be harnessed for additional energy production (Aragón-Briceño et al., 2017). Many pre-treatment techniques as thermal, biological, chemical, mechanical, physical and combinations has been studied by several researchers with the objective of enhance the sludge biodegradability by releasing the carbon and organic compounds from the microbes cells to the aqueous phase but the main drawback has been the economic constraints for scale them up and commercialize them (Pilli et al., 2015).

Hydrothermal processing is currently being considered as an alternative technology to further harness energy from sewage sludge and digestate (He et al., 2013, Zhao et al., 2014) and to reduce the issues related to current disposal of final solid products. Hydrothermal processes (HTPs) involve the treatment of biomass in hot compressed water that can produce either solid hydrochar, a biocrude or a syngas, depending on process temperature and pressure. Some researchers have already identified the potential of sewage sludge as an energy source due its high organic matter content (Danso-Boateng et al., 2015, Kim et al., 2014). HTPs applied to sewage sludge processing not only help to inactivate pathogens and further bacterial activity after disposal, but also produce valuable by-products like hydrochar.

However, during the HTP process water rich in organic compounds is produced and it cannot be disposed into the environment without further treatment (Becker et al., 2014). The solubilisation of organic compounds resulting from the hydrolysis of complex molecules in sewage sludge, makes the process water a potential feedstock for methane production via anaerobic digestion, which is something that very few researchers have covered in recent years (Aragón-Briceño et al., 2017, Wirth and Mumme, 2013, Becker et al., 2014, Mumme et al., 2011, Wirth et al., 2012).

Despite of HTP's commercial applications are still under development, in comparison with other waste treatment processes for sewage sludge (i.e., AD, composting, incineration, etc.), the treatment of high-moisture waste biomass like sewage sludge is considered one of the most promising area for the consolidation of HTPs (Mumme et al., 2015). Therefore, the challenge is to provide a smooth integration for coupling HTPs with existing infrastructure and treatment units at waste water treatment works in order to meet environmental targets regarding the safe disposal of sewage sludge and other operational targets linked to waste minimisation, recovery of valuable resources embedded in sewage sludge and overall reduction of treatment costs. The main objective of this study is to investigate the changes suffered by sewage sludge samples collected along treatment process units in a conventional WWTW, when subjected to hydrothermal processes at different temperatures. Results are processed to evaluate and compare products yields and characteristics, as well as the biomethane potential of the resulting process waters. Research finding are used to propose new process configurations for WWTWs in order to integrate HTPs as part of a comprehensive sewage sludge management strategy.

6.2. Results and discussions

6.2.1.Mass balance

In **Figure 6.1a** the product distribution of sewage sludge at different temperatures after thermal treatment are presented. The different sewage sludge collected were tested with the higher concentration of solids found among all the different points of the WWTW that was at 2.5% of solids concentration and loaded into the hydrothermal reactor. This with the aim of solubilise as much organic compounds into the process water

The mass of solid fraction was reduced after thermal treatment up to 72%. During the thermal treatment the solid lost led to the increase of the water soluble products due the solubilisation of organic and inorganic compounds from the original biomass into the liquid phase (Aragón-Briceño et al., 2017, Zabaleta et al., 2017, Ekpo et al., 2015, Keymer et al., 2013, Qiao et al., 2011).

Higher temperatures (250°C) showed more solubilisation of solids into the liquid fraction (see **Figure 6.1**) due the severity of the process. The primary sludge presented a solids reduction of 32% after the 160°C treatment and increased up to 60% at the 250°C treatment. The secondary sewage sludge showed the highest solid reduction (up to 72%) among the different sewage sludge in both thermal treatments. This might be due the biomass from the SS was more susceptible to hydrolysis through thermal treatments than the other sewage sludge (PS and Mix). The MIX sewage sludge presented a solid reduction as the treatment temperature increased (up to 52% and 64% at 160°C and 250°C treatment respectively). Furthermore, all digestates (PS, SS and MIX) showed higher solids reduction after the 250°C treatment compared with the 160°C treatment. That means the severity of the process helps to dissolve the remained organic matter contented in the digestate and therefore to harness their properties.

The solid distribution is shown in **Figure 6.1**. Between 8 to 43% of the biomass solids were converted to gaseous components and just between 13 to 34% were transferred to the liquid fraction. Zabaleta et al. (2017) stated that most of the gaseous components are mainly composed by CO_2.

It is important to highlight that most of the energy content is within the hydrochar and secondly in the process water which has the potential to produce methane. For that reason, a lot of gasification results can prove to be inconvenient for harnessing the properties of the feedstock. **Figure 6.1** shows that lower process temperatures did not generate a lot of gasification. The primary sludge treated at 160°C showed the best conditions for a feedstock because ony 8% was gasified and 24% of the total solids was solubilised.

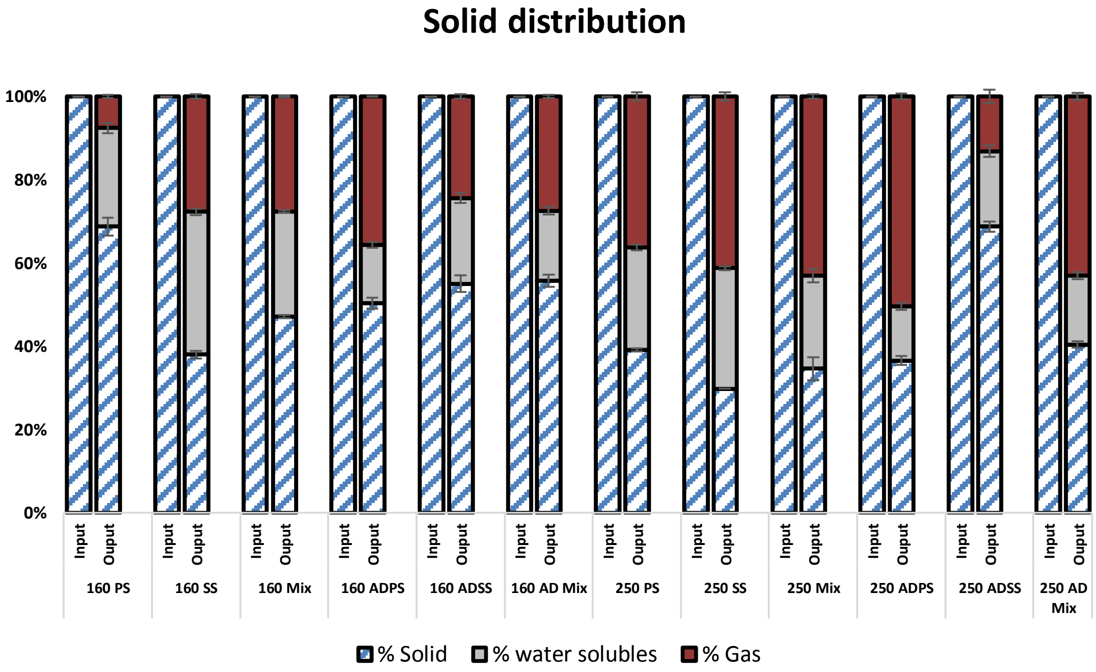


Figure 6.1.- Mass balance solid distribution of the thermal treatments of different sewage sludge at different temperatures.

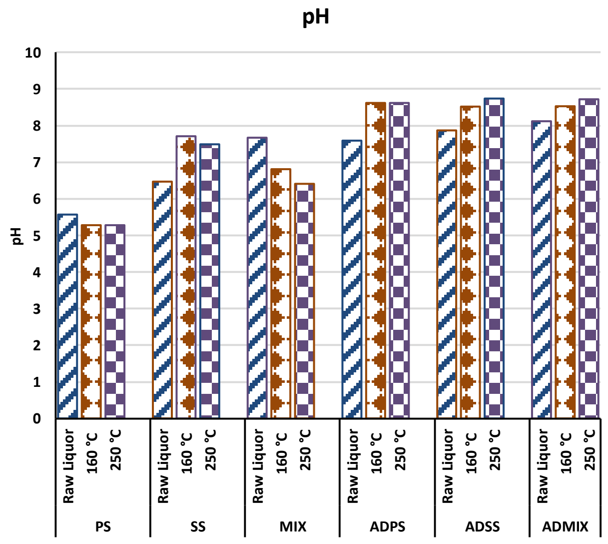
6.2.2.Characteristics of the process waters

6.2.2.1.pH

The pH is a feedstock dependant parameter tha has been proved to suffer changes during the thermal treatment because the organic compounds reactions (Qiao et al., 2011). The formation of ammonium and alkaline compounds can contribute to the pH increasing as the VFAs and acid compounds resulting from the hydrolysis contribute to the pH reduction (Aragón-Briceño et al., 2017). Although, the buffering capacity of the sample is other factor that may hinder the initial hydrolysis step in the thermal process (Berge et al., 2011a).

The pH of the different sewage sludge can be observed in **Figure 6.2a**. It seems that the samples that came from biological treatments (SS and digestates) prior thermal treatment favoured the production of alkaline compounds that made the pH increase. On the other hand, the rest of the samples which did not have a biological treatment prior the thermal treatment (PS and MIX) presented and slightly drop of the pH after the thermal treatments which suggest the formation of acid compounds. Some researchers have reported different pH values in PWs coming from different sewage sludge. For instance PWs coming from synthetic faecal sludge reported pH values from 3.8 to 7.8 at different treatment temperatures (140-200°C) (Nyktari et al., 2017), pH values from 7.04 to 9.15 were reported in sewage digestate at treatment temperatures between 160 to 250°C (Aragón-Briceño et al., 2017) and for PW coming from primary sludge treated at 200°C the pH value reported was 7.7.

a)



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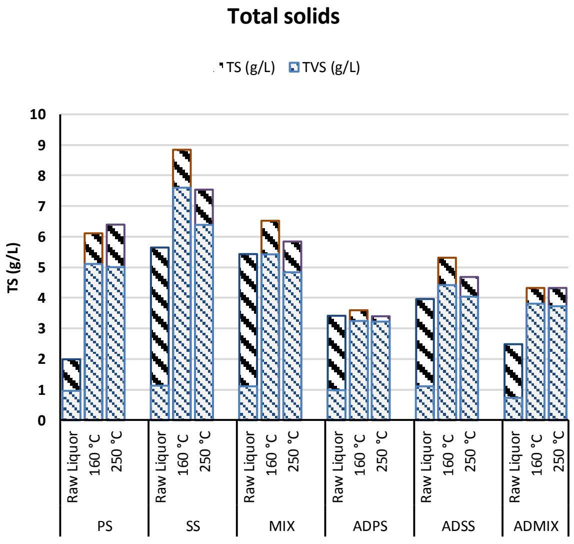


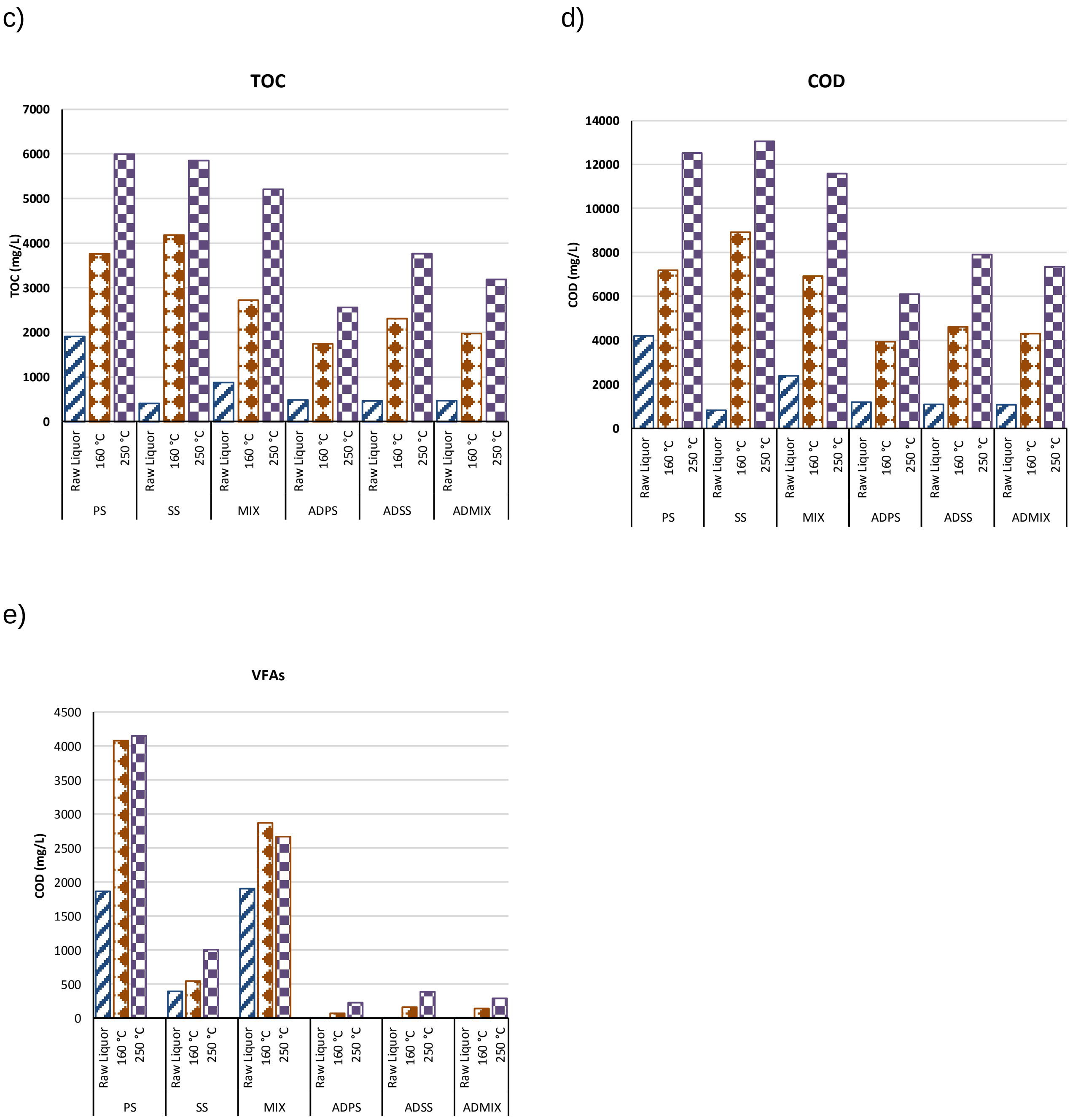


Figure 6.2.- (a) pH and concentration of (b) Total Solids(TS) and Total Volatile Solids (TVS), (c) Total Organic Carbon (TOC) (d) Chemical Oxygen demand (COD) and (e) Volatile Fatty Acids (VFAs) of the different sewage sludge's process waters after the different thermal treatment.

6.2.2.2.Total Solids and Total Volatile Solids

In the **Figure 6.2b** is shown the total solid (TS) and total volatile solid (TVS) concentration of the raw liquors and process waters from different sewage sludge after different thermal treatments. As stated by Aragón-Briceño et al. (2017), the thermal treatments favours solids solubilisation (organics and inorganics) into the process waters due the hydrolysis process. For that reason, there was an increase of the TS and TVS concentration in all the different sewage sludge after the thermal treatment.

The PS had the highest TS solubilisation after thermal treatment of 160°C and 250°C (307 and 321% respectively). This might be attributed to the high concentration of organics and inorganics available for hydrolysis unlike others sewage sludge that have been biologically treated. TVS represents most of the organics that are contented in the different sewage sludge which increased significantly after thermal treatments (from 2 to 6 times). Although the TVS fraction of the TS of liquors from the different sewage sludge prior thermal treatment ranged from 20 to 49%, but after thermal treatments, the TVS fraction increased up to 95%. The SS presented the highest TVS solubilisation which might be due its high amount of organics coming from the biomass of activated sludge were hydrolysed and released into the process water during the thermal treatment.

Furthermore, the non-AD sludge showed a higher TS and TVS solubilisation than those which have been anaerobic digested previously. This might be during the AD treatment, organic compounds are consumed and transformed into biogas. However, still a big amount of organics remain into the AD sludge that can be harness with the thermal treatments.

6.2.2.3.Chemical oxygen demand and Total Organic carbon

In **Figure 6.2c and 6.2d** the TOC and COD concentration of liquid fraction from different sewage sludge of non-treated and thermally treated are presented. As the temperature reaction increased the TOC and COD concentration increased. This was due the severity of the reaction enhanced the solubilisation of the organics and inorganics. During the thermal treatments there is a solubilisation of the organics and inorganics due the hydrolysis reflected in the increase of the COD and TOC levels in the liquid fraction (Aragón-Briceño et al., 2017, Ekpo et al., 2015, Keymer et al., 2013).

The COD concentration of the non-treated sludge (filtered fraction) increased after the thermal treatments up to 3, 16 and 5-fold in process waters for the PS, SS and MIX respectively up to 5, 7 and 7.3-fold in process waters for PS, SS and MIX digestates respectively. Previous studies reported an increase of 7-fold of the COD concentration for sewage digestate after 160 and 250°C treatments (Aragón-Briceño et al., 2017).

The different non-AD treated sludge presented higher solubilisation rates than the AD treated sludge. The SS showed the highest COD solubilisation rate with 357 and 522 mg of COD per gram of feedstock, followed by the PS with 288 and 501 mg of COD per gram of feedstock, and the MIX sludge with 277 and 464 mg of COD per gram of feedstock respectively at 160 and 250°C treatment. On the other hand, digestates presented lower solubilisation rates ranging from 158 to 316 mg of COD per gram of Feedstock. This might be due sludge without previous AD treatment have more organic matter available compared with those which not.

The TOC concentrations showed that the carbon solubilisation were higher in non-AD treated sludge rather than those which had a previous AD treatment (see **figure 6.2c**). PS, SS and MIX presented an increase up to 3, 14.5 and 5.9-fold respectively after thermal treatment and up to 5, 8 and 6.8-fold for PS, SS and MIX digestates. This means that the increase on the TOC concentration varied depending on the sewage sludge treated. Aragón-Briceño et al. (2017) reported a 10-fold increase in the TOC concentration of sewage digestate after 160 and 250°C treatments.

The TOC solubilisation rates went up to 167 and 240 for the non-AD treated sludge and 92 and 151 mg of TOC per gram of feedstock at 160 and 250°C treatment respectively for the previous AD treated sludge.

