EFFECTS OF ULTRASOUND PRETREATMENT AND ANAEROBIC DIGESTION ON THE ENERGY POTENTIAL OF SLUDGE

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EMREHAN BERKAY ÇELEBİ

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submitted by **EMREHAN BERKAY ÇELEBİ** in partial fulfillment of the requirements for the degree of **Master of Science in Environmental Engineering Department, Middle East Technical University** by,

Prof. Dr. Gülbin Dural Ünver ____________________
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. F. Dilek Sanin ____________________
Head of Department, **Environmental Engineering**

Prof. Dr. F. Dilek Sanin ____________________
Supervisor, **Environmental Engineering Dept., METU**

Assoc. Prof. Dr. Ayşegül Aksoy ____________________
Co-Supervisor, **Environmental Engineering Dept., METU**

Examining Committee Members:

Assoc. Prof. Dr. Tuba Hande Ergüder Bayramoğlu ____________________
Environmental Engineering Dept., METU

Prof. Dr. F. Dilek Sanin ____________________
Environmental Engineering Dept., METU

Assoc. Prof. Dr. Ayşegül Aksoy ____________________
Environmental Engineering Dept., METU

Assist. Prof. Dr. Robert W. Murdoch ____________________
Environmental Engineering Dept., METU

Assist. Prof. Dr. Çiğdem Moral ____________________
Environmental Engineering Dept., Akdeniz University

Date: August 14, 2015

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Emrehan Berkay Çelebi

Signature:

ABSTRACT

EFFECTS OF ULTRASOUND PRETREATMENT AND ANAEROBIC DIGESTION ON THE ENERGY POTENTIAL OF SLUDGE

Çelebi, Emrehan Berkay

M.S., Department of Environmental Engineering

Supervisor: Prof. Dr. F. Dilek Sanin

Co-Supervisor: Assoc. Prof. Dr. Ayşegül Aksoy

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The by-product of wastewater treatment, sludge, is generated in tons everyday all around the world. As environmental regulations in Turkey are becoming stricter during the European Union adaptation period, the previously wide-spread disposal method of landfilling the sludge will not be applicable. Instead, dried sludge is expected to be used in revenue generating methods like land application or combustion. Combustion can be thought of as more beneficial as it uses sludge as an energy source. However, it is not the only way to exploit the energy potential of sludge; anaerobic digestion also provides energy as biogas. While it is known that anaerobic digestion reduces the calorific value of the sludge, this effect is not yet fully investigated. Thus, the primary purpose of this study was to determine the effect of anaerobic digestion (with or without sonication pretreatment) on the calorific value of sludge. Additionally the study investigates the optimal sludge management strategy that maximizes the energy gain. After the inital experiments that determined the sonication duration as 10 minutes, anaerobic batch reactors with 2.5 L active volumes were used to track the changes in the fuel properties of sludge during digestion. Results showed that sonication provided a 340% increase in sCOD, a 15% increase in biogas production and a 32% increase in methane production. Using the data from the experiments, the energy analysis showed that the optimal method is the combination of thickening, dewatering, thermal drying and combustion. Adding digestion and ultrasound pretreatment to this scenario reduces the overall gain.

Keywords: Anaerobic digestion, calorific value, combustion, sludge, ultrasound pretreatment

ÖZ

ULTRASONLA ÇAMUR PARÇALAMA VE ANAEROBİK ÇÜRÜTMENİN ÇAMURUN ENERJİ POTANSİYELİNE ETKİLERİ

Çelebi, Emrehan Berkay

Yüksek Lisans, Çevre Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. F. Dilek Sanin
Ortak Tez Yöneticisi: Doç. Dr. Ayşegül Aksoy

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Atıksu arıtımının yan ürünü olan çamurdan dünyanın her yerinde günde tonlarca üretilmektedir. Avrupa Birliği uyum sürecinde Türkiye'nin çevre mevzuatı katılaşırken, eskiden yaygın olarak başvurulan çamur bertaraf metodu olan düzenli depolama, bundan sonra uygulanamayacaktır. Bu sebeple, kurutulmuş çamurun, ek kazanç oluşturan, toprakta kullanım veya yakma gibi metotlarla değerlendirilmesi beklenmektedir. Yakma işleminde çamurun enerji potansiyelinden yararlanıldığı için, daha faydalı olduğu düşünülebilir. Ancak, çamurun enerji potansiyelini değerlendiren tek yol yakma değildir; anaerobik çürütme işleminde de biyogaz formunda enerji üretilir. Anaerobik çürütmenin çamurun kalorifik değerini düşürdüğü bilinse de, bu etki tam olarak araştırılmamıştır. Bu yüzden, bu çalışmanın amacı, anaerobik çürütmenin (ultrasonla parçalamayla birlikte veya değil) çamurun kalorifik değeri üzerindeki ektisini ortaya koymaktır. Ek olarak, bu çalışmada, çamurdan elde edilebilecek toplam enerjiyi maksimize edecek strateji de araştırılmıştır. Ultrasonlama düzeyinin 10 dakika olarak belirlendiği öncül deneyleri takiben, 2.5 L aktif hacimli, daha büyük kesikli anaerobik reaktörler kullanılarak çürüme sırasında çamurun yakıt özelliklerindeki değişim takip edilmiştir. Sonuçlar, çKOİ miktarında %340, biyogaz üretiminde %15, ve metan üretiminde %32 artış göstermektedir. Deneylerden elde edilen veriler kullanılarak yapılan enerji analizine göre, çamurdan elde edilen enerji miktarını maksimize eden yöntem, çamur yoğunlaştırma, susuzlaştırma, termal kurutma ve yakma proseslerinin kombinasyonudur. Bu senaryoya anaerobik çürütme ve ultrasonlama eklendiğinde, toplam enerji miktarı azalmaktadır.