The proximate analyses in the process waters showed a carbon solubilisation after the thermal treatments as well (see **Table 6.1**). The Secondary sludge presented higher carbon solubilisation in the liquid fraction after the thermal treatments from 11.8% in the original feedstock liquor to

35.9 and 39.8% of 160 and 250°C process waters respectively. Most of the secondary sludge's organic material in the solid fraction is mainly activated sludge bacteria which releases organics and inorganics within the liquid fraction during the thermal treatment. The primary sludge showed a low increasing in carbon percentage (from 27.6 up to 33.3%). This might be because the primary sludge comes from the settlement solids of the raw wastewater that carries all the complex organics and inorganics, mostly in the solid fraction, that are less susceptible to hydrolysis. The Mix sludge elemental carbon increased from 19 to 38% after both thermal treatments. The elemental carbon of process waters coming from the different digestates ranged from 38 to 43%.

The elemental carbon values of digestates were slightly lower than reported by Aragón-Briceño et al. (2017) for sewage digestate who obtained from 46 to 68% elemental carbon within the process water. The carbon solubilisation comes from the AD biomass which is hydrolysed during the thermal treatments. Nonetheless, despite of the different AD sludge presented high carbon solubilisation during the thermal treatment; most of the carbon released within liquid fraction seems to be less suitable for methane production than the carbon solubilized within the liquid fraction from non-AD treated sludge.

6.2.2.4.Volatile Fatty Acids (VFAs)

Figure 6.2e shows the VFAs concentration of the liquid fraction coming from the different sewage sludge prior and after different thermal treatments. Aragón-Briceño et al. (2017) reported that the VFA concentration increases as the reaction temperature increases in sewage digestate and is due solubilisation coming from the solid fraction of sewage. According to the reported by Aragón-Briceño et al. (2017) and Nyktari et al. (2017), the acetic acid makes the highest contribution to VFAs produced during the thermal treatment..

The VFAs concentration in process waters from PS did not vary significantly despite of the different treatment temperatures. The VFAs concentrations were 4083 and 4155 mg of COD/L for 160 and 250°C respectively. The

160°C treatment presented higher VFAs solubilisation than the 250°C treatment in the process waters coming from the MIX sludge where the concentrations were 2875 and 2672 mg of COD/L respectively. For the biologically treated sludges (secondary sludge and digestates), the process temperature influenced the VFAs solubilisation showing an increase in the concentration as the the temperature increased. Furhtermore, the VFAs concentration were lower compared with non-biologically treated sludge.This might be that the primary sludge has not received any previous treatment that has degraded the organics contented in it, unlike secondary sludge and digestates where all the organic’s carbon compounds have been degraded by different bacteria.

Table 6.1.-Proximate analyses of the Process waters.

Sample	Ultimate analysis				
	C (%)	H (%)	N (%)	O^a (%)	S (%)
Primary Sludge	27.59	4.40	3.79	64.03	0.18
Secondary Sludge	11.81	1.26	14.92	71.92	0.09
Mix Sludge	19.37	2.37	4.85	73.41	0.00
AD Primary Sludge	31.07	4.03	3.64	60.51	0.75
AD Secondary Sludge	19.68	2.49	2.30	74.57	0.96
AD Mix Sludge	24.45	3.03	2.64	68.95	0.93
Process Waters from 160 °C - 30 min- 5 Bar					
Primary Sludge	31.60	4.93	6.34	56.29	0.83
Secondary Sludge	35.92	5.28	8.79	48.84	1.17
Mix Sludge	38.39	5.68	6.95	48.02	0.96
AD Primary Sludge	39.01	5.46	9.50	44.46	1.56
AD Secondary Sludge	38.82	5.59	9.79	44.02	1.78
AD Mix Sludge	38.38	5.41	9.66	44.82	1.73
Process Waters from 250 °C - 30 min- 40 Bar					
Primary Sludge	33.35	5.22	6.76	53.77	0.90
Secondary Sludge	39.82	5.79	8.58	44.43	1.38
Mix Sludge	38.36	5.71	8.18	46.75	1.01
AD Primary Sludge	43.49	6.56	10.28	37.65	2.03
AD Secondary Sludge	37.98	6.02	9.83	44.30	1.86
AD Mix Sludge	40.69	6.18	9.63	41.39	2.11

[a] Calculated as difference between sum of C,H,N,S.

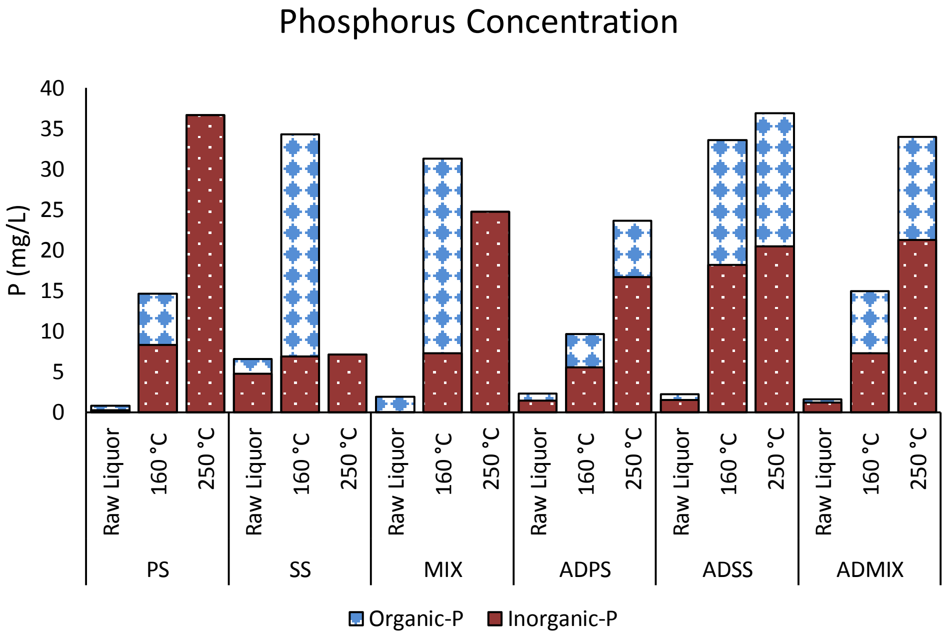
6.2.2.5.Phosphorus

Figure 6.3a shows the phosphorus concentration of the liquid fraction of the different sewage sludge prior and after thermal treatment at different temperatures. The phosphorus solubilisation is carried on during the thermal process due the organic phosphorus compounds (complex phospholipids, DNA and phosphates monoesters) break down into phosphate (Dai et al., 2015, Ekpo et al., 2015). Although, the fate of P is highly feedstock dependent during hydrothermal treatment and is linked to the levels of metals presented in the feedstock (Aragón-Briceño et al., 2017, Ekpo et al., 2015)

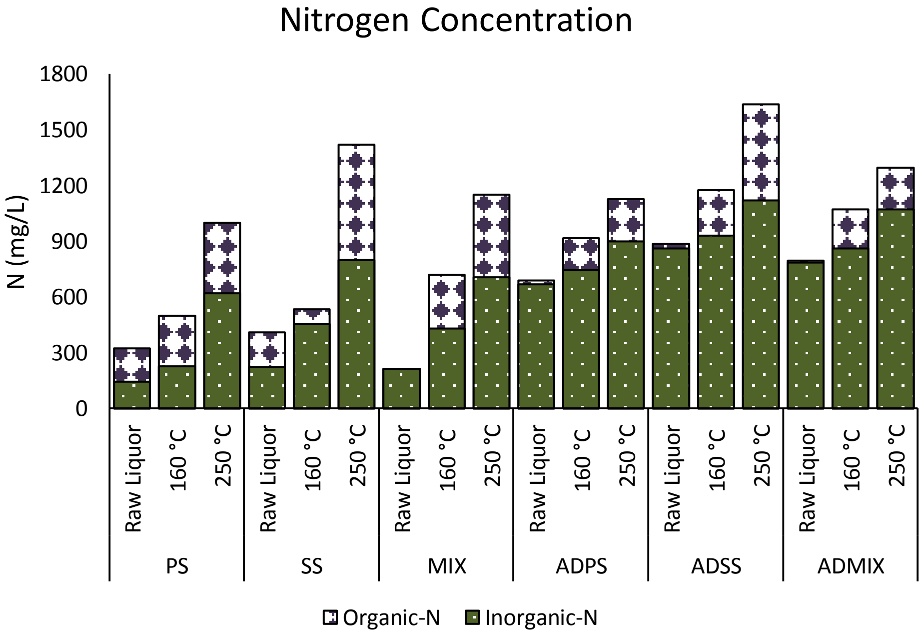
There was a clear influence of the temperature in the phosphorus solubilisation from the solid part among the different sewage sludge with exception of the secondary and mix sludge. The higher temperature was applied, the higher phosphorus solubilisation was obtained in AD treated sludge. Although it can be assumed that most of the phosphorus is contained in the solid fraction since the raw liquors presented low phosphorus concentration. There was a solubilisation up to 10% of Phosphorus at 250°C and up to 12% of Phosphorus at 160°C (See **Figure 6.3d**). However, the phosphorus concentrations in process waters coming from secondary sludge suggest that 250°C treatment enhanced the phosphorus fixation within the hydrochar unlike the 160 °C that improved the phosphorus solubilisation.

Aragón-Briceño et al. (2017) reported that hydrothermal treatments at lower temperatures improves the extraction of organic P in sewage digestate than higher temperature treatments. Nonetheless, the 250°C treatment showed a higher inorganic phosphorus production (up to 3 times) in most of the different sewage compared with organic phosphorus production. Moreover, 160°C treatment showed the same trend on digestates related to higher inorganic phosphorus production.

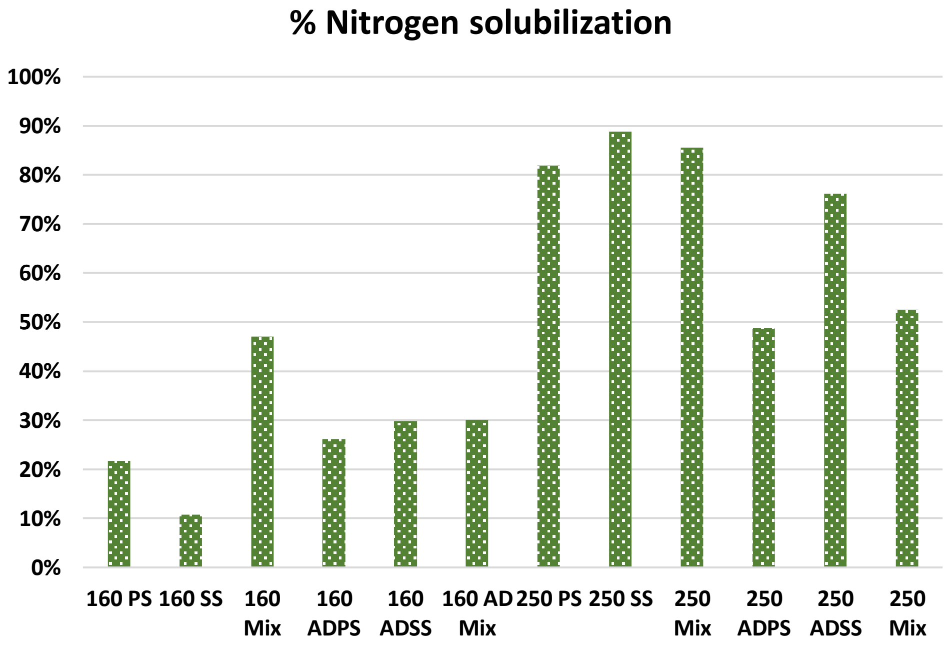
a)


Phosphorus Concentration
P (mg/L)
0
5
10
15
20
25
30
35
40
Raw Liquor
160 °C
250 °C
PS
SS
MIX
ADPS
ADSS
ADMIX
Organic-P
Inorganic-P

b)


Nitrogen Concentration
N (mg/L)
0
300
600
900
1200
1500
1800
Raw Liquor
160 °C
250 °C
PS
SS
MIX
ADPS
ADSS
ADMIX
Organic-N
Inorganic-N

c)



d)

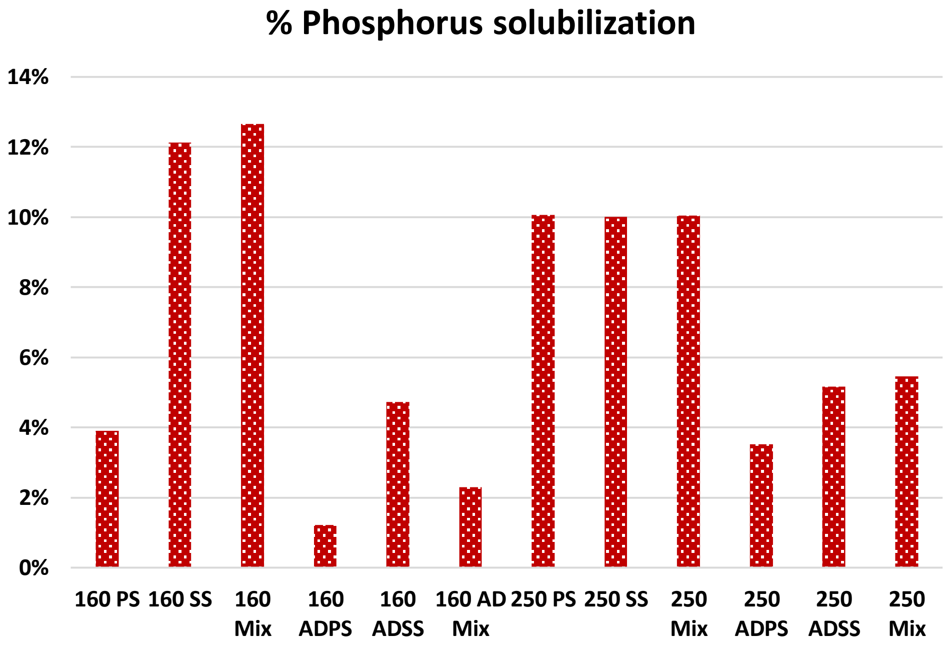


Figure 6.3.- Concentration of phosphorus and nitrogen of the different sewage sludge after the different thermal treatment: (a), Total Phosphorus and Reactive Phosphorus, (b) Total Kjeldahl Nitrogen (TKN) and Ammonia and solubilisation of the c) Nitrogen and d) Phosphorus.

6.2.2.6.Nitrogen

In previous studies have been proven that during thermal treatment the proteins in sewage sludge hydrolyse forming ammonium which is released into the process waters (Aragón-Briceño et al., 2017).

In **Figure 6.3b** the organic and inorganic nitrogen concentration of the liquid fraction of the different sewage sludge prior and after different thermal treatments are shown. The Total nitrogen solubilisation was influenced with the temperature applied to the different sewage sludge. As the temperature increased, the total nitrogen concentration increased. After the thermal treatment, the soluble nitrogen concentration increased up to 540% in the non-AD treated sludge at 250°C and up to 340% at 160°C and for the digestates there were an increase up to 70% at 250°C and up to 36% at 160°C. These findings match with the results of Aragón-Briceño et al. (2017) in which the nitrogen concentration increased up to 50% at 250°C treatment and up to 45% at 160°C.

The ammonia concentration (Inorganic Nitrogen) in the process waters increased after thermal treatments showing higher solubilisation in non-AD treated sludge (up to 204 and 431% at 160 and 250°C respectively) compared with digestates (up to 109 and 136% at 160 and 250°C respectively).

6.2.3.Anaerobic digestion and biomethane potential of process waters (BMP)

The BMP of different sewage sludge and their process waters derived from thermal treatment are presented in **Figure 6.4**. Thermal treatment enhanced the BMP of the different non-AD treated sludge up to 170%. The process waters coming from 250°C treatment showed higher BMP values than 160°C process waters (up to 68%), excepting process waters coming from secondary sludge digestate where the BMP did not vary significantly regardless the temperature (12%).

The non-AD treated sludge presented higher BMP than digestates (up to 52%). The Mix sludge due its high organic matter content, presented BMPs of 252 and 351 mL of CH_4 per g of COD at 160 and 250°C respectively that represented an increasing of 92 and 168% with respect to the untreated Mix sludge. The secondary sludge showed close BMP values in the different thermal treatments with 276 mL of CH_4 per g of COD at 160°C and 312 mL of CH_4 per g of COD at 250°C treatment. Thermal processes enhanced the BMP of the primary sludge increasing it up to 152% in the process water (208 and 325 mL of CH_4 per g of COD for 160 and 250°C process waters respectively) compared with the untreated sludge (129 mL of CH_4 per g of COD).

On the other hand, digestates without thermal treatment showed BMP values of cero, meaning in non organic matter was available for methane conversion. After the thermal treatment, digestates BMP values increased from 0 up to 232 mL of CH_4 per g of COD. There was not a significant difference between 160 and 250°C treatment for process waters coming from ADSS and ADMIX. However the BMPs of process waters coming from ADPS showed that the temperature influenced increasing the BMP value in 68% as the temperature increased.

Previous studies investigating the anaerobic digestion of HTC have reported using PW from municipal sewage sludge treated at 170°C methane yields of 256.6mL of CH_4 per g of COD (Qiao et al., 2011); for PW from sewage sludge digestate treated between 160 to 250°C, the methane yields ranged from 178 to 277mL of CH_4 per g of COD (Aragón-Briceño et al., 2017, Wirth et al., 2015) and for PW coming from PS treated at 200°C, the methane yield was 335mL of CH_4 per g of COD (Nilsson E, 2017).

There was a significant rising on the COD degradation in the process waters in comparison with the untreated sludge (see **Table 6.2**) (up to 97% of COD degradation). The thermal treatment reduces the concentration of complex organic matter during the hydrolysis which is reflected in the increasing of COD degradation during the anaerobic digestion (Becker et al., 2013). The 160°C process waters coming from non- AD treated sludge (PS, SS and MIX) presented higher COD degradation than 250°C process waters. This is because at higher temperatures it is more susceptible to produce toxics as furans, phenols and other recalcitrant products that may affect the anaerobic bacteria (Hübner and Mumme, 2015). Nonetheless the 250°C process waters coming from the AD treated sludge presented higher COD consumption than the 160°C process waters.