Anahtar Kelimeler: Anaerobik çürütme, çamur, kalorifik değer, ultrasonla parçalama, yakma

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To my dearest, my love…

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CHAPTER 1

INTRODUCTION

Sludge, the by-product of wastewater treatment, is generated in large amounts every day. Typical production rates vary between 30 and 100 g/capita/day depending on the treatment scheme involved (Sanin, Clarkson, and Vesilind, 2010). The overall quantity of sludge is expected to increase as the number of people connected to treatment plants increases, making the management and disposal methods more crucial for the environment. Current management approach includes stabilization and dewatering followed by landfilling, land application or combusting. In Europe, combusting and land application are gaining more popularity (Kelessidis and Stasinakis, 2012), while in Turkey, up to the present date, landfilling has been the most commonly applied disposal method. Turkey's case however, will no longer be sustainable as the environmental legislations become stricter resulting from the European Union adaptation period. The EU landfill directive (1999/31/EC), which has already been adapted into Turkish legislation (Regulation of Landfilling of Wastes), states that landfilling will require the sludge to have at least 50% solids content and at most 5% organic carbon, making the conventional scheme of stabilization, dewatering and landfilling practiced in Turkey illegal with the start of 2015. Thus, it is likely that land application or combustion, both of which can be considered as revenue generating methods, will start gaining popularity in the very near future. Already, some of the bigger treatment plants situated in İstanbul, İzmit and Antalya have modified their processes to include drying and combustion at either on-site or off-site locations.

Combustion of sludge can be achieved in incineration plants where the intent is mainly to get rid of waste or in existing co-combustion facilities, like cement factories, by replacing some of the original fuel with dried sludge. In both cases, the calorific value of sludge is utilized (Werther and Ogada, 1999), whereas in landfilling or land application, this energy content is disregarded completely. Another benefit is that, the ash remaining after incineration or co-combustion is easier to dispose of than sludge itself as it is much less hazardous. Furthermore, sludge ash can be incorporated into cement itself without compromising its integrity (Onaka, 2000; Wzorek, 2012). Finally, with co-combustion, the original fuel that the sludge replaces is conserved for a longer period of time, a benefit that incineration does not share.

Important parameters for the co-combustion of sewage sludge include its elemental composition, calorific value, water content, flue gas content and ash content (Werther and Ogada, 1999). Calorific value (or lower heating value), indicates the amount of heat energy released during combustion. Raw, undigested sludge can yield about 17000 J/g, if digestion is applied, this value is reduced to about 10000 J/g (Werther and Ogada, 1999). Both these values are substantial, compared to the 25000 J/g that can be typically obtained from high quality coal and about 6000 J/g of lignite, indicating that from an energy gain point-of-view, sludge can replace a medium quality coal. As the by-product of wastewater treatment, sludge consists mainly of water when it is formed. Through thickening followed by polymer aided dewatering, solids content may reach 35%, in other words the remaining 65% of sludge will still be water (Metcalf and Eddy, 2003). The combustion procedure is negatively affected by the presence of water, as it may reduce the combustion temperature, so, it is vital that sludge is dried from 35% solids to at least 90% to mitigate the adverse effects (Werther and Ogada, 1999). However, it should be noted that drying is a heat intensive process. Combustion characteristics, flue gas composition and ash content are also taken into consideration during co-combustion, mainly to see how the system will diverge from regular conditions when a new fuel is partially introduced.

When combustion is considered, the main emphasis is on energy gain, however, there are other ways of exploiting the energy potential of sludge. If anaerobic digestion is employed during stabilization, the produced biogas will mainly include methane, the primary component of natural gas. Nowadays, studies on anaerobic digestion focus on increasing the digestion rate, with the aim of reducing reactor size and energy requirements, and improving digestion and biogas generation by subjecting sludge to different pretreatment or conditioning processes (Braguglia, Gianico, and Mininni, 2012; Müller, 2001; S. I. Pérez-Elvira, Nieto Diez, and Fdz-Polanco, 2006; Wang, Kuninobu, Kakimoto, Ogawa and Kato, 1999). During the hydrolysis step of anaerobic digestion, complex forms of organics are broken down into smaller forms, and for sludge, this part takes the longest. Heat treatment, acid, ozone and ultrasound pretreatments help improve this part, and yield more digestible organics for the following steps, after hydrolysis of sludge (S. I. Pérez-Elvira et al., 2006; Xu, He, Yu, and Shao, 2011). While these procedures are beneficial to the overall digestion process, they consume significant amounts of energy on top of the requirements of anaerobic digestion itself. Another important point that must be raised is that all the digestion procedures reduce the calorific value of sludge, yielding less energy if sludge combustion takes place after digestion (Werther and Ogada, 1999).