These findings match with the reported in previous studies where the COD degradation during the anaerobic digestion ranged between 62 to 88% in HTC process waters from sewage sludge (Nyktari et al., 2017, Aragón-Briceño et al., 2017, Wirth et al., 2015).

The percentage of biodegradability (BD) increased as the temperature treatment increased (see **Table 6.2**). The MIX sludge showed the highest biodegradability among all the other sludge, prior (57%) and post 160 and 250°C treatment (82 and 89% respectively). The SS presented a BD of 29% and after the 160 and 250°C treatments, the process waters BD incased to 70 and 79%. The BD of the PS (33%) increased after thermal treatments to 53% and 82% of 160°C and 250°C process waters.

The biogas composition of process waters is shown in **Table 6.2**. The untreated sludge presented methane percentage of 72, 66 and 72% for PS, SS and Mix Sludge respectively. The 160°C and 250°C treatment produced a biogas with methane percentage between 60 to 79% and from 60 to 77%respectively. With exception of the process water coming from primary sludge, the 250°C treated process waters presented higher methane percentage in the biogas than the 160°C process waters and untreated sludge. These results are similar to those obtained by Wirth and Mumme (2013) in HTC liquor from corn silage where they obtained 70% of methane.

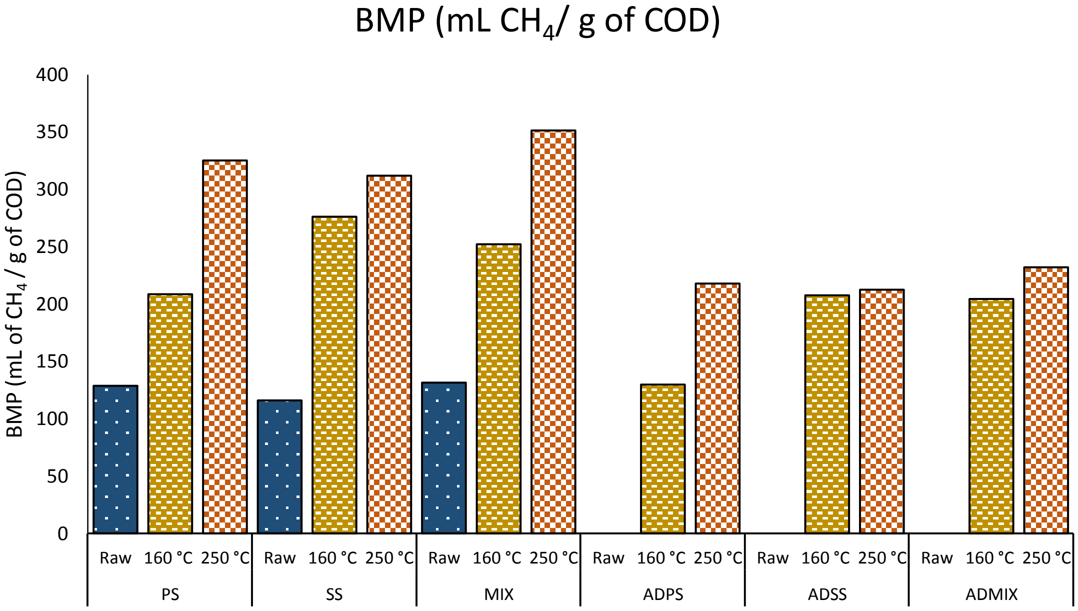


Figure 6.4.- BMP of the liquid fraction of the different sewage sludge prior and after thermal treatment.

Table 6.2.- BMP, biogas composition and COD removal of the process waters.

Sample	BMP (mL CH_4/ g of COD)	BMP Boyle's eq. (mL CH_4 / g COD)	BD Boyle's eq.	Biogas composition		COD REMOVAL
				%CH4	%CO2	
Primary Sludge	129	181	71%	72	28	38%
Secondary Sludge	116	350	33%	66	34	48%
Mix Sludge	131	419	54%	72	28	44%
AD Primary Sludge	0	359	0%	0	0	0%
AD Secondary Sludge	0	353	0%	0	0	0%
AD Mix Sludge	0	347	0%	0	0	0%
Hydrochars from 160 °C - 30 min- 5 Bar						
Primary Sludge	208	460	45%	66	34	97%
Secondary Sludge	276	485	57%	69	31	83%
Mix Sludge	325	492	66%	68	32	86%
AD Primary Sludge	130	467	28%	61	39	57%
AD Secondary Sludge	207	554	37%	70	70	42%
AD Mix Sludge	204	517	39%	79	79	37%
Hydrochars from 250 °C - 30 min- 40 Bar						
Primary Sludge	325	294	110%	60	60	53%
Secondary Sludge	312	373	84%	73	27	68%
Mix Sludge	351	306	115%	77	23	75%
AD Primary Sludge	218	378	58%	70	30	59%
AD Secondary Sludge	212	363	58%	72	28	59%
AD Mix Sludge	232	345	67%	74	26	60%

6.2.4.Hydrochar characteristics

6.2.4.1.Physical characteristics

Table 6.3 shows hydrochar yields and proximate characteristics. According to Danso-Boateng et al. (2015) and Ekpo et al. (2015) the reaction temperature affects the hydrochar yields. Hydrochar yields varied from 38 to 69% for sludge treated at 160°C and from 20 to 40% for sludge treated at 250°C. The Secondary sludge presented the lowest hydrochar yields after both thermal treatments at 160 and 250°C (38 and 30% respectively). The yields obtained in this study were lower in comparison with other values reported for hydrochar coming from sewage sludge that ranged between 57 to 81.1% (Aragón-Briceño et al., 2017, Ekpo et al., 2015, Danso-Boateng et al., 2015).

The ash content is strong related with the energy that we can harness from the hydrochar. If the ash content of a hydrochar is high, the less energy densification is presented. Ash content seems to increase as the reaction temperature increases. The ash content of the raw feedstock ranged from 25.7 to 36.4%. After the 160°C treatment the ash content increased to 12-27% and after the 250°C treatment the ash content increased to 53-61%.

The ash content of digestate hydrochars are similar to reported by reported by Berge et al. (2011a) (55.8%) and slightly higher than Aragón-Briceño et al. (2017) (36.9%) at 250°C.

The volatile matter of the feedstock decreased as the reaction temperature increased. The 250°C treatment had more influence in the volatile matter reduction that the 160°C treatment. The volatile matter reduction ranged from 1 to 10% when the sludge as treated at 160°C and ranged from 14 to 29% when the sludge was treated at 250°C. However in both thermal treatments the digestates had higher volatile matter reduction than the non-AD treated sludge.

Table 6.3.-Proximate analyses of the feedstock (control) and hydrochar.

Sample	Proximate Analyses				Yield (%)
	Moisture (%)	Ash (%db)	Volatile matter (%db)	Fixed carbon [a] (% db)	
Primary Sludge	6.80	25.67	57.87	9.66	
Secondary Sludge	7.29	28.20	54.81	9.70	
Mix Sludge	7.35	27.31	56.01	9.33	
AD Primary Sludge	7.48	36.26	48.02	8.25	
AD Secondary Sludge	6.60	35.12	49.85	8.43	
AD Mix Sludge	7.11	36.36	48.46	8.07	
Hydrochars from 160 °C - 30 min- 5 Bar					
Primary Sludge	4.87	28.75	57.30	9.09	69
Secondary Sludge	5.51	35.88	53.36	5.25	38
Mix Sludge	5.69	31.84	55.22	7.25	47
AD Primary Sludge	5.47	44.18	43.95	6.40	50
AD Secondary Sludge	5.40	43.87	44.97	5.76	55
AD Mix Sludge	5.43	43.56	44.50	6.52	56
Hydrochars from 250 °C - 30 min- 40 Bar					
Primary Sludge	2.94	40.53	47.50	9.03	39
Secondary Sludge	2.86	45.26	42.28	9.59	30
Mix Sludge	2.82	42.47	48.22	6.49	35
AD Primary Sludge	2.76	56.08	35.49	5.68	37
AD Secondary Sludge	3.19	55.43	35.60	5.78	40
AD Mix Sludge	2.96	55.73	35.84	5.47	40

[a] 100 - (moisture + ash + volatile matter).

6.2.4.2.Elemental composition in hydrochar

The ultimate analyses of the different sewage sludge and hydrochars are shown in **Table 6.4**. The untreated PS presented the same carbon content value after the 160°C treatment (40.3%) but after the 250°C treatment the carbon content in the PS sludge was reduced to 37.4%. The ADPS sludge presented lower carbon content (31.1%) than the PS due the prior biological treatment received. Unlike the PS, the ADPS´s carbon content was reduced to 28.9 and 27.3% after 160 and 250°C treatment respectively. The SS presented carbon content of 33.5% and after 160°C treatment it showed a small reduction on the carbon content to 33.1% but after the 250°C treatment there was an increase to 36.1% showing carbon densification. The ADSS carbon content (32.2%) suffered a reduction after the 160 and 250°C treatments (29.4 and 27.5% respectively). The Mix Sludge carbon content (35.5%) suffered carbon densification increasing its carbon content after 160 and 250°C thermal treatments (37.5 and 35.8% respectively). The ADMix carbon content (30.9%) presented a reduction after 160 and 250°C treatments (29.9 and 26.6%).The carbon reduction in hydrochars from different sewage sludge is similar to the observed by Ekpo et al. (2015) where the sewage digestate suffered a reduction up to 8% after thermal treatment. The carbon content of the different sewage sludge are similar to those reported by Aragón-Briceño et al. (2017) (33- 38%), Danso-Boateng et al. (2015) (36.6-39.2%) and Berge et al. (2011a) (32.6%).

There was a reduction in the nitrogen content between 0.5 to 2.3% after thermal treatment, presented in the hydrochars, in comparison to the original feedstock. This nitrogen reduction is given by the nitrogen released into the process waters during the thermal process (Aragón-Briceño et al., 2017).

Oxygen content of hydrochars was lower compared to the original feedstock due the decarboxylation reactions carried out during carbonisation process (Danso-Boateng et al., 2015).

Table 6.4.- Ultimate analyses of the feedstock and hydrochar.

Sample	Ultimate analysis					HHV (Mj kg^{-1})	Energy densification (Mj Kg^{-1})	Energy Yield (%)
	C (%)	H (%)	N (%)	O^{a} (%)	S (%)			
Primary Sludge	40.3	6.6	3.3	23.7	0.4	18.9	-	-
Secondary Sludge	33.5	5.5	4.1	28.5	0.2	14.2	-	-
Mix Sludge	35.5	5.8	3.3	28.0	0.1	15.4	-	-
AD Primary Sludge	31.1	5.1	3.0	24.0	0.5	13.5	-	-
AD Secondary Sludge	32.2	5.2	3.4	23.5	0.6	14.2	-	-
AD Mix Sludge	30.9	5.0	3.0	24.1	0.7	13.3	-	-
Hydrochars from 160 °C - 30 min- 5 Bar								
Primary Sludge	40.3	6.3	2.1	22.5	0.1	18.2	0.99	67.8
Secondary Sludge	33.1	5.3	3.3	21.7	0.7	14.6	1.06	40.2
Mix Sludge	37.5	6.0	2.6	21.6	0.5	17.5	1.14	53.5
AD Primary Sludge	28.9	4.5	2.1	19.8	0.5	12.8	0.94	47.6
AD Secondary Sludge	29.4	4.6	2.4	19.1	0.6	13.2	0.93	51.1
AD Mix Sludge	29.9	4.6	2.5	18.9	0.6	13.5	1.01	56.3
Hydrochars from 250 °C - 30 min- 40 Bar								
Primary Sludge	37.4	5.3	1.0	15.6	0.1	16.8	0.93	36.4
Secondary Sludge	36.1	4.6	1.9	11.6	0.5	16.5	1.19	35.5
Mix Sludge	35.8	5.2	1.1	15.2	0.3	16.9	1.10	38.1
AD Primary Sludge	27.3	3.8	1.1	11.4	0.3	12.3	0.93	34.2
AD Secondary Sludge	27.5	3.8	1.3	11.6	0.4	12.2	0.90	35.8
AD Mix Sludge	26.6	3.7	1.1	12.6	0.3	12.0	0.90	36.5

[a] Calculated as difference between sum of C,H,N,S,ash.

6.2.4.3.Energy characteristics in hydrochar

The High Heating Value (HHV) of hydrochars coming from the non-AD treated sludge generally increase with exception of the PS (See **Table 6.4**). HHVs of SS and MIX sludge after hydrothermal treatment were higher than their original sample without treatment with a maximum of 16.5 and 17.5 Mj kg^{-1} respectively. The AD prior the thermal treatment influenced in the HHVs of the hydrochar. The digestates and the PS after the thermal treatment showed a HHV reduction betwwen 4 to 14%. The Assessment of the combustion behaviour of the hydrochar were not been performed. Hydrochar´s HHV are similar with the values reported by Berge et al. (2011a) for anaerobic digestion waste (13.7 Mj Kg^{-1}), Danso-Boateng et al. (2015) (17.2 – 18.4 Mj Kg^{-1}) and Aragón-Briceño et al. (2017) (14.3 – 17.8 Mj Kg^{-1}).

The energy densification of sewage derived solids and digestates is quite low (from 0.90 to 1.19) compared to thermally treated swine and chicken manure (1.27 and 1.49 respectivelty) and indicates that a significant amount of the energy in the original feedstock is accumulated in the process waters(Ekpo et al., 2015).

6.2.5.Energy balance

The integration of thermal treatments prior or following AD has proven not only the improving in dewaterability characteristics of the sludge by reducing the moisture in the solid fraction, but also it was found that improves the energy production if the solid fraction is included as a fuel source (Aragón-Briceño et al., 2017).

Table 6.5 shows the energy produced by different sewage sludge, hydrochars and process waters per kg of feedstock from different process configurations based on the HHVs, theoretical and experimental BMP. It was included configurations of conventional AD, two different thermal pre-treatments and post-treatments (160 and 250°C) integrated with AD processing. This study only considered the energy consumed by the thermal treatments and it was calculated based on the energy required to heat water in a closed system is small in comparison to that required to evaporate water in traditional dry thermochemical conversion process (Aragón-Briceño et al., 2017, Berge et al., 2011b).

The results show the net energy balance of all the scenarios from different sewage sludge were positives when the hydrochar is considered as a fuel source (See **table 6.5**). The PS sludge presented the highest net energy production (16.5 Mj*Kg^{-1}) in all the scenarios followed by the SS sludge (12.3 Mj*Kg^{-1}) and Mix Sludge (12.1 Mj*Kg^{-1}).

The thermal treatments as pre-treatments increased the net energy balance of the different sewage sludge compared with the conventional AD system. After the 160°C pre-treatment, the net energy balance increased from up to 8% for PS, from up to 136% for SS and up to 57% for MIX sludge. After the 250°C pre-treatment, the net energy production increased up to 11% for the PS, up to 200% for SS and up to 66% for MIX sludge. In addition, the slurry pre treatment (solid and liquid fraction) presented up to 57% higher net energy balance compared when PWs is anaerobic digested and the hydrochar is taken as a fuel source. When the PWs are considered as the only energy source when thermal treatments are applied as pre-treatments, the net energy balance of the system reduces significantly resulting in some a negative energy balance. For that reason it is important the hydrochar inclusion as a fuel source within the system in order to make a more self-sustainable.

The Integration of the conventional AD and the thermal treatment as a post-treatment showed in some scenarios higher net energy balance compared with the pre-treatments. The net energy balance increased up to 38, 141 and 137% for PS, SS and Mix Sludge respectively when 160°C thermal treatment was applied and up to 15, 61 and 58% when 250°C was applied. In addition, the net energy balance only when the biogas is considered as the only energy source is significantly higher in comparison of the values obtained from the process waters when the thermal treatments are applied as pre-treatments.

Table 6.5.- Energy production and consumption per kg of feedstock. Considering 20% of solids loading.

		[b]Energy produced from CH4 per kg of feedstock (Mj)	[a]Energy produced in char per kg of feedstock (Mj)	Overall energy produced per Kg of feedstock (Mj)	[c]Energy consumed in the HTx per Kg of feedstock (Mj)	Overall Net Energy Balance per Kg of feedstock (Mj)	Net Energy Balance only biogas considered per Kg of feedstock(Mj)
Primary	Conventional AD Sludge	12.0	-	12.0	-	12.0	12.0
	160TT + AD Slurry[d]	15.6	-	15.6	2.5	13.0	13.0
	250TT + AD Slurry[d]	17.5	-	17.5	4.2	13.3	13.3
	160TT + AD P.W.	1.7	12.5	14.2	2.5	11.7	-0.8
	250TT + AD P.W.	6.8	6.6	13.4	4.2	9.3	2.7
	AD sludge + 160T + AD P.W.	12.61	6.43	19.0	2.5	16.5	10.1
	AD sludge + 250T + AD P.W.	13.51	4.50	18.0	4.2	13.8	9.3
Secondary	Conventional AD Sludge	4.1	-	4.1	-	4.1	4.1
	160TT + AD Slurry[d]	12.2	-	12.2	2.5	9.7	9.7
	250TT + AD Slurry[d]	16.5	-	16.5	4.2	12.3	12.3
	160TT + AD P.W.	2.7	5.5	8.3	2.5	5.8	0.2
	250TT + AD P.W.	4.5	4.9	9.4	4.2	5.2	0.3
	AD sludge + 160T + AD P.W.	5.1	7.3	12.4	2.5	9.9	2.6
	AD sludge + 250T + AD P.W.	5.9	4.9	10.8	4.2	6.6	1.7
Mix	Conventional AD Sludge	4.3	-	4.3	-	4.3	4.3
	160TT + AD Slurry[d]	14.0	-	14.0	2.5	11.5	11.5
	250TT + AD Slurry[d]	16.3	-	16.3	4.2	12.1	12.1
	160TT + AD P.W.	1.9	8.2	10.2	2.5	7.7	-0.6
	250TT + AD P.W.	4.5	5.9	10.3	4.2	6.2	0.3
	AD sludge + 160T + AD P.W.	5.2	7.5	12.7	2.5	10.2	2.7
	AD sludge + 250T + AD P.W.	6.1	4.9	11.0	4.2	6.8	2.0

[a] Values were determined according to the HHV of the hydrochars. [b] Values were obtained from the experimental BMP potential of the process waters and the relationship 1m^3 = 35.8Mj (Passos and Ferrer, 2014). [c] Energy consumed were determined based in energy required to heat water from 25°C to 250°C in 500mL reactor. D Values obtained from Boyle's equation of the hydrochar.

6.3. Conclusions

In conclusion, hydrothermal treatments improved the characteristics of the sewage sludge producing hydrochars and process waters rich in soluble organic matter and nutrients. Hydrochars from the different digestate sludge showed to have poorer production and energy characteristics than the hydrochars coming from the different non-AD treated sewage sludge. Nevertheless, the hydrochar’s energy characteristics are enough to enhance the overall energy production. The organics and nutrients solubilisation demonstrated to be feedstock dependant showing better solubilisation to the different non-AD sewage sludge in comparison to the different digestate sludge. Process waters showed to be suitable option for biomethane production, especially process waters coming from the digestate sludge which showed a significant improvement in biogas production. Most of the potential energy production comes from the hydrochar. Therefore, the energy production of the HTP treated sludge was higher when the hydrochar was considered than non HTP treated sludge. The integration of the HTPs as post-treatment after AD showed to a sustainable option in terms of energy production but still more studies needs to be done.

6.4. Summary

In this chapter, the potential of hydrothermal processing as a novel alternative for sewage sludge treatment was evaluated. Primary, secondary and digestate sludge were treated using hydrothermal processes. The effect of process temperature was evaluated with regard to product yields, biomethane potential and solubilisation of organic carbon and nutrients. Tests at 160 and 250°C for 30-minute reaction time were carried out. Hydrochar yields ranged from 38 to 68% at 160°C and from 29 and 40% at 250°C. The soluble fraction of organic carbon increased up to 313.7% in primary sludge, 1427.7% in secondary sludge and 292.9% in digestate sludge, after thermal treatments. Experimental BMP values showed that hydrothermal treatment enhanced methane production in all sludge samples processed. The integration of the HTPs as post-treatment after AD showed to be the best option in terms of energy production.

6.5. Publications and awards derived from this chapter

- “Outstanding Poster Award” at the 15th IWA World Conference on Anaerobic Digestion (2017). Beijing, China.
- ***Aragón C.**, Camargo-Valero M. and Ross A. (2018). Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatment. In proceedings of the XIII Latin American Workshop and Symposium on Anaerobic Digestion (DAALXIII). Medellin, Colombia
- ***Aragón C.**, Camargo-Valero M. and Ross A. (2018). Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatment. In proceedings of the 4th AD Network (a BBSRC NIBB) Early Career Researcher conference. University of Birmingham, Birmingham, United Kingdom.
- ***Aragón C.**, Camargo-Valero M. and Ross A. (2017). “Evaluation and comparison of product yields and bio-methane potential from hydrothermally pre-treated sewage sludge” In proceedings of the 15th IWA World Conference on Anaerobic Digestion. Beijing, China.

Chapter 7. Mass and Energy Integration Study of Hydrothermal Processing with Anaerobic Digestion of Sewage Sludge

7.1. Introduction

The use of sewage sludge as a resource for renewable energy generation is gaining growing attention. The sewage sludge coming from waste water treatment works (WWTs) has been commonly treated by anaerobic digestion (AD) due its large organic matter content which leads the biogas production and brings multiple environmental benefits (Aragón-Briceño et al., 2017, Kim et al., 2014, Berglund and Börjesson, 2006). It is considered an efficient and sustainable technology for sludge treatment and disposal (Pilli et al., 2015). The water industries in the UK, generate approximately 800GW/h of electrical energy from sewage sludge (Mills et al., 2014). The integration of anaerobic digestion into the WWTW has become the most benefit alternative for SS treatment because of the energy generation from methane helps to reduce the net energy consumption of the overall treatment. According to Berglund and Börjesson (2006), 40-80% of the energy content of the biogas produced corresponds to the overall energy input in a large-scale biogas plant. Furthermore the inclusion of the AD brings associate benefits as mass reduction, odour removal and pathogen reduction (Pilli et al., 2015). Nevertheless, one of the main limiting steps of the AD process is the solubilisation of the organics through hydrolysis resulting in just one half of the organic matter in sewage sludge is susceptible to anaerobic biodegradation (Abelleira-Pereira et al., 2015, Hindle, 2013). For that reason, the resulting digested sludge (digestate) from the anaerobic digestion still contains large amounts of non-easy biodegradable organic matter that can be harnessed for additional energy production (Aragón-Briceño et al., 2017). Several researchers have studied different pre-treatment techniques (thermal, biological, chemical, mechanical, physical and combinations) with the aim of enhance the sludge biodegradability but the economic constraints for scale them up and commercialize them has been the main downside (Pilli et al., 2015).

In recent years, some researchers has proposed the hydrothermal carbonisation process (HTC) as an alternative to harness better the properties from the sewage sludge and reducing the waste generation (Aragón-Briceño et al., 2017, Zhao et al., 2014, He et al., 2013). HTC main objective is to transform biomass into a carbon-rich product applying heat (200-250°C) and pressure during a certain period of time (Biller and Ross, 2012, Wirth et al., 2015, Danso-Boateng et al., 2015). The main advantage of HTC is that it is carried out in presence of water avoiding the energy-intensive drying step required for thermal processes (Aragón-Briceño et al., 2017, Biller and Ross, 2012). Furthermore, the resulting products from the HTC are a solid hydrochar that can be used as a soil amender or fuel source and a process water rich in carbon and organics that can be used for produce biogas (Wirth et al., 2015, Becker et al., 2014, Wang et al., 2010).

There are some companies who has developed HTC at commercial scale as Terranova Energy, SunCoal Industries, AVA-CO2 and Ingelia. According to the studies carried on by Child (2014) and Lucian and Fiori (2017), a HTC plant might cost from €1.5 up to €10million depending the treatment capacity (8,000 to 50,000 tonnes of feedstock). Nevertheless, most of them focus on hydrochar production using mostly lignocellulocic biomass and just few use sewage sludge as main feedstock. Moreover, the integration of HTC as a post-step after the AD is a recent approach that is still under development and some authors suggest that the integration of a hydrothermal treatment step into waste water systems are energy positive (Aragón-Briceño et al., 2017, Mumme et al., 2015).

Some studies have found that the biogas production of the thermal hydrolysis as pre-treatment is better that the hydrothermal treatments as post-treatment but the use of hydrochars despite of being considered a low-grade fuel gives an added value boosting up the energy production up to 179% compared with the 43% of the thermal hydrolysis. This makes the integration of hydrothermal treatment as post-treatment a promising option to harness the energy from sewage digestate (Aragón-Briceño et al., 2017). Nonetheless, those studies just mention the energetic benefits of integrating hydrothermal processes with AD but did not considered other implications as energy consumption, potential economic benefits and mass and energy balances (Aragón-Briceño et al., 2017).

In order to meet with the environmental targets embedded in sewage sludge as waste minimisation, valuable products recovering and the overall reduction of treatment costs, the challenge is to provide integration studies for coupling HTC with the existing infrasctructure and treatment units at the WWTWs.

The main objective of this study is to assess the integration of the HTC with AD through mass and energy balances from proposed process configurations from different sewage sludge based on the results obtained from experimental analyses. Results are processed to evaluate and compare the products yields, waste generation, energy implications and potential economic benefits in order to integrate HTC as part of a comprehensive sewage sludge management strategy.

7.2. Material and methods

7.2.1.Process description

The overall process of integrating hydrothermal processing with anaerobic digestion of sewage sludge is divided in four main processing areas. Firstly, the feed (PS, SS or MIX sludge) undergoes mesophilic anaerobic digestion processing (37°C) producing digestate (ADPS, ADSS or ADMIX) and biogas. The next process is compound by a thickener which concentrate the digestate to 15% of solids. Next, the thickened digestate is submitted to thermal processing (160 or 250°C) converting it into process water and hydrochar. The thermal recovery efficiency from the heat exchanger is considered in this stage. Then, a centrifuge is used to separate the hydrochar (solid fraction) from the process water (liquid fraction). The hydrochar is considered as a potential fuel source based in their HHV but non-energy recovery process is considered. On the other hand the process water is anaerobically treated at mesophilic conditions in a second reactor producing biogas as well. The biogas produced by the first and second reactors are mixed combusted in a combine heat power (CHP) unit to produce the energy for the system. The energy produced from the biogas is used to cover the energy requirements of the hydrothermal system and the exceeding energy is used for other equipment.

The aim of the process configuration is to integrate the hydrothermal treatment as a post-treatment to the anaerobic digestion of sewage sludge. The use of different sewage digestate is to compare the energy production between them since the primary sludge contains high organic matter. Therefore, as stated by Pérez-Elvira and Fdz-Polanco (2012), the best option will be to segregate primary and secondary sludge in order to produce more energy in the overall system.

The assumptions adopted as a basis for the mass and energy balance of the different scenarios build in this study are presented in **Table 7.1**.

7.2.2.Mass and energy balance

This study is based on the experimental results obtained from laboratory experiments of this research carried on at University of Leeds (UK). Six scenarios were built with three different sewage sludge (Primary, Secondary and Primary-Secondary Mix) treated with two different hydrothermal temperatures.

7.2.2.1.Sludge and anaerobic treated sludge samples

Primary (PS), secondary (SS) and 1:1 mix of primary-secondary (MIX) sludge were obtained as it was described in section 3.2 and processed by anaerobic treatment for 30 days in the lab, before further hydrothermal processing. Resulting samples were named as follows: digested primary sludge – ADPS; digested secondary sludge – ADSS; and digested mix of PS and SS – ADMIX.

Table 7.1.- Process assumptions and calculation basis considered for the mass and energy balances of the different scenarios.

Description	Sc1	Sc2	Sc3	Sc4	Sc5	Sc6	Data Source	Reference
Sludge to be treated (Kg/h)	1000	1000	1000	1000	1000	1000	Assumed	-
Feeding sludge	PS	SS	Mix	PS	SS	Mix	Considered	-
Solids concentration (%DS)	15	15	15	15	15	15	Assumed	-
Anaerobic Digestion temperature (°C)	37	37	37	37	37	37	Experimental Values	Section 3.2.5
Anaerobic Digestion retention time (Day)	21	21	21	21	21	21	Experimental Values	Section 3.2.5
Raw sludge COD removal during AD (%)	38	48	44	38	48	44	Experimental Values	Table 6.2
Process Water COD removal during AD (%)	47	42	37	59	59	60	Experimental Values	Table 6.2
Thermal treatment temperature (°C)	160	160	160	250	250	250	Experimental Values	Section 3.6
Thermal treatment retention time (H)	0.5	0.5	0.5	0.5	0.5	0.5	Experimental Values	Section 3.6
Recovery of heat energy from thermal treatment (%)	85	85	85	85	85	85	Literature	Shemfe et al. (2015) and Sridhar Pilli et al. (2015)
Methane production of raw sludge (m^3 of methane/Ton of COD)	129	116	226	129	116	226	Experimental Values	Table 6.2
Methane production of Process Water (m^3 of methane/Ton of COD)	130	207	204	218	212	232	Experimental Values	Table 6.2
Energy required for thermal treatment ($MJ*Kg^{-1}$ of dry feedstock)	3.6	3.6	3.6	5.9	5.9	5.9	Literature	Aragón-Briceño et al. (2017) and Berge et al. (2011b)
Hydrochar yield	50	55	56	37	40	40	Experimental Values	Table 6.3
Hydrochar HHV (MJ)	12.8	13.2	13.5	12.3	12.2	12.0	Experimental Values	Table 6.4
Solids separator Energy consumption (kW/DTon) - Centrifuge	108	108	108	108	108	108	Literature	Liu et al. (2013)
Energy required for Mixing in the AD (kWh/Dton)	18.3	18.3	18.3	18.3	18.3	18.3	Literature	Berglund and Börjesson (2006)

7.3. Results and discussions

7.3.1.Mass balance

The experimental data obtained from the lab experiments and considerations were used for assess the mass and energy balance of the different thermal treatments integrated to anaerobic digestion and built the scenarios shown in **Figure 7.1** and **Figure 7.2.** Six scenarios were built, compared and assessed considering three different sewage sludge (PS, SS and Mix) treated at two different temperatures (160 and 250°C). For this study 1000Kg as initial amount of sewage sludge was considered with 15% w/w of initial solid concentration. The initial solids concentration considered for the scenarios was based on the minimum solid concentration that shows positive energy balance.

In **Table 7.2** it is shown the COD and solid reduction of the proposed scenarios. The percentage of solids removed comes from the sum of solids volatilized during the thermal treatment and solids converted to biogas during the AD treatment. The results showed that higher thermal treatments trended to reduce more solids (See **Table 7.2**). The scenarios with the 160°C hydrothermal treatment integrated showed a solids reduction between 47 to 56% and the scenarios with the 250°C hydrothermal treatment integrated presented between 62 to 68%. The PS and MIX scenarios did not show significantly differences in terms of solids reduction. However the secondary sludge's scenarios, regardless the temperature treatment, presented the lowest percentage of solids removal with 47% at 160°C thermal treatment and 62% with 250°C thermal treatment.

The overall COD reduction comes from the sum of COD volatilized during the thermal treatment and COD converted to biogas during the AD treatment. During the thermal treatment, most of the COD volatilized is normally converted into CO_2 (Zabaleta et al., 2017). The COD reduction showed a similar trend as the solids reduction where higher temperatures presented higher reduction. The Mix sludge presented the higher COD reduction with 58% at 160°C and 66% at 250°C thermal treatments. This was followed by the PS and SS where the COD reduction were 56 and 46% at 160°C and 61 and 51% at 250°C respectively. The COD remained within the process water after the AD treatment represented only the 4-7% for the all scenarios with 160°C thermal treatment and 5-8% for all the scenarios with 250°C thermal treatment of the overall intial COD concentration. This means that most of the COD degraded is used for energy generation either from biogas or hydrochar. Moreover, the remaining liquid waste (AD processed water) might be used for irrigation due its high amount of nutrients or reused into the thermal treatment if more liquid is required for co-processing the sewage sludge with other biomass.

In **Table 7.2** is shown the methane and hydrochar production of proposed scenarios. The methane production showed not to be related with the COD and solids reduction. Scenarios 1 and 4, that used PS as initial feedstock, presented the best methane production with 57 and 67.5% respectively. This might be due the high organic content in the feedstock that has no receive any previous treatment. On the other hand the SS’s scenarios (2 and 5) presented lower methane production when both thermal treatments are integrated with 20.3 and 22.7% (160 and 250°C respectively). This might be due the previous biological treatment received which makes the COD less available for methane conversion.

The amount of hydrochar produced during the hydrothermal treatment varied in all the scenarios because its feedstock and process conditions dependence. Scenarios 1 to 3 presented higuer hydrochar production than scenarios 4 to 6. This is because as the temperature increase, less hydrochar is produced (Danso-Boateng et al., 2015). Moreover, the PS´s scenarios showed the lowest hydrochar production with 75.6 and 54.8Kg in scenarios 1 and 4 respectively. The MIX and SS’s scenarios presented similar hydrochar production with 82.5 and 83.6 Kg in scenarios 2 and 3 when the treatment temperature was 160°C and 59.7 and 60.6Kg in scenarios 5 and 6 when the treatment temperature was 250°C respectively.

Table 7.2.- Mass balance of the proposed scenarios.

	Sludge	Process Temperature (°C)	%Solids removed	%COD removed	Methane produced/ton of Sludge (m^3)	Hydrochar Produced (Kg)/ton of sludge
Scenario 1	PS	160	56%	56%	57.0	75.6
Scenario 2	SS	160	47%	46%	20.3	82.5
Scenario 3	MIX	160	56%	58%	21.4	83.6
Scenario 4	PS	250	68%	61%	67.5	54.8
Scenario 5	SS	250	62%	51%	22.7	59.7
Scenario 6	MIX	250	68%	66%	25.0	60.6

Scenarios 3 and 6 showed the most suitable for integrate HTC with AD for those existing AD plants due it means that there would be less modifications on the current WWTWs configurations. However, in terms of by-products production, the different approaches showed in scenarios 1 and 4 are the best options and can be considered as an alternatives for smaller plants without secondary treatment. On the other hand the approaches from scenarios 2 and 5 are not convenient due its low overall biogas and hydrochar production and quality.

One of the most promising process for phosphorus recovery in the waste water sector is through formation and precipitation of ammonium magnesium phosphate (struvite) (Molinos-Senante et al., 2011). In **Table 7.3** is presented the nitrogen and phosphorus balance and the potential struvite production per ton of sludge of the different scenarios. Some authors have demonstrated that during the thermal treatment there is a nitrogen and phosphorus solubilisation (Aragón-Briceño et al., 2017, Dai et al., 2015, Ekpo et al., 2015). Most of the nitrogen extracted is contented within the liquid fraction. The scenarios 2 and 5 extracted the highest nitrogen concentration; this due the SS that is mainly biomass from the aerobic treatment which their main function is to remove nitrogen and phosphorus from the waste water. Furthermore, most of the nitrogen solubilized during thermal treatment was ammonia, which may be used for struvite precipitation.