In light of these facts regarding sludge, its anaerobic digestion and combustion, the arising question is “what is the optimal sludge management method if one wishes to maximize the net energy gain?”. It is known that anaerobic digestion consumes energy for its operation while also providing some in the form of biogas. If ultrasound pretreatment is applied beforehand, both the consumed and the produced energies increase. Dewatering is necessary for all disposal methods, and again, demands energy. If combustion is selected for final disposal, drying and its energy requirements also need to be taken into consideration, before finally harvesting the energy from combustion.

The purpose of this study is to investigate the optimal way to handle the wastewater treatment sludge that maximizes the energy gain. With this aim, sludge samples were taken from Ankara Central Wastewater Treatment Plant, the optimal ultrasound pretreatment level was experimentally determined using the results of two biochemical methane potential tests. Then, another anaerobic digestion test consisting of bigger batch reactors was conducted on both pretreated and non-pretreated sludge to quantify the exact difference between treatment levels and biogas productions of the two types of sludge. Calorific values of the sludge were measured during all the experiments, to reveal the total energy loss from anaerobic digestion. Finally, an energy balance was constructed to see how each treatment step including ultrasound pretreatment, anaerobic digestion, dewatering, drying, combustion, and land application influences the following steps and the end result; the optimal method was selected as the suggested treatment and disposal scheme of municipal sludge.

CHAPTER 2

LITERATURE SURVEY

2.1. Sludge Management

Sludge is one of the by-products of wastewater treatment. As wastewater is treated via physical, chemical and biological means, sludge is formed. Conventionally, it consists of settleable solids in the wastewater and the bacteria used in biological treatment, however, different processes like chemical precipitation may produce sludge with varying properties (Metcalf and Eddy, 2003; Sanin et al., 2010). Sludge has many objectionable qualities which require several methods of treatment to stabilize its organic activities and reduce its water content (Metcalf and Eddy, 2003). Traditionally, sludge is firstly thickened, reducing the water content by more than 50%, then a form of stabilization is applied, reducing its organic and pathogen content, making it safer to be handled (Metcalf and Eddy, 2003; WEF and ASCE/EWRI, 2009). Last steps are again related to the water present within the sludge, application of dewatering turns the sludge into a semi-solid form, increasing the solids content up to 35%. From then on, solids content can be further increased to above 90% via drying methods, if necessary (Kurt, Aksoy, and Sanin, 2015; Metcalf and Eddy, 2003; WEF and ASCE/EWRI, 2009).

After being treated within the plant, there are a few options for the disposal of sludge. Until 2000s, landfilling was the most popular method in Europe, with more than 50% of the sludge being disposed of this way (Werther and Ogada, 1999). With the implementation of the directive on landfilling of sludge (1999/31/EC) by the European Commission, sludge was required to have at least 50% solids content and at most 5% organic carbon. After this point, trends began to shift towards other disposal alternatives (Stehlík, 2009). Figure 2.1 shows the distribution of sludge disposal methods in Europe before 2000, while Figure 2.2 shows the country-based distribution in the period of 2005 to 2009 (Kelessidis and Stasinakis, 2012; Werther and Ogada, 1999). This preference of revenue generating methods like land application or thermal processes are expected to continue in the future. Already, over 50% of the sludge produced in Europe is being used in land application, along with more than 20% of the sludge being thermally disposed of (Escala, Zumbühl, Koller, Junge, and Krebs, 2013). Moreover, countries like Switzerland and the Netherlands have fully switched to incineration due to the unavailability of land (PURE, 2012). Details regarding land application and thermal processes as final sludge disposal methods are given in the sections below.

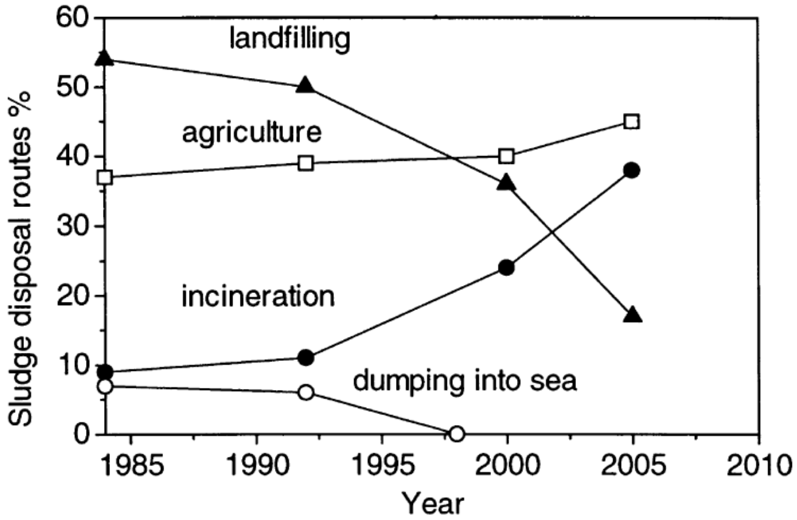


Figure 2.1: Distribution of sludge disposal methods in Europe between 1985 and 2000 (Werther and Ogada, 1999).

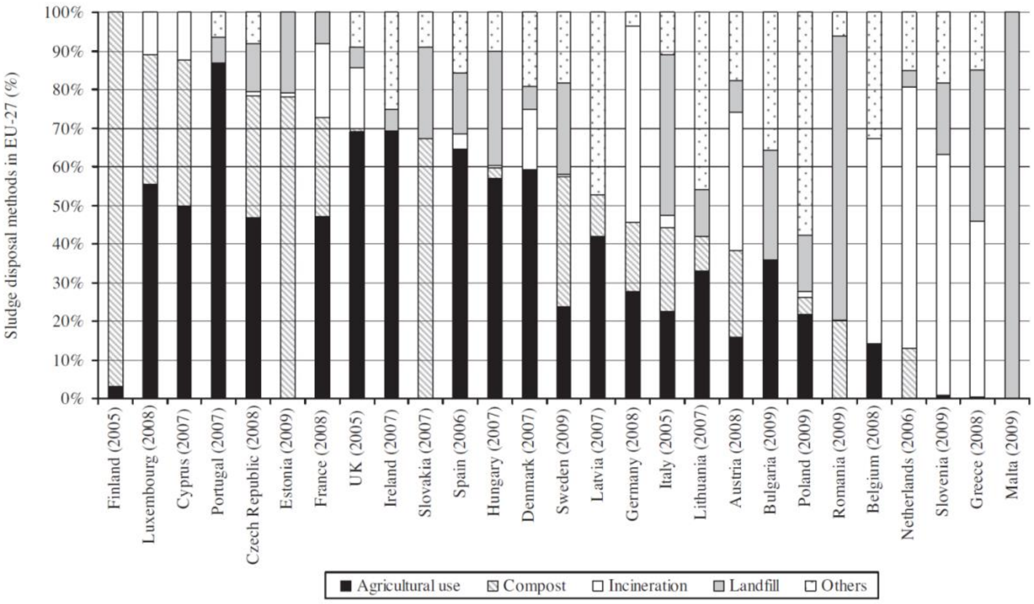


Figure 2.2: Country based distribution of sludge disposal methods in Europe, years 2005 – 2009 (Kelessidis and Stasinakis, 2012).

2.1.1. Final Disposal: Land Application

Sewage sludge is found to be able to replace commercial fertilizers with its high organic and nutrient content (Laturnus, von Arnold, and Grøn, 2007). Among providing a beneficial final disposal method, land application of sludge also helps the soil retain more water, while increasing its overall fertility in addition to the energy saved from replacing industrial fertilizers (Werther and Ogada, 1999). These qualities increase the popularity of land application, making it the most common method in USA and Canada as a sustainable and economical solution to the problem of sludge disposal (Laturnus et al., 2007). The benefits are well documented with several studies being published on this disposal method assessing the positive effects on the soil conditions (Wong, Li, Fang, and Su, 2001) and the quality and the quantity of the produce (Pedreño, Gómez, Moral, and Mataix, 1996; Vannoordwijk, Schoonderbeek, and Kooistra, 1993).

Despite all the benefits, municipal sludge contains pathogens, trace organics, and heavy metals, and their introduction to agriculture is considered to propose significant health risks (Manara and Zabaniotou, 2012). Besides its potentially harmful contents, constant production of sewage sludge and the seasonal need for fertilizers in agriculture seldom match, turning land application into unreliable as a consistent disposal method at best (Fytili and Zabaniotou, 2008). Combination of these drawbacks with the public's negative opinion on using sludge in agriculture result in the reassessment of the sustainability of this method (Fytili and Zabaniotou, 2008; Kelessidis and Stasinakis, 2012).

2.1.2. Final Disposal: Thermal Processes

Various thermal processes can be utilized as sludge disposal. Figure 2.3 displays the categorization of these processes which are grouped into three main headings: mono-combustion, co-combustion, and alternative processes (Werther and Ogada, 1999). Mono-combustion involves direct combustion of sewage sludge in appropriate systems like multiple hearth furnace or fluidized bed reactors. In co-combustion processes, sludge replaces part of the original fuel in a given combustion system, waste combusting cement factories can be given as an example (Onaka, 2000; Werther and Ogada, 1999). Alternative processes mainly include further applications on the sludge to improve its fuel characteristics including processes such as pyrolysis and gasification (Moldoveanu, 2010; Werther and Ogada, 1999).