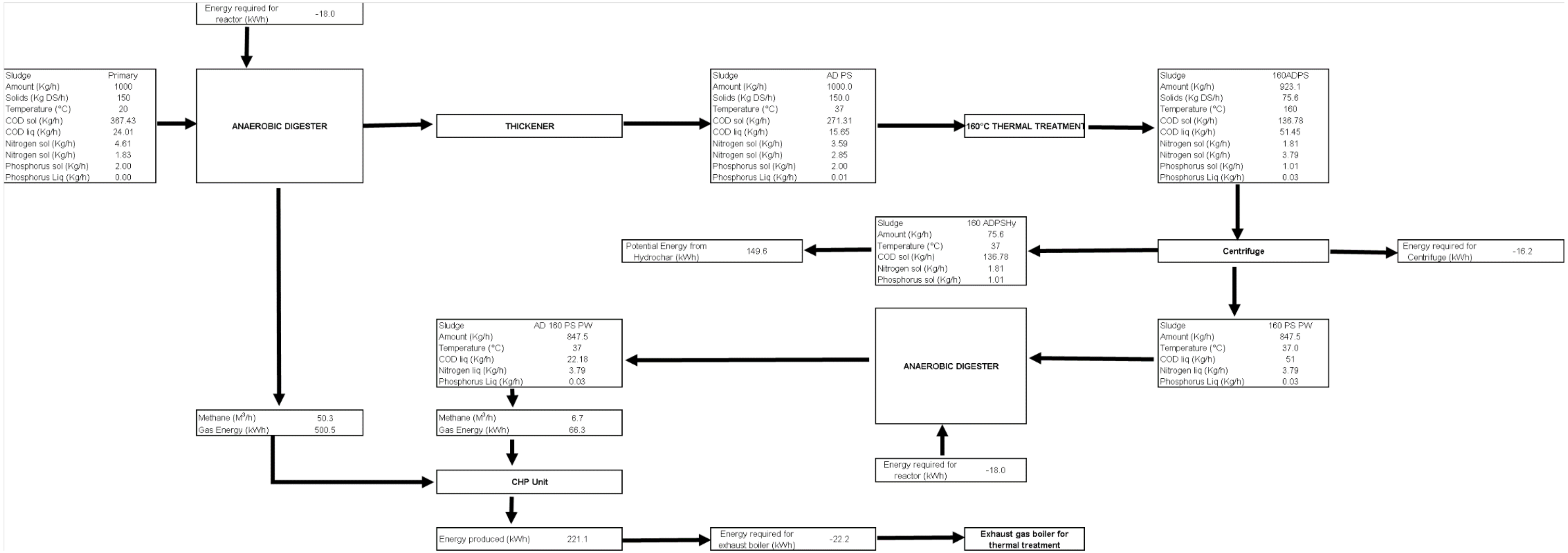
On the other hand, most of the phosphorus remained within the solid fraction. The phosphorus extraction ranged from 0.03 to 0.07Kg per ton of sludge in those scenarios (1 to 3) with 160°C treatment and 0.8Kg per ton of sludge in those scenarios (4 to 6) with 250°C treatment. The majority phosphorus extracted was inorganic phosphorus (PO_3^{-3}) ranging from 50 to 75% of the total phosphorus extracted. **Table 7.3** shows the potential struvite production of the different proposed scenarios. The highest struvite production were presented in scenarios 4 to 6 which corresponds to those treated with highest reaction temperature.

Table 7.3.- Nitrogen and Phosphorus balance and struvite production of the proposed scenarios.

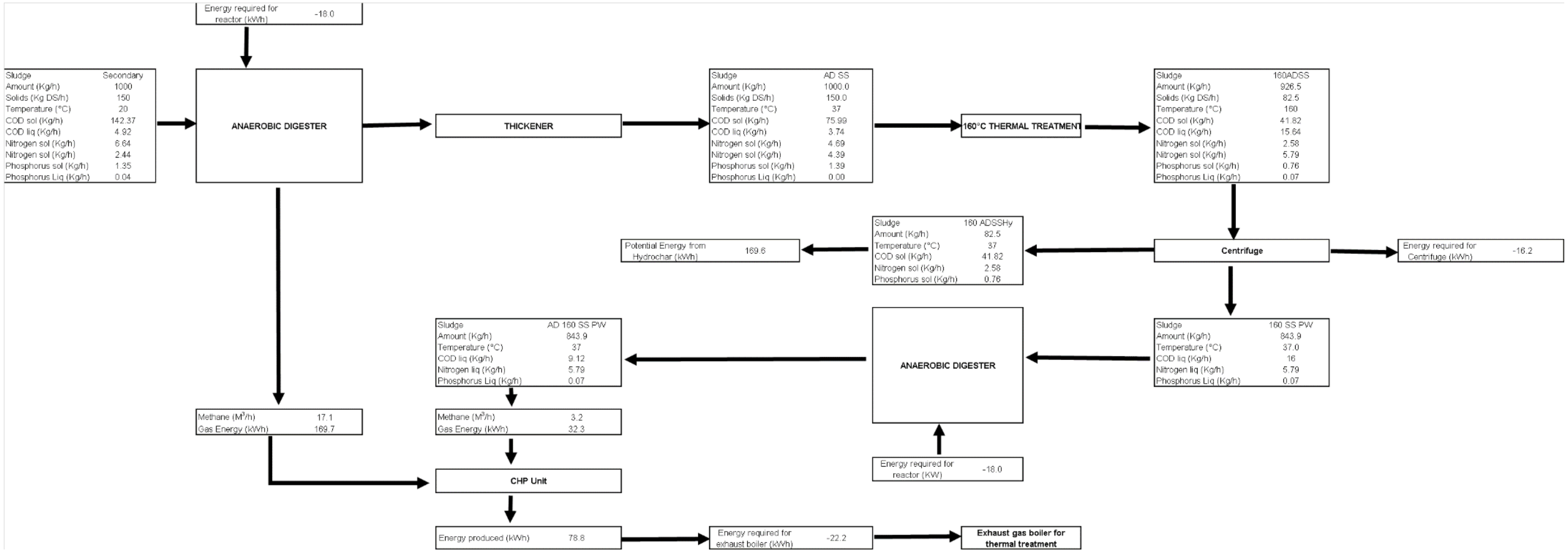
	***Nitrogen$_{Sol}$ (Kg)**	***Nitrogen$_{Liq}$ (Kg)**	***Ammonia (Kg)**	***Phosphorus$_{Sol}$ (Kg)**	***Phosphorus$_{Liq}$ (Kg)**	***PO_3 (Kg)**	***Mg Addition (Kg)**	***Struvite Production (Kg)**
Scenario 1	1.8	3.8	3.1	1.0	0.03	0.02	0.00	0.02
Scenario 2	2.6	5.8	4.6	0.8	0.07	0.04	0.01	0.04
Scenario 3	2.3	4.8	3.8	0.8	0.04	0.02	0.00	0.02
Scenario 4	1.3	4.6	3.7	0.7	0.08	0.06	0.01	0.06
Scenario 5	1.9	6.8	4.7	0.6	0.08	0.04	0.01	0.04
Scenario 6	1.6	5.7	4.7	0.6	0.08	0.05	0.01	0.05

*per ton of sludge

a)


Energy required for reactor (kWh) -18.0
Sludge Primary
Amount (Kg/h) 1000
Solids (Kg DS/h) 150
Temperature (°C) 20
COD sol (Kg/h) 367.43
COD liq (Kg/h) 24.01
Nitrogen sol (Kg/h) 4.61
Nitrogen sol (Kg/h) 1.83
Phosphorus sol (Kg/h) 2.00
Phosphorus Liq (Kg/h) 0.00
ANAEROBIC DIGESTER
THICKENER
Sludge AD PS
Amount (Kg/h) 1000.0
Solids (Kg DS/h) 150.0
Temperature (°C) 37
COD sol (Kg/h) 271.31
COD liq (Kg/h) 15.65
Nitrogen sol (Kg/h) 3.59
Nitrogen sol (Kg/h) 2.85
Phosphorus sol (Kg/h) 2.00
Phosphorus Liq (Kg/h) 0.01
160°C THERMAL TREATMENT
Sludge 160ADPS
Amount (Kg/h) 923.1
Solids (Kg DS/h) 75.6
Temperature (°C) 160
COD sol (Kg/h) 136.78
COD liq (Kg/h) 51.45
Nitrogen sol (Kg/h) 1.81
Nitrogen sol (Kg/h) 3.79
Phosphorus sol (Kg/h) 1.01
Phosphorus Liq (Kg/h) 0.03
Centrifuge
Energy required for Centrifuge (kWh) -16.2
Sludge 160 ADPSHy
Amount (Kg/h) 75.6
Temperature (°C) 37
COD sol (Kg/h) 136.78
Nitrogen sol (Kg/h) 1.81
Phosphorus sol (Kg/h) 1.01
Potential Energy from Hydrochar (kWh) 149.6
Sludge 160 PS PW
Amount (Kg/h) 847.5
Temperature (°C) 37.0
COD liq (Kg/h) 51
Nitrogen liq (Kg/h) 3.79
Phosphorus Liq (Kg/h) 0.03
ANAEROBIC DIGESTER
Energy required for reactor (kWh) -18.0
Sludge AD 160 PS PW
Amount (Kg/h) 847.5
Temperature (°C) 37
COD liq (Kg/h) 22.18
Nitrogen liq (Kg/h) 3.79
Phosphorus Liq (Kg/h) 0.03
Methane (M³/h) 6.7
Gas Energy (kWh) 66.3
Methane (M³/h) 50.3
Gas Energy (kWh) 500.5
CHP Unit
Energy produced (kWh) 221.1
Energy required for exhaust boiler (kWh) -22.2
Exhaust gas boiler for thermal treatment

b)


Energy required for reactor (kWh) -18.0
Sludge Secondary
Amount (Kg/h) 1000
Solids (Kg DS/h) 150
Temperature (°C) 20
COD sol (Kg/h) 142.37
COD liq (Kg/h) 4.92
Nitrogen sol (Kg/h) 6.64
Nitrogen sol (Kg/h) 2.44
Phosphorus sol (Kg/h) 1.35
Phosphorus Liq (Kg/h) 0.04
ANAEROBIC DIGESTER
THICKENER
Sludge AD SS
Amount (Kg/h) 1000.0
Solids (Kg DS/h) 150.0
Temperature (°C) 37
COD sol (Kg/h) 75.99
COD liq (Kg/h) 3.74
Nitrogen sol (Kg/h) 4.69
Nitrogen sol (Kg/h) 4.39
Phosphorus sol (Kg/h) 1.39
Phosphorus Liq (Kg/h) 0.00
160°C THERMAL TREATMENT
Sludge 160ADSS
Amount (Kg/h) 926.5
Solids (Kg DS/h) 82.5
Temperature (°C) 160
COD sol (Kg/h) 41.82
COD liq (Kg/h) 15.64
Nitrogen sol (Kg/h) 2.58
Nitrogen sol (Kg/h) 5.79
Phosphorus sol (Kg/h) 0.76
Phosphorus Liq (Kg/h) 0.07
Potential Energy from Hydrochar (kWh) 169.6
Sludge 160 ADSSHy
Amount (Kg/h) 82.5
Temperature (°C) 37
COD sol (Kg/h) 41.82
Nitrogen sol (Kg/h) 2.58
Phosphorus sol (Kg/h) 0.76
Centrifuge
Energy required for Centrifuge (kWh) -16.2
Sludge AD 160 SS PW
Amount (Kg/h) 843.9
Temperature (°C) 37
COD liq (Kg/h) 9.12
Nitrogen liq (Kg/h) 5.79
Phosphorus Liq (Kg/h) 0.07
ANAEROBIC DIGESTER
Sludge 160 SS PW
Amount (Kg/h) 843.9
Temperature (°C) 37.0
COD liq (Kg/h) 16
Nitrogen liq (Kg/h) 5.79
Phosphorus Liq (Kg/h) 0.07
Methane (M^3/h) 17.1
Gas Energy (kWh) 169.7
Methane (M^3/h) 3.2
Gas Energy (kWh) 32.3
Energy required for reactor (KW) -18.0
CHP Unit
Energy produced (kWh) 78.8
Energy required for exhaust boiler (kWh) -22.2
Exhaust gas boiler for thermal treatment

c)

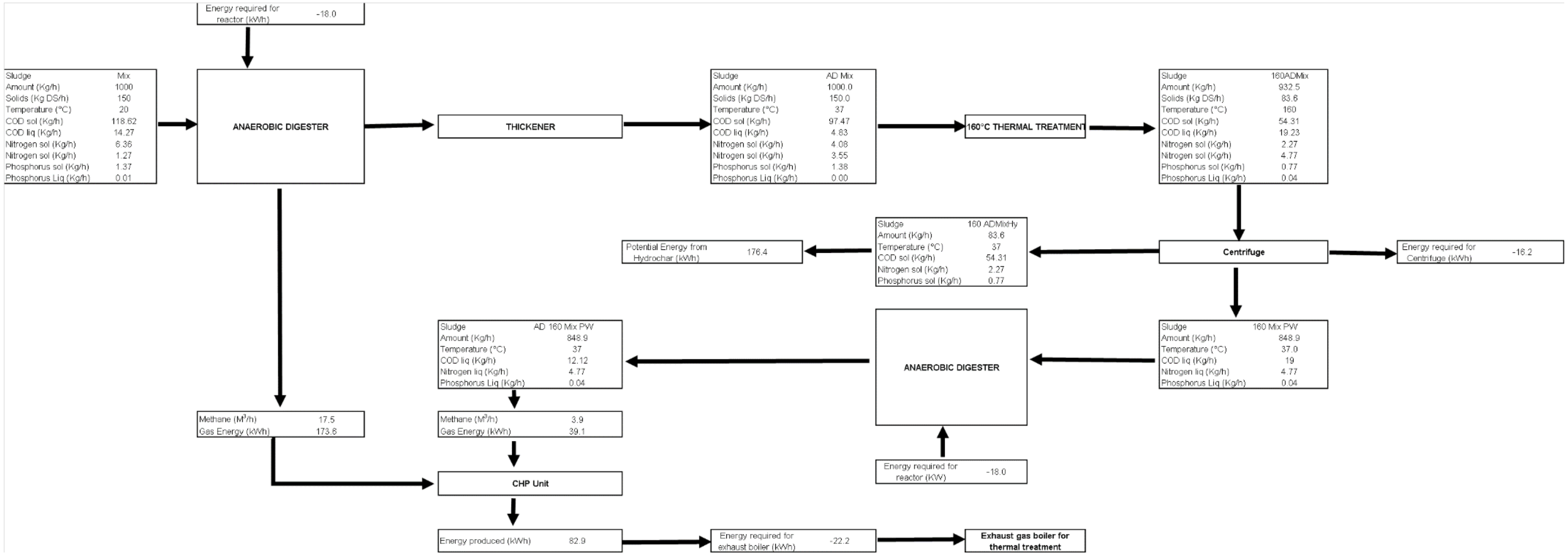
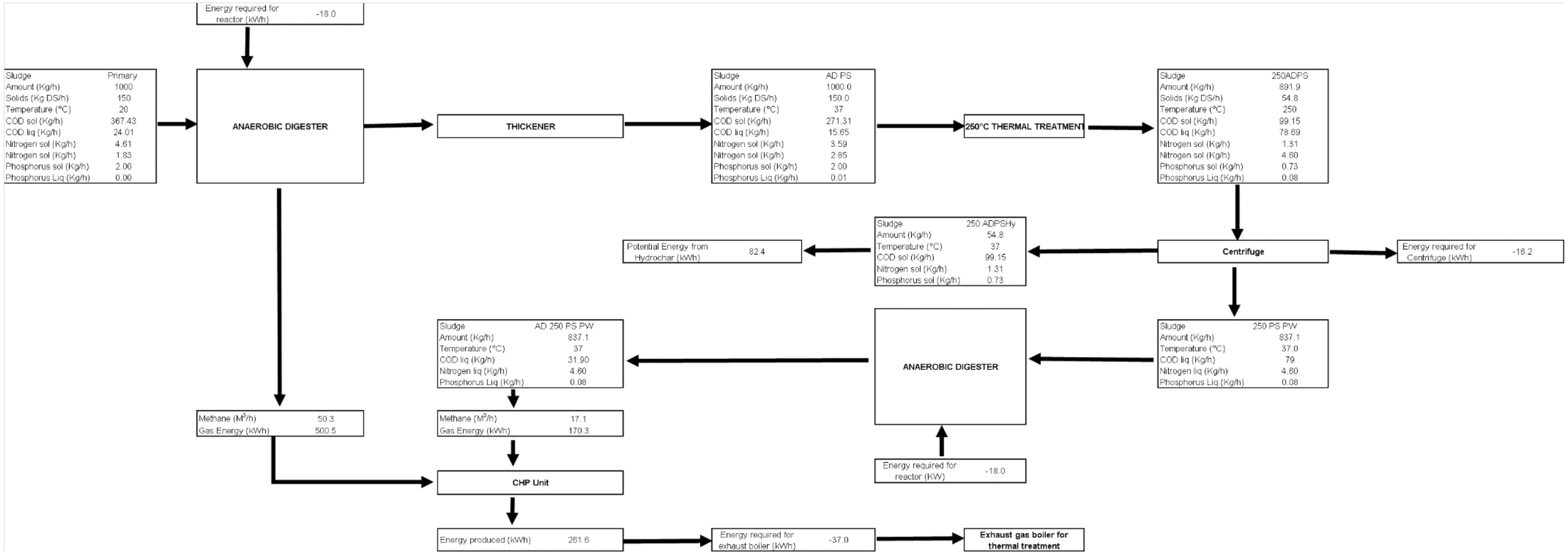
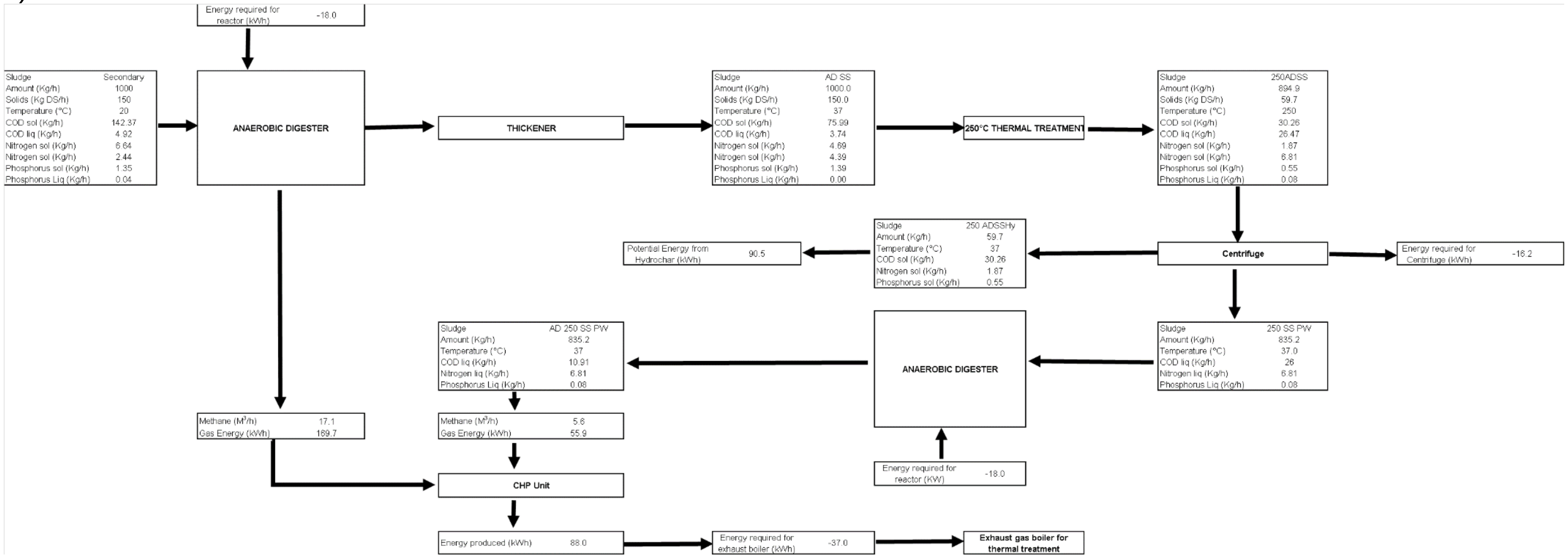