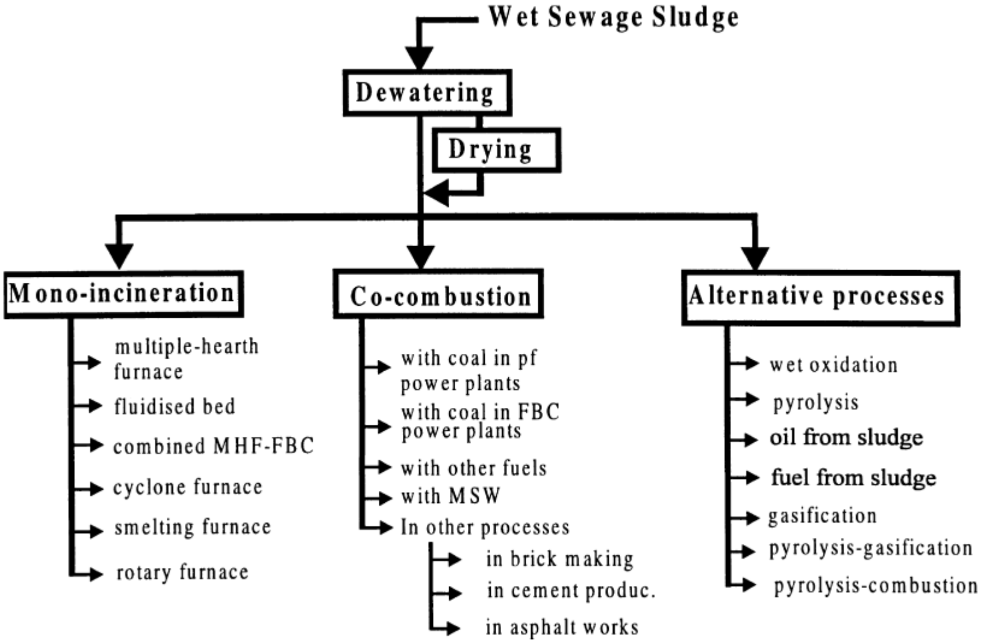


Figure 2.3: Thermal processing of sewage sludge (Werther and Ogada, 1999).

One reason for sludge's adaptability for these thermal processes results from its relatively high calorific value (Werther and Ogada, 1999). As depicted in Table 2.1, sludge taken from different parts of the treatment scheme has comparable calorific values to that of coal, once it is dried (Fytili and Zabaniotou, 2008; Manara and Zabaniotou, 2012).

Table 2.1: Calorific values of different fuels along with types of sludge (Fytili and Zabaniotou, 2008; Manara and Zabaniotou, 2012).

Fuel	Calorific Value (MJ/kg)
Coal	14.6 - 26.7
Wood	16.0 - 20.0
Gas-oil	45.5
Natural Gas	38.0
Synthetic Coal Gas	10.8
Raw Sludge (Dried)	23.0 - 29.0
Activated Sludge (Dried)	16.0 - 23.0
Anaerobically Digested Primary Sludge (Dried)	9.0 - 13.0

Combustion can be defined as the oxidation of a fuel in the presence of an oxidant, leading to the release of heat (Borghi and Destriau, 1998). Following this definition, fuels are materials that produce useable heat when reacted with an oxidant. In a traditional sense, primary fuels consist of carbon based fossil materials while alternative fuels include renewable materials with high organic content, like sewage sludge (McAllister, Chen, and Fernandez-Pello, 2011; Werther and Ogada, 1999). Although both methods are applicable, studies on sewage sludge combustion tend to focus on co-combustion systems, rather than mono-combustion (Werther and Ogada, 1999).

Co-combustion in cement factories is wide-spread, besides sewage sludge, solid wastes, food wastes, tyres and other similar wastes can be disposed of this way (Aranda Usón, López-Sabirón, Ferreira, and Llera Sastresa, 2013). It is found that although using alternative fuels could cause issues with the flame characteristics due to the presence of higher amounts of volatile solids, the quality of the cement - once sludge ash is mixed in - and the overall performance of combustion is unaffected (Aranda Usón et al., 2013; Onaka, 2000; Wzorek, 2012). Other than cement kilns, coal fired power plants are also suitable co-combustion sites (Stelmach and Wasielewski, 2008). Replacing 1% (by weight) of the coal was reported to have minor reductions in the efficiency of the boiler and the temperature of the combustion chamber, without hindering the overall process (Stelmach and Wasielewski, 2008). In addition to the effects on the combustion process, emissions can also be affected by the presence of sludge. When sludge combusted with coal in a fluidized bed reactor, emissions of HCN, HCl, SO_2 and N_2O were found to increase in the flue gas (Deng et al., 2009). However, emissions and these increases are proportional to the constituents and amount of sludge within the combusted mixture, and when only a minor amount of the original fuel is replaced, the emissions are not altered significantly (Deng et al., 2009). On the whole, with co-combustion, the heating value of sludge is utilized, some of the original fuel is conserved for a longer period of time and the remainder of the sludge is more easily disposed of (Onaka, 2000; Werther and Ogada, 1999).

Listed under the alternative technologies in Figure 2.3, pyrolysis and gasification have also been applied to sewage sludge. Pyrolysis is the process that occurs between 300 to 350 °C during which a solid material is forced to decompose, forming smaller molecules as the chemical bonds break with the application of heat, subsequently, reforming into bigger particles (Moldoveanu, 2010). Gasification can be defined as the process of converting a solid fuel into a gaseous fuel, eventually ending up with H_2, CO and CH_4 (Higman and van der Burgt, 2008). Products of these processes are char, the solid part, tar, the condensed liquid part and syngas, the useful combustible gas with a calorific value of approximately 10 MJ/m^3 (Mun, Kang, and Kim, 2009; Seggiani, Vitolo, Puccini, and Bellini, 2012). There are several problems associated with these processes that halt their spread as disposal methods for sludge, like the emissions of NO_x or HCN (Chen, Namioka, and Yoshikawa, 2011), and the produced tars harming the equipment and the overall process (Mun et al., 2009).