Figure 7.1.- Mass and energy balance scenarios of the a) Primary Sludge, b) Secondary Sludge and c) Mix Sludge at 160°C thermal treatment.

a)


Energy required for reactor (kWh) -18.0
Sludge Primary
Amount (Kg/h) 1000
Solids (Kg DS/h) 150
Temperature (°C) 20
COD sol (Kg/h) 367.43
COD liq (Kg/h) 24.01
Nitrogen sol (Kg/h) 4.61
Nitrogen sol (Kg/h) 1.83
Phosphorus sol (Kg/h) 2.00
Phosphorus Liq (Kg/h) 0.00
ANAEROBIC DIGESTER
THICKENER
Sludge AD PS
Amount (Kg/h) 1000.0
Solids (Kg DS/h) 150.0
Temperature (°C) 37
COD sol (Kg/h) 271.31
COD liq (Kg/h) 15.65
Nitrogen sol (Kg/h) 3.59
Nitrogen sol (Kg/h) 2.85
Phosphorus sol (Kg/h) 2.00
Phosphorus Liq (Kg/h) 0.01
250°C THERMAL TREATMENT
Sludge 250ADPS
Amount (Kg/h) 891.9
Solids (Kg DS/h) 54.8
Temperature (°C) 250
COD sol (Kg/h) 99.15
COD liq (Kg/h) 78.69
Nitrogen sol (Kg/h) 1.31
Nitrogen sol (Kg/h) 4.60
Phosphorus sol (Kg/h) 0.73
Phosphorus Liq (Kg/h) 0.08
Potential Energy from Hydrochar (kWh) 82.4
Sludge 250 ADPSHy
Amount (Kg/h) 54.8
Temperature (°C) 37
COD sol (Kg/h) 99.15
Nitrogen sol (Kg/h) 1.31
Phosphorus sol (Kg/h) 0.73
Centrifuge
Energy required for Centrifuge (kWh) -16.2
Sludge AD 250 PS PW
Amount (Kg/h) 837.1
Temperature (°C) 37
COD liq (Kg/h) 31.90
Nitrogen liq (Kg/h) 4.60
Phosphorus Liq (Kg/h) 0.08
ANAEROBIC DIGESTER
Sludge 250 PS PW
Amount (Kg/h) 837.1
Temperature (°C) 37.0
COD liq (Kg/h) 79
Nitrogen liq (Kg/h) 4.60
Phosphorus Liq (Kg/h) 0.08
Methane (M³/h) 50.3
Gas Energy (kWh) 500.5
Methane (M³/h) 17.1
Gas Energy (kWh) 170.3
Energy required for reactor (KW) -18.0
CHP Unit
Energy produced (kWh) 261.6
Energy required for exhaust boiler (kWh) -37.0
Exhaust gas boiler for thermal treatment

b)


Energy required for reactor (kWh) -18.0
Sludge Secondary
Amount (Kg/h) 1000
Solids (Kg DS/h) 150
Temperature (°C) 20
COD sol (Kg/h) 142.37
COD liq (Kg/h) 4.92
Nitrogen sol (Kg/h) 6.64
Nitrogen sol (Kg/h) 2.44
Phosphorus sol (Kg/h) 1.35
Phosphorus Liq (Kg/h) 0.04
ANAEROBIC DIGESTER
THICKENER
Sludge AD SS
Amount (Kg/h) 1000.0
Solids (Kg DS/h) 150.0
Temperature (°C) 37
COD sol (Kg/h) 75.99
COD liq (Kg/h) 3.74
Nitrogen sol (Kg/h) 4.69
Nitrogen sol (Kg/h) 4.39
Phosphorus sol (Kg/h) 1.39
Phosphorus Liq (Kg/h) 0.00
250°C THERMAL TREATMENT
Sludge 250ADSS
Amount (Kg/h) 894.9
Solids (Kg DS/h) 59.7
Temperature (°C) 250
COD sol (Kg/h) 30.26
COD liq (Kg/h) 26.47
Nitrogen sol (Kg/h) 1.87
Nitrogen sol (Kg/h) 6.81
Phosphorus sol (Kg/h) 0.55
Phosphorus Liq (Kg/h) 0.08
Potential Energy from Hydrochar (kWh) 90.5
Sludge 250 ADSSHy
Amount (Kg/h) 59.7
Temperature (°C) 37
COD sol (Kg/h) 30.26
Nitrogen sol (Kg/h) 1.87
Phosphorus sol (Kg/h) 0.55
Centrifuge
Energy required for Centrifuge (kWh) -16.2
Sludge AD 250 SS PW
Amount (Kg/h) 835.2
Temperature (°C) 37
COD liq (Kg/h) 10.91
Nitrogen liq (Kg/h) 6.81
Phosphorus Liq (Kg/h) 0.08
ANAEROBIC DIGESTER
Sludge 250 SS PW
Amount (Kg/h) 835.2
Temperature (°C) 37.0
COD liq (Kg/h) 26
Nitrogen liq (Kg/h) 6.81
Phosphorus Liq (Kg/h) 0.08
Methane (M^3/h) 17.1
Gas Energy (kWh) 169.7
Methane (M^3/h) 5.6
Gas Energy (kWh) 55.9
Energy required for reactor (KW) -18.0
CHP Unit
Energy produced (kWh) 88.0
Energy required for exhaust boiler (kWh) -37.0
Exhaust gas boiler for thermal treatment

c)

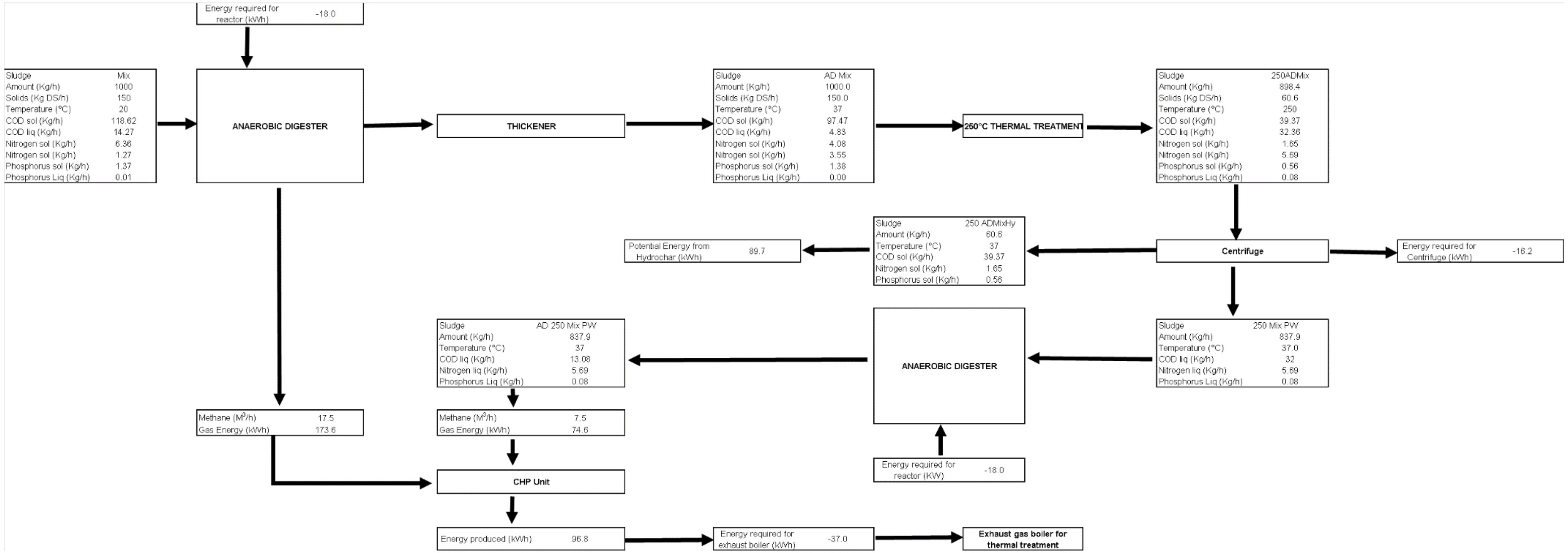


Figure 7.2.- Mass and energy balance scenarios of the a) Primary Sludge, b) Secondary Sludge and c) Mix Sludge at 250°C thermal treatment.

7.3.2.Energy balance

In **Table 7.4** a summary of the energy balance from the different porposed scenarios are presented. The energy production coming from methane were higher in those scenarios with the highest reaction temperature treatment. The scenarios 1 and 4, where the PS was treated, presented the highest energy production (221.1kWh and 261.6kWk respectively) because of their methane production. These were followed by scenarios 3 and 6 (MIX) which produced 82.9 and 96.8kWh respectively, and scenarios 1 and 5 (SS) which produced the least energy from biogas with 78.8 and 88kWh respectively.

The energy production from methane showed to be enough to cover the energy needs of the system proposed scenarios (See **Table 7.4**). Most of the proposed scenarios presented a positive energy balance with exception of scenario 5. Scenarios 1 and 4 showed to be a suitable option in terms of net energy balance, producing extra 146.7 and 172.5 kWh per ton of sludge treated, followed by scenarios 3, 6 and 2 with 8.5, 7.6 and 4.4 kWh extra respectively. The extra energy produced can be used either for the total WWTWs energy needs or for selling.

Despite of hydrochar's characteristics from the different sewage sludge were like a low-grade fuel, the energy production was enhanced with the inclusion of the energy that come from the hydrochar. According to Aragón-Briceño et al. (2017), between 56 to 59% of the energy produced comes from the hydrochar. The scenarios with lower process temperature (1, 2 and 3) showed more potential energy from the hydrochar with 149.6 , 169.6 and 176.4 kWh per ton of sludge in comparison with higher process temperature scenarios (4, 5 and 6) with 82.4, 90.5 and 89.7 kWh per ton of sludge. This is because the hydrochar production are higher at lower process temperature scenarios compared with scenarios with higher process temperature. The hydrochar fraction represented a contribution on the overall energy production between 40 to 68% for scenarios with 160°C treatment and between 24 to 51% for the scenarios with 250°C treatment. Therefore, the inclusion of the hydrochar as an energy source was directly reflected on the net energy balance which would contribute to the energy up to 97% for scenarios with 160°C treatment and up to 100% for the scenarios with 250°C treatment. In previous studies, it has been demonstrated that the implementation of the thermal treatment at the end of the process favours the overall energy production up to 179% in comparison with the traditional AD (Aragón-Briceño et al., 2017). Nevertheless, more mass and energy balance calculations and considerations regarding to solids combustion need to be done in order to obtain an energy estimation of the hydrochar as a fuel source.

Table 7.4.- Energy balance of the proposed scenarios.

	Sludge	Process Temperature (°C)	*Energy consumed (kWh)	*Energy produced from Methane (kWh)	*Net Energy balance (kWh)	*Potential Energy from the hydrochar (kWh)	*Net Energy balance (kWh) / Hy considered
Scenario 1	PS	160	74.4	221.1	146.7	149.6	296.3
Scenario 2	SS	160	74.4	78.8	4.4	169.6	173.9
Scenario 3	MIX	160	74.4	82.9	8.5	176.4	284.6
Scenario 4	PS	250	89.2	261.6	172.5	82.4	254.8
Scenario 5	SS	250	89.2	88.0	-1.2	90.5	89.3
Scenario 6	MIX	250	89.2	96.8	7.6	89.7	97.0

*per ton of sludge

7.3.3.Economics

In United Kingdom the tariff rates for electricity exportation from renewable sources is established by the Office of Gas and Electricity Markets (Ofgem, 2018). This is a non-ministerial government department and an independent National Regulatory Authority, recognised by EU Directives and governed by the Gas and Electricity Markets Authority (GEMA). The tariff rates for anaerobic digestion depends on the plant capacity for electricity generation. In this study, the lowest tariff of 4.73 p/kWh was considered as the based tariff for the electricity produced by the methane (Ofgem, 2018). The same tariff was considered for potential electricity production from the hydrochar since there is not a clear information about it.

In **table 7.5** the summary of economic benefits of integrate HTC with AD are shown. The potential benefit from methane production ranged from £0 to £8.2 per ton of sewage sludge treated. The economic analysis for the PS scenarios (1 and 4) presented the highest benefit and showed an increase when the reaction temperature is higher (£6.9 per ton of sludge at 160°C and £8.2 per ton of sludge at 250°C). The MIX scenarios (3 and 6) showed a benefit of £0.4 per ton of sludge, regardless the reaction temperature. The SS scenario 2 had the benefit of £0.2 per ton of sludge at 160°C reaction temperature and £0 per ton of sludge at scenario 5 because its negative balance.

The benefit from the hydrochar production was slightly higher compared with the biogas production. The benefit showed to and increase when the reaction temperature is lower. Although, it seems that at 250°C reaction temperature the benefit is the same for the different sewage sludge (£4 per ton of sludge). The potential benefit from the hydrochar production might be increased if the co-processing with other feedstocks is considered in order to increase the quality properties of the hydrochar (Zhai et al., 2017).

For this study, the price of the struvite was considered based on that average price for the struvite in the fertilizer market is £424.6 per ton (Molinos-Senante et al., 2011).The potential benefit per ton of sludge ranged from £8 to £16 when 160°C treatment was applied and between £18 to £23 when the 250°C was applied. Nonetheless, despite of the cost of phosphorus recovering as struvite can be expensive ranging from £1.8 up to £7.1 per kg of P recovered, the struvite production from the process waters still showed to be a good opportunity area for increase the overall profit, especially if feedstocks with high phosphorus content are co-processed with the sewage sludge (Mayer et al., 2016, Molinos-Senante et al., 2011).

Table 7.5.- Potential economic benefits of integrating HTC with AD.

	Sludge	Process Temperature (°C)	Electricity production profit from methane per ton of sewage sludge (£)	Electricity production profit from Hydrochar per ton of sewage sludge (£)	[a]Struvite production profit per ton of sewage sludge (£)	Total profit per ton sludge (£)
Scenario 1	PS	160	6.9	7.1	8.2	22.2
Scenario 2	SS	160	0.2	8.0	16.1	24.4
Scenario 3	MIX	160	0.4	8.3	8.1	16.9
Scenario 4	PS	250	8.2	3.9	23.4	35.5
Scenario 5	SS	250	0	4.3	18.0	22.3
Scenario 6	MIX	250	0.4	4.2	21.0	25.6

[a] exchange rate £1=€1.1197 (Bank of England, 2018).

In 2010, the average sewage sludge generation per person in UK was 22.5kg of dry sewage sludge annually (DEFRA, 2012b, Office for National Statistics, 2013). Considering that a large size WWTW provides services to a 100,000 population, which means a production of 15,000 ton of sewage sludge annually (15% of dry solids). In addition, according to Lucian and Fiori (2017) the price of an HTC plant treating 20,000 tons a year might reach £1,349,107. Considering these facts, the benefits from the integration of and HTC plant into a WWTW might be estimated.

The economic benefit from biogas production would be up to £122,355, from hydrochar production would be up to £125,124 and from struvite production (without considering the price of Mg addition and pH regulation process) would be up to £351,569 per year depending the scenario (See **Table 7.6**). The scenarios where the 250°C treatment was applied showed the highest potential profit with £532,358 and £386,037 for scenarios 4 and 6 respectively (See **Table 7.6**).

To determine the return of investment time (ROI), the annual maintenance was considered (8% of the total cost of the plant) and a 5% of annual interest considered that the loan comes from an EU scheme (Lucian and Fiori, 2017). Considering these aspects, the net profit decreases significantly (see **Table 7.6**). The ROI varied from 5 to 17 years for the energy positive scenarios. The PS and Mix sludge’s scenarios with the higher temperature process had lower ROI time with 5 and 10 years respectively.

Table 7.6.- Potential economic benefits of scaling up the scenarios.

	Sludge	Process Temperature (°C)	*Profit per year of a WWTP supplying population of 100,000 (£)	**Maintenance cost per Year (£)	Net Profit per year (£)	***ROI (years)
Scenario 1	PS	160	333,637	107,928.57	225,708	17
Scenario 2	SS	160	365,598	107,928.57	257,670	12
Scenario 3	MIX	160	253,042	107,928.57	145,114	NA
Scenario 4	PS	250	532,358	107,928.57	424,430	5
Scenario 5	SS	250	333,777	107,928.57	225,849	17
Scenario 6	MIX	250	384,037	107,928.57	276,109	10

* Production of 15,000 ton of sludge with 15% of Solids per year.

**Considered on 8% of the total cost of a 20,000 ton HTC plant with a cost of (Lucian and Fiori, 2017).

**Considered as a Loan from the EU with a 5% annually interest.

The Scenarios 6 and 4 showed to be the most suitable scenarios in overall terms because of the organic matter removal, energy harnessing and economic feasibility. However many tests and considerations need to be done for have a complet understand about the HTC-AD integration. For instance, the cost of WWTW´s modifications should be considered and included and capacity of the WWTW´s. Furthermore the inclusion of a CHP unit and turbine need to be considered if the hydrochar produced are planned to be used as an energy source.

7.4. Conclusions

Hydrothermal carbonisation showed to be a suitable option for integration with anaerobic digestion. Higher temperatures (250°C) seems to have more economically and environmentally benefits. Scenarios that involved primary and Mix sludge showed to be the most sustainable options because of the organic matter removal, energy harnessing and economic feasibility, but still many aspects have to be considered as the cost of WWTW´s modifications or the addition of the complementary equipment for the hydrochar use as an energy source. Although co-processing feedstocks with AD sludge need to be considered as an option due it might enhance the energy properties of the liquid and solid products and therefore the overall profit. Further research is needed, incorporating real data available for HTC and AD (carried out especially using large scale plants) in terms of operation and energy use to provide a more detailed analysis for developing a standard cost benefit analysis of the intended integrated approach.