2.2. Anaerobic Digestion

Besides the thermal processes that directly produce energy from sludge, a form of stabilization can also help exploit some of the energy potential of sludge: anaerobic digestion. As a stabilization method, it is deemed to be necessary before certain final disposal methods since it reduces the amount of organics and pathogen content of sludge, eventually converting some part of them to methane and carbon dioxide (Parkin and Owen, 1986).

Depicted in Figure 2.4, anaerobic digestion takes place in three stages, in addition to a preliminary step required for wastes with high amounts of complex organics:

> Preliminary Step – Hydrolysis: In this preliminary step, complex organics which may also be insoluble are broken down into simpler, bioavailable organics like sugars, fatty acids, and amino acids. Compounds that are able to be absorbed into the cell through the cell wall are called bioavailable, it is imperative that organics within the sludge have this property, so that the following steps can progress with ease (Parkin and Owen, 1986). Achieved through extra-cellular enzymes, this step takes the longest, especially for sewage sludge (Müller, 2001; WEF and ASCE/EWRI, 2009). Thus, it is called as the rate-limiting step in anaerobic digestion. It is this step, that some of the pretreatment technologies aim to fasten, with the aim of increasing the overall rate of digestion (S. I. Pérez-Elvira et al., 2006)
>
> Acidogenesis: Soluble organics already present, or produced through hydrolysis are converted to long-chain fatty acids, including propionic and butyric acid (Parkin and Owen, 1986; WEF and ASCE/EWRI, 2009).
>
> Acetogenesis: In this step, previously formed long-chain fatty acids are broken down to carbon dioxide, hydrogen and acetic acid by acetogens (Parkin and Owen, 1986; WEF and ASCE/EWRI, 2009).

Methanogenesis: The final step of anaerobic digestion, methanogenesis involves the production of methane via two pathways: acetoclastic methanogenesis and hydrogenotrophic methanogenesis (WEF and ASCE/EWRI, 2009). The former one is the main pathway, producing most of the methane, while the latter helps stabilize the whole process, preventing the accumulation of volatile acids which in turn result in a reduction of the pH, also known as digester souring (WEF and ASCE/EWRI, 2009).

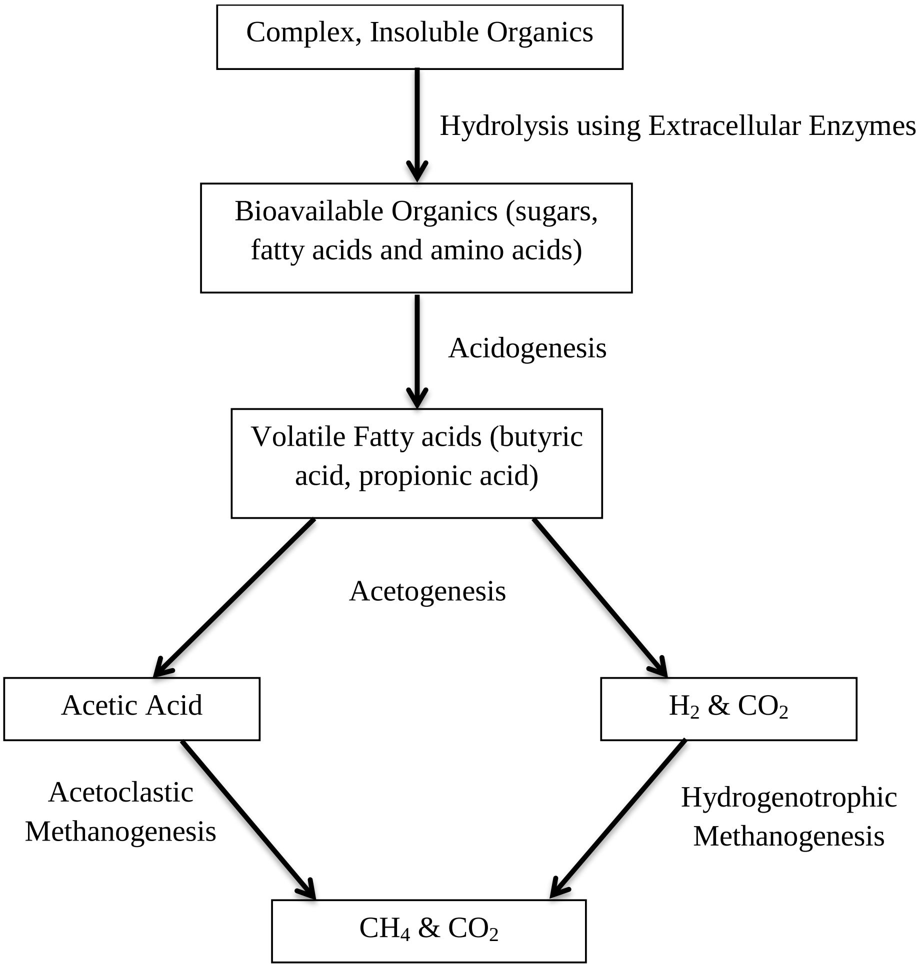


Figure 2.4: Pathways of anaerobic digestion (Parkin and Owen, 1986; WEF and ASCE/EWRI, 2009)