7.5. Summary

In this chapter, the potential of integration of HTC with AD for sewage sludge treatment was evaluated. Mass and energy balances were carried out from six proposed process configurations from different sewage sludge (pirmary, secondary and 1:1 Mix) in order to evaluate the waste generation, nutrients potential fate, net energy production and potential profit. The results showed the HTC at Higher temperatures (250°C) seems to have more economic and environmental benefits. Scenarios that involved primary and mix sludge seemed to be the most suitable options in terms of the organic matter removal, energy harnessing and economic feasibility.

Chapter 8. General Discussions

8.1. Introduction

In recent years, sewage sludge management has been considered one of the biggest concerns in the wastewater industry for the environmental impacts linked to its high content of pollutants. Hydrothermal Treatments are a good option for converting wet biomass such as sewage sludge into high-value products. The digestate following anaerobic treatment of sewage sludge has high organic matter content despite initial conversion into biogas and is normally spread on land or composted; however, this does not fully harness its full potential. In fact, sewage sludge digestate is a potential feedstock for hydrothermal processing and this route may produce higher value products. According to Mumme et al. (2015) and Sridhar Pilli et al. (2015) the integration of the HT step into the waste water systems is suggested to be energy positive. However, HT as a post-treatment step after AD is an approach that are still under research and development, but preliminary findings have shown that this approach could be even more effective with regard to overall energy production from sewage sludge (Aragón-Briceño et al., 2017). Therefore, further research on process conditions and overall benefits from hydrothermal processes as a post-treatment step after AD is still needed.

In this proposed research project, it was considered that the use of Hydrothermal Treatments is not only a suitable option to effectively handling sewage sludge, considering future vetoes on sludge-to-land practices, but also we believe that they can help to obtain valuable by-products.

The study of hydrothermal processes integration with anaerobic digestion based in wastewater treatment have included several laboratory observations and experiments in four areas: (a) Hydrochar valorisation, (b) Process water valorisation, (c) Nutrients fate and (d) Feasibility of hydrothermal treatment integration with AD. This chapter summaries the new findings found as part of the research work in these four areas, which will contribute to improve the knowledge about hydrothermal treatments on sewage sludge.

8.2. Hydrochar valorisation

The production of hydrochar through HTC has the potential to become an environmental friendly conversion process. Hydrochar is a carbon-rich solid that has been reported to have rich nutriment properties for terrestrial plants and has been proposed as a source for soil amendment and also has the potential to be co-fired with coal. The hydrochar is a novel material that has been probed in many applications as water purification material, fuel cell catalysis, energy storage, CO_2 sequestration, drug delivery and gas sensors (Biller and Ross, 2012, Danso-Boateng et al., 2015, He et al., 2013). According to Kruse and Dahmen (2018) the studies related with hydrochar and HTC have suffered a notorious development since the past years, which highlights the importance of developing a market for hydrochar with the emphasis on integration HTC within the “bio-refinery” concept. This represents a good opportunity for all the biological treatments such as AD that can be benefited by the production of hydrochars from HTC.

The revalorisation of the sewage sludge and especially the digestate, is one of the key points on this research. Kim *et al*. (2014) demonstrated that hydrothermal carbonisation can be used to convert sewage digestate into a solid fuel by increasing the high heating value and carbon content in the resulting hydrochar. Hydrochars have H/C and O/C ratios comparable to that of low-grade coal but a higher calorific value that such coals, for that reason can be used as a fuel source. Furthermore, the addition of hydrochars can boost up to 179% the energy production in the HT-AD system if they are used as an energy source (Aragón-Briceño et al., 2017). In this regard, this research focused mainly on assessing the production, energy properties, carbon and nutrient content of the hydrochars.

In the first objective, the effect of process temperature on the hydrochar characteristics coming from digestate was studied as a first step towards the evaluation of the new approach which is the integration of hydrothermal treatments as post-treatment. According to Danso-Boateng *et al*. (2015) and Ekpo *et al*. (2015), hydrochar yields are influenced by reaction temperature and time. Hydrochar production decrease with increasing temperature and reaction time. It was found that the highest yield of hydrochar was obtained at 220°C (73.4%), followed by the yields reported at 160°C (68.8%) and at 250°C (56.8%).

Hydrothermal treatments showed a carbon densification. The carbon content of the hydrochars obtained after hydrothermal treatment increased from 34.8% of the original digestate to 35.5 and 38% at 160°C and 250°C treatments respectively and decreased to 33.2% after the 220°C treatment. Similar results were reported by Danso-Boateng et al. (2015) (36.63-39.24%) and Berge et al. (2011) (32.6%) for primary and digestate sludge. It is important to highlight that it is sometimes challenging to make direct comparisons between hydrothermal treatments conducted by different researchers due to differences in reactor configurations, reaction conditions and solid loadings, all of which have a large influence on the characteristics of the products during carbonisation (Berge et al., 2011).

The HHV of hydrochars is mostly influenced by the temperature and increase as the reaction temperature increases (Danso-Boateng *et al*., 2015); however, this is feedstock dependent and not true for all feedstocks (Smith *et al*., 2016). The HHV of the original digestate is increased from 16.61 Mj kg^{-1} to a maximum of 17.80 Mj kg^{-1} when the maximum reaction temperature is applied, representing only a marginal energy densification between 2 to 8% compared with other studies where the energy densification achieve values up to 28% for hydrochars coming from primary sludge. However, it has to be taken into account that digestates have a lower carbon content compared with primary sewage sludge due to anaerobic digestion in which organic carbon is released during its conversion into biogas (CH_4 and CO_2). In this case, the HHV of the hydrochars generally increased but only slightly. On the other hand the HHV of the hydrochar coming from the 220°C treatment was lower than the original feedstock. Many authors have shown a reduced heating value for hydrochars produced from certain feedstocks compared to the original feedstocks (Berge *et al*., 2011a; Zhang *et al*., 2014). The HHV of the hydrochars produced are within a similar range to those reported by Danso-Boateng et al. (2015) for digestate and for wastewater solids and sludge (17.2 - 18.4 Mj kg^{-1}). This indicates that for sewage derived solids and digestates, the energy densification is quite low compared to other feedstocks and shows that a significant amount of the energy in the original feedstock is in the soluble water fraction (process waters), which may be recovered via anaerobic digestion. Furthermore the hydrochars produced can be classified as a low-quality fuel due to its HHV characteristics and their high ash content.

Since the hydrochar quality from sewage digestate improved as the reaction temperature increased, the second objective was to assess the influence of solid loading on hydrochar characteristics from sewage digestate treated a 250°C. The hydrochar production generally increased with increasing solid loading in agreement with the results reported for food waste by Zabaleta et al. (2017). The hydrochar yields ranged from 67.9% at 2.5 wt% loading to 75.6% at 25% loading. The yields obtained in this study are similar with the values reported by Danso-Boateng et al. (2015) (60.5 to 81.1%) although slightly higher than the yield reported by Aragón-Briceño et al. (2017) (56.8%) for a different sewage sludge.

The carbon content of the hydrochars increase when increasing solid loading rate but there is only a slight increase in carbon content compared to the original feedstock from 33.3 to a maximum of 34.4% of the maximum solid loading percentage (30%). Previous reports have observed the carbon content in the hydrochar from digestate within a range from 10 to 39% (Aragón-Briceño et al., 2017, Danso-Boateng et al., 2015, Ekpo et al., 2015, Berge et al., 2011a). However carbon yields are highly dependent upon feedstock composition and the process conditions (temperature, pressure, solid loading, etc.) (Funke and Ziegler, 2010). The carbon content of the hydrochars is reduced after HTC compared to the feedstock, which is unusual and only observed for certain feedstocks such as sewage digestate.
The HHVs of the hydrochars are only slightly higher than the original feedstock and increased from 14.4 MJ kg^{-1} to 16.5 MJ kg-1 at 30 wt% solid loading. This low level of energy densification is typical for feedstocks such as sewage digestates which tend to result in larger levels of solubilisation of the organic carbon (Danso-Boateng et al., 2015). There is a slight increase in HHV as solid loading increases and this corresponds to a higher carbon content in the hydrochar product as the loading increases. The HHV of the

hydrochars produced were higher compared with the values reported by Berge et al. (2011a) for digestate (13.7 MJ Kg^{-1}) and lower than the values reported by Danso-Boateng et al. (2015) (17.2 – 18.4 MJ Kg^{-1}) and Aragón-Briceño et al. (2017) (17.8 MJ Kg^{-1}).

In oder to provide a smooth integration for coupling HTPs with existing infrastructure and treatment units at waste water treatment works, the third stage of this project focused on investigate the changes suffered on hydrochars from sewage sludge samples collected along treatment process units in a conventional WWTW, when subjected to anaerobic digestion and hydrothermal processes at different temperatures. Hydrochar production varied from 38 to 69% for sludge treated at 160°C and from 20 to 40% for sludge treated at 250°C. The SS had the lowest hydrochar yields in both thermal treatments at 160 and 250°C (38 and 30% respectively) followed by MIX (47 and 35% respectively) sludge and PS (69 and 39%). When the different sludge were submitted to AD treatment before the hydrothermal treatment, the hydrochar production increased for the SS and MIX sludge at both thermal temperatures and reduced for the PS digestate that was slightly lower than the other digestates. The yields obtained in this study were lower in comparison with other values reported for hydrochar coming from sewage sludge that ranged between 57 to 81.1% (Aragón-Briceño et al., 2017, Ekpo et al., 2015, Danso-Boateng et al., 2015). This suggests that the anaerobic digestion prior the thermal treatment helps to improve the hydrochar production for the SS and MIX sludge and has the opposite effect for the PS.

The carbon content varied depending of the sewage sludge treated. The PS carbon content after the 160°C treatment did not show any change (40.3%) compared with the untreated sludge. On the other hand after the 250°C treatment the carbon content in the PS sludge was reduced to 37.4%. The ADPS sludge presented lower carbon content than the PS due the prior biological treatment received (31.1%). Unlike the PS, the ADPS´s carbon content was reduced to 28.9 and 27.3% after 160 and 250°C treatment respectively. The SS carbon content (33.5%) showed an slightly decrease after the 160°C treament (33.1%), but after the 250°C treatment there was an increase in the carbon content (36.1%) showing carbon densification. The

ADSS carbon content (32.2%) suffered a reduction after the 160 and 250°C treatments (29.4 and 27.5% respectively). The Mix Sludge carbon content (35.5%) suffered an increase after 160 and 250°C thermal treatments (37.5 and 35.8% respectively). The ADMIX carbon content (30.9%) presented a reduction after 160 and 250°C treatments (29.9 and 26.6%). The carbon reduction in hydrochars from different sewage sludge is similar to the observed by Ekpo et al. (2015) where the sewage digestate suffered a reduction up to 8% after thermal treatment. The carbon content of the different sewage sludge are similar to those reported by Aragón-Briceño et al. (2017) (33- 38%), Danso-Boateng et al. (2015) (36.6-39.2%) and Berge et al. (2011a) (32.6%). The overall carbon reduction among the hydrochar from different sewage sludge showed that there was a solubilisation reflected on the TOC and COD concentration increase of the process waters.

The High Heating Value (HHV) of hydrochars coming from the non-AD treated sludge generally increased with exception of the PS. HHVs of SS and MIX after hydrothermal treatment were higher than their original sample without treatment with a maximum of 16.5 and 17.5 Mj kg^{-1} respectively.

The AD prior the thermal treatment affected the hydrochar quality when the digestate is submitted to thermal treatment. The different sewage digestates and the raw PS after the thermal treatment showed a HHV reduction between 4 to 14%. Hydrochar´s HHV are similar with the values reported by Berge et al. (2011a) for anaerobic digestion waste (13.7 Mj Kg^{-1}), Danso-Boateng et al. (2015) (17.2 – 18.4 Mj Kg^{-1}) and Aragón-Briceño et al. (2017) (14.3 – 17.8 Mj Kg^{-1}). The energy densification of sewage derived solids and digestates is quite low (from 0.90 to 1.19) compared to thermally treated swine and chicken manure (1.27 and 1.49 respectivelty) and indicates that a significant amount of the energy in the original feedstock is accumulated in the process waters(Ekpo et al., 2015).

In this research work, the application of the HTC to sewage sludge showed to be a feasible option to revalorize it producing hydrochars rich in carbon and with good energy value. It was also demonstrated that the production of the hydrochar, carbon content and energy properties at high temperatures (250°C) are improved when the solids loading of the thermal treatment is increased. The AD prior the thermal treatment reduce the quality of the hydrochars significantly but the production of the biogas is a benefit that has to be considered. However due hydrochar characteristics depend on the feedstock composition, temperature and solids loading conditions, more studies focused on the improvement of the quality of hydrochars from sewage sludge need to be done.

8.2.1.Process water valorisation

Hydrothermal processing also generates a liquid by-product or “process water" rich in organic compounds that cannot be directly disposed into the environment, but that has been proved to be suitable for methane production via anaerobic digestion (Almeida, 2010, Becker et al., 2014, Kim et al., 2014, Stemann et al., 2013, Wirth et al., 2015, Zhao et al., 2014). However as it was mentioned before, the specific hydrochar and process water characteristics are highly dependent on the choice of feedstock and the process parameters (Zabaleta et al., 2017, Wirth et al., 2015). Therefore, the properties of the process waters need to be measured in order to determine the potential for using as a feedstock for biogas production.

The integration of HTC into a wastewater system as post-treatment step after AD offers a potential energetic and economic benefits for dewatering digestate producing a bio-coal that can be used in a coal fired power plant and enhanced biogas production by recycling process water into the AD unit (Aragón-Briceño et al., 2017).

For that reason, in this research project, the methane potential was considered one of the most important characteristics to consider due its potential for energy production. The influence of the temperature conditions during the HTC on the process water characteristics was studied in the first objective. This aim was to determine the suitability of process waters for anaerobic digestion depending on the temperature of thermal treatment. The organic carbon and COD solubilisation were two of the most important factors that were considered.

The increasing of soluble organic carbon and COD concentration within the process waters is given due the hydrolysis of organic material during the thermal treatment (Wirth *et al*., 2015). The concentration of soluble COD increased 7-fold after hydrothermal treatment, increasing from 1,843 mg/L in the initial digestate, to 12,992 mg/L after 220°C treatment; 12,642 mg/L after 160°C treatment; and 12,164 mg/L after 250°C treatment. The same trend is observed for TOC concentrations which shows a 10-fold increase from 461 to 4,879 mg of TOC per litre. This demonstrates that for this type of feedstock, a large degree of solubilisation occurs following hydrothermal treatment, in agreement with previous reports from similar treatments (Ekpo et al., 2015, López Barreiro et al., 2015).

The BMP assays were carried out using different process waters in order to evaluate their suitability for anaerobic digestion and biogas production. The COD degradation efficiency was 69.1%, 79.6% and 63.8% for the 160°C, 220°C and 250°C process waters respectively. This proves that the organic fraction solubilised within the process waters can be degraded by anaerobic digestion. These figures are lower than the results obtained by Wirth *et al*. (2015), who reported COD degradation efficiencies between 84 and 107% in process waters from anaerobically digested sewage sludge after HTC at 200°C for 6 hours.

Previous studies using hydrothermal processes as a pre-treatment for anaerobic digestion have shown an increase in methane yields in BMP tests, due the additional solubilisation of organic matter achieved via thermal hydrolysis (Keymer *et al.*, 2013). After hydrothermal treatment, the BMP values for process waters following hydrothermal treatment increased between 29% and 58% compared with the control sample (175 mL of CH_4/ g of COD). The highest methane yields values were for the processed water of 220°C treatment (277 mL of CH_4/ g of COD) followed by 160°C treatment (260 mL of CH_4/ g of COD) and 250°C treatment (225.8 mL of CH_4/ g of COD). However, the BMP result of the 250°C treatment was considered underestimated since there was not a full consumption of VFAs during the assay time.

Another important point to discuss is the biodegradability of the process waters. The biodegradability values provide more robust data for predicting overall enhanced energy recovery, which can be used to better calculate and assess energy balances for integrating AD and HTC at WWTWs. The process waters from 160 and 220°C treatments had 96% of biodegradability compared with the 56% of the process waters from 250°C treatment. Based on the results in this study (1st objective), it is likely that lower temperature hydrothermal treatment is more advantageous than higher temperature for processing sewage sludge digestate. Nevertheless, the value of biodegradability in the digestate treated at 250°C does not represent the complete potential as this test was still generating methane after 21 days so this result may underestimate the highest BMP.

Since the best hydrochar characteristics were obtained at 250°C treatment, in objective 2 this process temperature was selected to evaluate the effect of solids loading on the process waters characteristics. Furthermore, the levels of water soluble products generally increase with reaction severity due the combination of solubilisation of inorganics and increase in production of soluble organics hydrocarbons that may favor the biogas production (Ekpo et al., 2015, Keymer et al., 2013, Qiao et al., 2011).

The solubilisation of carbon is due hydrolysis, releasing inorganic and organic compounds such as acetic acid, butanoic acid, alkenes, phenols, etc (Danso-Boateng et al., 2015). Therefore, it is reflected in the increasing amount of COD and TOC measured in the process waters. The COD solubilisation ranged between 240 to 360mg of COD per gram of feedstock processed and between 100 and 140mg of Carbon per gram of feedstock processed. That corresponds to an increase in solubilisation from 3 to 4.5 times higher than the initial sample of sewage digestate based on COD and between 4 to 6 times higher based on the TOC (80mg of COD per gram of feedstock and 20mg of Carbon per gram of feedstock). However the solubilisation is improved when the solid loading is lower than 15% and the solubilisation becomes constant beyond 15% of solid loading. A similar trend is seen for food waste at different solid loadings by Zabaleta et al. (2017) in which studies, the ratio between TOC and the dry mass of the feedstock reduced as the solid loading increased. This influence of solubility is important as it is possible that additional washing of hydrochars may liberate additional soluble hydrocarbons into the process water, this in turn may improve the properties of the hydrochars for further applications. Moreover, the solubilisation of the organics in process waters is a factor that must be considered when the anaerobic digestion is applied as a treatment route to avoid to surpass the limits that can inhibit methanogenesis due to over-acidification.