Anaerobic digestion process can be affected by a number of parameters including temperature, pH and alkalinity and presence of toxic substances (Wang et al., 1997). Anaerobic digestion can be achieved in two ranges of temperature. The most common temperature range, used in the majority of the full-scale digesters is given as 30 to 38 °C, named mesophilic digestion (Gray, 2010; Parkin and Owen, 1986). For a significant increase in biogas production and volatile solids destruction rate, the temperature range can be increased to 40 to 50 °C becoming thermophilic digestion (Metcalf and Eddy, 2003). Although thermophilic digestion is preferable in terms of digestion performance, the energy required to sustain higher temperatures prevents its spread into mainstream use (Parkin and Owen, 1986; WEF and ASCE/EWRI, 2009). Another concern with temperature lies with its fluctuations during the process. Microbial groups involved at each step, particularly methanogens are sensitive to changes in temperature, so much that a 1 °C change may result in undesirable consequences (WEF and ASCE/EWRI, 2009).

Alkalinity and the pH of the system play an important role in anaerobic digestion. As was the case with temperature change, methanogens are susceptible to changes in pH. The most desirable methane production is found to occur in a pH range of 6.8 to 7.2 (WEF and ASCE/EWRI, 2009). During the reactions, pH is lowered through the production of volatile acids, but also kept stable through the buffering capacity of the alkalinity resulting from carbon dioxide and ammonia, from methanogenesis (Metcalf and Eddy, 2003; Parkin and Owen, 1986).

There are several substances that were found to be toxic to anaerobic digestion, particularly heavy metals, cations of several light metals, oxygen, sulfide, ammonia and some organic compounds including types of benzenes and aldehydes (Parkin and Owen, 1986; WEF and ASCE/EWRI, 2009). Should their concentrations increase beyond the limits set for methanogens, which are the most sensitive group, the final step of anaerobic digestion is inhibited or eventually completely halted. This leads to the previously explained phenomenon of souring, due to the build-up of volatile fatty acids (WEF and ASCE/EWRI, 2009).

When mesophilic anaerobic digesters are operating properly, with the aforementioned conditions are satisfied, a situation akin to the one depicted in Table 2.2 can be observed (WEF and ASCE/EWRI, 2009). For digesters fed with a combination of primary and secondary sludges a biogas yield of 0.8 to 1 m^3/kg VS destroyed is common (WEF and ASCE/EWRI, 2009). Of this produced biogas, 60 to 70% should be methane and 30 to 35% should be carbon dioxide. If the carbon dioxide level increases beyond this point, it may be an indication of the problems within the digester (WEF and ASCE/EWRI, 2009).

Table 2.2: Typical operating parameters of mesophilic anaerobic digesters (WEF and ASCE/EWRI, 2009)

Parameter	Value
Volatile Solids Destruction	45 to 55%
Biogas Methane Content	60 to 70%
Biogas Carbon Dioxide Content	30 to 35%
pH	6.8 to 7.2
Alkalinity	2500 to 5000 mg $CaCO_3$/L

2.3. Pretreatment of Sludge

Sludge digested in the anaerobic digesters of municipal treatment plants generally consist of primary and secondary sludges (WEF and ASCE/EWRI, 2009). Secondary sludge, especially, is hard to digest as it consists mostly of settled bacteria whose cell walls require extended durations of hydrolysis (Müller, 2001). Different ways of pretreatment have emerged, particularly to tackle this issue. These pretreatment methods can be grouped into four distinct categories; mechanical treatment, chemical treatment, biological treatment and thermal treatment (Müller, 2001).

Mechanical pretreatment employs physical effects such as pressure, translational or rotational energy to disrupt and break the cell walls of bacteria. This way, the bound water and the soluble organics are released and are available for the next steps of digestion (Müller, 2001). Mechanical methods include high pressure homogenizer, lysate centrifuge, high performance pulse technique, and ultrasound pretreatment (Müller, 2001; Strünkmann, Müller, Albert, and Schwedes, 2006).

Chemical pretreatment methods involve the addition of chemicals that break down the cell walls of bacteria to speed up the hydrolysis step. The effective chemicals can be listed as ozone, Fenton's reagent, chlorine, and various acids and alkalies (Kim et al., 2003; Müller, 2001; S. I. Pérez-Elvira et al., 2006).

Biological pretreatment methods focus on disintegration with enzymatic reactions or by autolytic processes. Addition of certain enzymes have been found to trigger the disintegration of gram-positive bacteria, along with providing further benefits on dewaterability (Barjenbruch and Kopplow, 2003; Müller, 2001; Yamaguchi, Yao, and Kihara, 2006).

Thermal pretreatment can be defined as the application of heat to the sludge, increasing the temperature to the range of 60 to 200 °C in order to destroy the cell walls of the bacteria (Müller, 2001; Weemaes and Verstraete, 1998). With temperatures close to the higher end, over 20% increase in soluble organic contents have been observed (Weemaes and Verstraete, 1998). However, heating the sludge over 200 °C was found to cause Maillard reactions, producing compounds that were harder to dewater (Eskicioglu, Kennedy, and Droste, 2006).