The effect of the solids loading on process waters BMPs showed a slight reduction in methane yield as the solid loading increases (up to 10%). This may be explained due the process waters generated from higher solid loadings may have higher levels of phenols as they were found by Berge et al. (2011a) in digestates. This is also reflected on the COD removal was from 55 to 81%, being the process water coming from 2.5% of solid loading with the higher COD removal and the worst with 55% of removal was the process water coming from 15% of solid loading.

The methane production seems to be slightly favoured by the solid loading because there is an increment on the methane percentage as the solid loading increase. Although, the methane concentration in the biogas ranged between 74 to 80%. These values are slightly higher than obtained by Wirth and Mumme (2013) in HTC liquor from corn silage (70%).

The biodegradability in the process water decreases as the solid loading increase and ranged from 75 to 89%. These results above 70% corroborate what is was mentioned in the first objective in which the 56% of biodegradability obtained from the 250°C treatment was underestimated. Furthermore, the biodegradability of the process waters increased from 36 to 89% compared with the digestate liquor (control). This demonstrates that the digestate still have some organic compounds that can be used to produce methane and can be solubilised through HTC.

In the third objective the aim was to assess the characteristics of the process waters coming from the different sewage sludge (AD and non-AD treated) at different temperature treatments in order to obtain information to build and propose different process configurations. In this study, it was found that when the temperature reaction increases, the TOC and COD concentration increases for all the process waters coming from the different sewage sludge. This is because the severity of the reaction favoured the solubilisation of the organics and inorganics. During thermal treatment, a solubilisation of organics and inorganics occurred due to hydrolysis or organic content which is reflected on the increase of the COD and TOC levels in the liquid fraction (Aragón-Briceño et al., 2017, Ekpo et al., 2015, Keymer et al., 2013). The COD concentration of the filtered non-AD treated sludge increased after the thermal treatments up to 3, 16 and 5-fold for the PS, SS and MIX respectively. The PS, SS and MIX digestates COD concentration also increased up to 5, 7 and 7.3-fold respectively after thermal treatment, showing there is still a substancial amount of organics in the AD sludge that can be harness with the thermal treatments. Previous studies reported an increase of 7-fold of the COD concentration for sewage digestate after 160 and 250°C treatments (Aragón-Briceño et al., 2017).

The TOC concentrations showed that the carbon solubilisation was favoured for non-AD treated sludge rather than those which had a previous AD treatment. After 160 and 250°C treatments, PS, SS and MIX showed an increased up to 3, 14.5 and 5.9-fold respectively but digestates of PS, SS and MIX just increased up to 5, 8 and 6.8-fold respectively. Furthermore, this showed that the increase on the TOC concentration varied depending on the sewage sludge treated. Aragón-Briceño et al. (2017) reported a 10-fold increase in the TOC concentration of sewage digestate after 160 and 250°C treatments.

The thermal treatment improved the BMP of all process waters coming from different sewage sludge. The process waters coming from 250°C treatment had higher BMPs than 160°C process waters, excepting process waters coming from secondary sludge digestate where the BMP did not vary significantly regardless the temperature. The Mix sludge presented BMPs of 252 and 351 mL of CH_4 per g of COD at 160 and 250°C respectively, which represented an increase of 11 and 55% with respect to the untreated Mix sludge, which can attributed to its high organic matter content. The secondary sludge presented higher BMP at 160°C (276 mL of CH_4 per g of COD) than primary sludge, but it seems there were no significant changes at 250°C treatment where the BMP was 312 mL of CH_4 per g of COD. Thermal processing enhanced primary sludge BMP values for the process waters increasing them up to 152% (208 and 325 mL of CH_4 per g of COD for 160 and 250°C process waters respectively) compared with the untreated sludge (129 mL of CH_4 per g of COD).

After the thermal treatment, the BMP values of the digestates increased. There was not a significant difference on the BMP values between 160 and 250°C treatment for process waters coming from ADSS and ADMIX. However, the the process temperature had an influence on the BMP values of process waters coming from ADPS. Previous studies investigating the anaerobic digestion of HTC have reported methane yields of 256.6mL of CH_4 per g of COD when using PW from municipal sewage sludge treated at 170°C (Qiao et al., 2011); for PW from sewage sludge digestate treated between 160 to 250°C, the methane yields ranged from 178 to 277mL of CH_4 per g of COD (Aragón-Briceño et al., 2017, Wirth et al., 2015) and for PW coming from PS treated at 200°C, the methane yield was 335mL of CH_4 per g of COD (Nilsson E, 2017).

There was a significant rising of the COD degradation in the process waters in comparison with the untreated sludge. The thermal treatment leads to a decreased of the concentrations of complex organic matter during the hydrolysis which is reflected in the increasing of COD degradation during the anaerobic digestion (Becker et al., 2013). The non-AD treated 160°C process waters had higher COD degradation than 250°C process waters because at high temperatures more toxics are produced as furans, phenols and other recalcitrant products that affect the anaerobic bacteria (Hübner and Mumme, 2015). Nonetheless, the 250°C AD treated process waters presented higher COD consumption than the 160°C AD treated process waters. These findings match with the values reported in other studies where the COD degradation during the anaerobic digestion ranged between 62 to 88% in HTC process waters from sewage sludge (Nyktari et al., 2017, Aragón-Briceño et al., 2017, Wirth et al., 2015).

Furthermore, the percentage of biodegradability (BD) increased as the temperature treatment increased. The MIX sludge presented the highest biodegradability among all, prior (57%) and post 160 and 250°C treatment

(82 and 89% respectively). The SS started with a BD of 29% and after the treatment at 160 and 250°C, the process waters showed a 70 and 79% of BD. The BD of the PS (33%) was enhanced by the treatment at 250°C which is evidenced by the increase of process water BD up to 82% and up to 53% for process water treated at 160°C.

Hence, it was demonstrated the feasibility of using the process waters coming from the HT treatments to produce biogas due its high carbon content. Moreover, the biogas showed methane concentrations ranging from 60 to 80% depending on the feedstock and reaction conditions. Nevertheless, more studies need to be done considering the recalcitrant and inhibitory products that can affect the biogas production.

8.2.2.Nutrients fate

It is known that the wastewater, especially sewage sludge, has the elements that allow it to be used as a fertiliser or soil improver (European Commission, 2015). This is because its richness in nutrients such as nitrogen and phosphorous that are valuable and useful along the organic matter. During thermal treatment great part of the nitrogen in ammonia form is solubilised from the sewage sludge as some part of the phosphorus as well. The track of the fate of nutrients represents an opportunity to determine the potential of the hydrochars to be used as soil amenders or nutrient recovery from the process waters produced during the thermal process.

The temperature process showed to have significant role regarding to the phosphorus solubilisation. In the experiment done for complete the first objective, the total soluble phosphorus concentration increased after 160°C and 250°C treatments (3% and 13.8% of P concentration, respectively) and decreased after 220°C treatment (21.5% of P). . This was accompanied by a reduction in P content in the solid fraction from 21.7% in the raw feedstock (Control) to 19.4 and 11% in the hydrochar after treatment at 160 and 250°C, respectively. On the other hand, the concentration of reactive phosphorus decreased with respect of the feedstock between 32.7 and 25.3% after hydrothermal treatment. This means, the fate of P during hydrothermal treatment is highly feedstock dependent and is linked to the levels of other metals present in the feedstock (Ekpo *et al*., 2015). The P associated with the hydrochar at 220°C increased once more to 37%, maybe due precipitation of some of the inorganic P with metals such as Al, Ca and Mg presented within the hydrochar.

The soluble nitrogen concentration increased with temperature from an initial concentration of 1,493 mgN/l to 2,066, 2,191 and 2,354 mgN/L as the initial levels of nitrogen in the solid fraction decreased from 58.3% to 42.4%, 38.9% and 34.3% for the treatments at 160, 220 and 250°C, respectively. The concentration of ammonium nitrogen was lower although gradually increased with temperature. This suggests that, during hydrothermal treatment, the proteins hydrolyse and ammonium is released increasing the nitrogen concentration in the process waters (Keymer et al., 2013, Wilson and Novak, 2009). In addition to carbon, the levels of hydrogen and nitrogen increase after hydrothermal treatment. Moreover, the sulphur content in the liquid fractions increased from 0.74% up to 2.81% after hydrothermal treatment; that may have implications for levels of H_2S in the final biogas (or precipitation of metal sulphides), if process waters are recycled back into anaerobic digesters.

The nitrogen content in the original digestate samples of the solid fraction (5.04 wt%) was higher than the figures found in the hydrochar after hydrothermal treatment at 160, 220 and 250°C (i.e., 4.19, 2.01 and 4.23 wt%, respectively). This suggests there was a 'sweet spot' where the nitrogen content was minimised. Reincorporation of nitrogen into the hydrochar may occur at higher temperatures as carbonisation reactions proceed more rapidly. A reduction in nitrogen content in the hydrochar corresponds to an increase in solubilised nitrogen.

In the second part, the effect of solids loading indicates there significant part of the phosphorus is solubilized (up to 27%) into the liquid fraction. Although, there was a saturation point that was reached with the reactive phosphorus remaining relatively constant beyond a solid loading of 15%. That means that the solubilisation of the phosphorus became constant to in solids loading beyond 15%. The solubilisation of phosphorus following HTC was due decomposition of complex organic phosphorus containing compounds (phospholipids, DNA and phosphates monoesters) and results in a combination of reactive (PO_4^{3-}) and organic phosphorus (Dai et al., 2015, Ekpo et al., 2015). The majority of the phosphorus (66.8 to 75.7%) therefore remains in the char.

Solid loading also significantly influenced the level of soluble nitrogen in the process water following HTC. The amount of nitrogen transferred from the feedstock into the water increased up to 48% of the total nitrogen contented into the liquid, leaving the nitrogen content of the hydrochar ranging between 15 to 50%. In this mean, despite of the nitrogen content in the solid fraction (hydrochar) suffered a slightly increase as the solids loading increased, there was still a reduction in the nitrogen content with respect to the original feedstock which corresponded to the nitrogen released into the process waters as dissolved ammonia (Aragón-Briceño et al., 2017).

In the third stage of this project, it was studied the fate of the phosphorus and nitrogen during the thermal treatment of the different sewage sludge. There was a solubilisation up to 10% of Phosphorus at 250°C and up to 12% of Phosphorus at 160°C among the different thermal treated sewage sludge. However, the phosphorus concentrations in process waters coming from secondary sludge suggest that 250°C treatment favoured the phosphorus fixation within the hydrochar unlike the 160 °C that favoured the phosphorus solubilisation. Aragón-Briceño et al. (2017) reported that hydrothermal treatments at lower temperatures favours the extraction of organic P in sewage digestate. Nonetheless, the 250°C treatment seems to favour the Inorganic phosphorus production (PO_4^-) in most of the different sewage sludge unlike the 160°C treatment that just favoured the inorganic phosphorus production in the different digestates.

The soluble nitrogen concentration increased up to 540% in the non-AD treated sludge at 250°C and up to 340% at 160°C treatment and increased uo to 70% and 36% for digestates at 250°C and 160°C treatment respectively. Although, there was higher ammonia solubilisation in non-AD treated sludge (up to 204 and 431% at 160 and 250°C respectively) rather than digestates (up to 109 and 136% at 160 and 250°C respectively. This means for all the different sludge the total nitrogen solubilisation is influenced by the temperature, as the temperature increase the total nitrogen concentration increases as well.

On the other hand, hydrochars presented a reduction in the nitrogen content of the in comparison to the original feedstock. This nitrogen reduction is given by the nitrogen released into the process waters during the thermal process (Aragón-Briceño et al., 2017).

The findings of this research project revealed that during the thermal treatments of sewage sludge more than 50% of the nitrogen contented within the solid fraction is released into the process waters, mostly in ammonia form. Contrarily to the phosphorus that showed a lower solubilisation (up to 30%) coming from the solid fraction into the liquid fraction.

8.3. Feasibility of hydrothermal treatment integration with AD

In recent years, some researchers has proposed the hydrothermal carbonisation process (HTC) as an alternative to harness better the properties from the sewage sludge and reducing the waste generation (Aragón-Briceño et al., 2017, Zhao et al., 2014, He et al., 2013). The main advantage of HTC is that it is carried out in presence of water avoiding the energy-intensive drying step required for thermal processes producing a solid hydrochar that can be used as a soil amender or fuel source and a process water rich in carbon and organics that can be used for produce biogas (Aragón-Briceño et al., 2017, Biller and Ross, 2012) (Wirth et al., 2015, Becker et al., 2014, Wang et al., 2010).

According to Child (2014), a HTC plant can cost from €3 up to €10million depending the treatment capacity. Nevertheless, most of them focus on hydrochar production using mostly lignocellulocic biomass and just few use sewage sludge as main feedstock.

The integration of HTC as a post-step after the AD is a recent approach under development that is suggested for the integration into waste water systems because its positive energy balance (Aragón-Briceño et al., 2017, Mumme et al., 2015).

In the fourth stage of this study, the objective was to assess the integration of the HTC with AD through mass and energy balances from proposed process configurations from different sewage sludge based on the results obtained from experimental analyses in previous stages of this research.

The scenarios showed a WWTP which provides service to a 100,000 people would have a potential economic benefit from biogas production up to £122,355, from hydrochar production up to £125,124 and from struvite production (without considering the price of Mg addition and pH regulation process) up to £351,569 per year depending the scenario. The scenarios where the 250°C treatment was applied showed the best potential benefit with £532,358 and £386,037 for scenarios 4 and 6 respectively.

The scenarios 4 and 6 (Primary sludge and Mix as main feedstocks respectively) showed the highest overall profit. However the scenario 6 should be considered the most suitable along scenario 3 for integration of HTC with AD for those existing AD plants because implies that there would be less modifications on the current WWTWs configurations.

This analyses can be considered as initial step to show the benefits of the integration of HTC with AD but still there are more variables that have to be considered in order to have a better prospect.

Chapter 9. Overall Conclusions and Recommendations

9.1. Research conclusions

The study aimed to assess alternatives to enhance the way how of the digestate is handled in the WWTP, by focusing on the use of hydrothermal processes and the potential of recovering energy and nutrients recovery. The following section summaries the key conclusions from the experimental studies.

Hydrothermal treatments improved the characteristics of the sewage digestate producing hydrochars and process waters rich in organic matter and nutrients. The influence of the temperature showed that lower process temperatures favour hydrochar production. However, the quality of the hydrochar improves as the temperature increases. Anaerobic digestion was demonstrated to be a suitable option to treat process waters from hydrothermal treatments for further biomethane production. Processing of digestate at 250°C resulted in a hydrochar that enhanced the net production of VFAs, although delayed methane production (longer lag phase). The addition of hydrochar (250°C) to the process water delayed VFA production during anaerobic digestion. Hydrothermal processing of process water and slurries at lower temperature (160-220°C) produced high levels of biogas, with no detrimental effect due the presence of hydrochar. The Boyle's equation had a closer match to the values provided by experimental biomethane potential (BMP) tests at lower temperature.

Solid loadings had an influence in the hydrochar composition and its energetic properties. The process waters were influenced by the solid loading increasing the concentration and reducing the solubilisation of the carbon and nutrients. There was a slightly influence in the methane potential of the process waters coming from the different solid loading. The energy balance is positive beyond 5% of solid loading when the hydrochars are considered as a fuel source and when they are not considered, the energy balance is positive beyond 15% of solid loading. The sewage digestate of 20% solids seems to be the best option for carbonisation in terms management and energy.

Hydrothermal treatments improved the characteristics of the different sewage sludge producing hydrochars and process waters rich in soluble organic matter and nutrients. Hydrochars from the different digestate sludge showed to have poorer production and energy characteristics than the hydrochars coming from the different non-AD treated sewage sludge. Nevertheless, adding the fact that previously the AD sludge has previously used for produce methane, the hydrochar’s energy characteristics are enough to enhance the overall energy production in the system and overcome the energy produced by the non-AD treated sludge. The organics and nutrients solubilisation demonstrated to be feedstock dependant showing better solubilisation to the different non-AD sewage sludge in comparison to the different digestate sludge. Process waters showed to be an option for biomethane production from sewage sludge, especially process waters coming from the digestate sludge which showed a significant improvement in biogas production. Most of the potential energy production comes from the hydrochar. Therefore, the energy production of the HTP treated sludge is higher when the hydrochar is considered than non HTP treated sludge. The integration of the HTPs as post-treatment after AD showed to be the best option in terms of energy production.

This study developed a model in ASPEN plus software that demonstrated HTC-AD scenarios have a significant positive energy balance when process water and hydrochar are considered as fuel sources.

Hydrothermal carbonisation showed to be a suitable option for integration with anaerobic digestion. Higher temperatures (250°C) seems to have more economically and environmentally benefits. Scenarios that involved primary and Mix sludge seemed to be suitable options because of the organic matter removal, energy harnessing and economic feasibility, but still many aspects have to be considered as the cost of WWTW´s modifications or the addition of the complementary equipment for the hydrochar use as an energy source.

9.2. Further research and considerations

Further research is needed to improve our understanding on handling digestate in the WWTP using hydrothermal treatments as viable alternative. The following recommendations can be suggested for future works:

- The BMP tests in this research were carried out in batch mode. For this reason more tests in continuous mode (CSTR) needs to be done to understand better the anaerobic digestion process and the capacity of the anaerobic bacteria to resist the accumulation of some inhibitory compounds.
- Further studies are needed to understand the influence of adding hydrochar on the quality and safety of the digestate for final disposal, as well as the impacts on AD processes due to process water recycling.
- Co-processing feedstocks with AD sludge should be considered as an option to enhance the quality of the liquid and solid products. Especially the combination of the sewage sludge with lignocellulosic products.
- In this study the energy characteristics of the hydrochar were calculated based on the elemental composition and the usage of Dulong's formula. It will be recommendable to carry on the analyses with a calorimetric pump.
- It would be advised to investigate the potential of the hydrochars as soil amenders in future research.
- Research on struvite precipitation in process waters needs would be recommendable.
- Most of the research carried out on HTC-AD integration is laboratory-based, making the assumptions to be difficult for real life occurrences. For an extensive energy balance as well as cost benefit analysis, it is essential to incorporate real data available for HTC and AD (carried out especially using large scale plants) in terms of operation and energy use. This will provide a more detailed analysis for developing a standard cost benefit analysis of the intended integrated approach.

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