2.4. Ultrasound Pretreatment

Ultrasound can be defined as the cyclic sound pressure frequency of which exceeds that of the human hearing limit. There have been many applications of ultrasound in the fields of biology, engineering, geology, geography and medicine (Mason and Lorimer, 2002). For sewage sludge, it can be used as a mechanical pretreatment method to reduce the time spent during hydrolysis (Mason and Lorimer, 2002; Show, Mao, Tay, and Lee, 2006; Weemaes and Verstraete, 1998).

When sonicated at low frequencies between 20 to 40 kHz, microbubbles form within the liquid medium. Once the local pressure in the liquid phase falls below the vapor pressure, these bubbles cause tiny explosions, a phenomenon called as cavitation (Tiehm, Nickel, and Neis, 1997). Cavitation escalates as sonication progresses, eventually leading to high pressure differences and local maximum temperatures close to 5000 K and pressures of about 500 bar (Tiehm, Nickel, Zellhorn, and Neis, 2001). Figure 2.5 shows how this process occurs schematically ("Ultrawaves," 2015). With these extreme conditions, radicals including •OH, HO_2• and H• and hydrogen peroxide may form within the sludge (Bougrier, Carrère, and Delgenès, 2005). Eventually, the high temperatures and pressures resulting from collapsing microbubbles rupture the cell walls, disrupting their integrity and releasing the contents of the bacteria to the liquid medium (Khanal, Grewell, Sung, and van Leeuwen, 2007). It was also found that, the occurrence and the size of these microbubbles are inversely proportional to sonication frequency, in other words, number and size of the bubbles are greater when lower frequencies are applied (Tiehm et al., 2001).

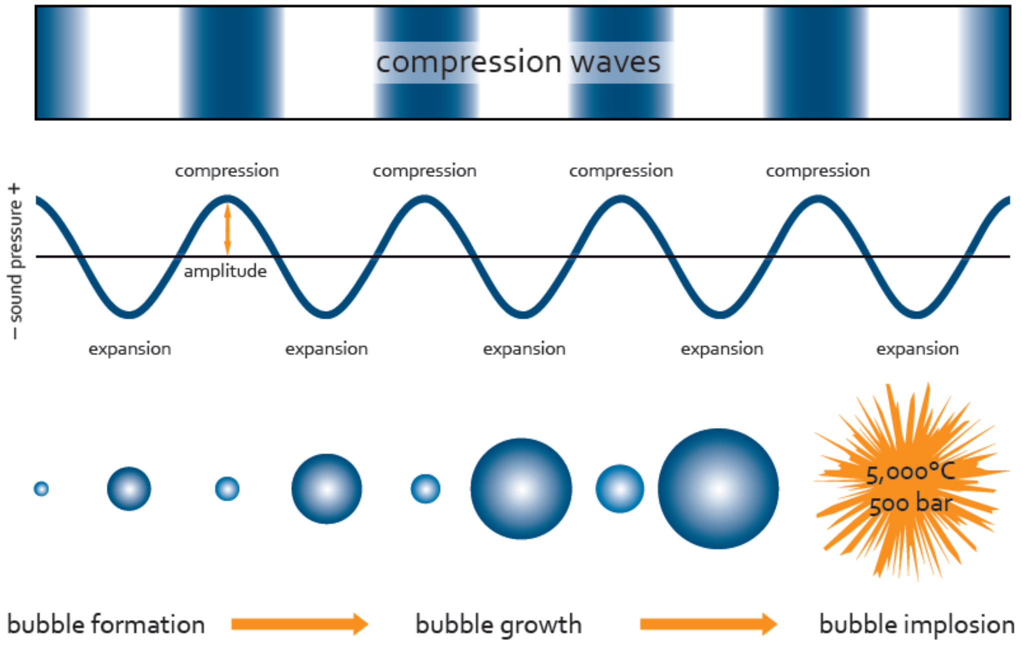


Figure 2.5: Schematic representation of the sonication procedure affecting sludge ("Ultrawaves," 2015).

Many studies have been conducted on the effect of sonication on the solubilization of organics present in the sludge, and its benefit on the overall anaerobic digestion procedure. According to the review conducted by Pérez-Elvira et al. (2006), sonication can yield up to 600% more sCOD along with 10 to 60% more biogas, when compared to digesters fed with non-pretreated sludge. Tiehm et al. (1997) demonstrated that sludge sonicated at a frequency of 31 kHz and a power of 6 kW released 6000 mg sCOD/L in 96 seconds, while 64 seconds resulted in a release of 4000 mg sCOD/L. A study by Show et al. (2006) showed that sCOD concentrations could increase by 100% when subjected to sonication at 20 kHz frequency with a density of 0.52 W/L for 60 seconds. Experiments of Wang et al. (1999) led to the conclusion that sonicating the sludge at 9 kHz frequency for 30 minutes did not increase the solubilization further. Braguglia et al. (2012) showed that sonication at 24 kHz frequency and 0.7 kWh/kg dry solids density increased the VS removal from 32% to 38%, and biogas production by 26%.

Many full-scale wastewater treatment plants have been including sonicators in their process scheme. These sonicators are placed before or after the thickeners that are used prior to anaerobic digesters. Other applications include sonication on some part of the return activated sludge, with the aim of increasing the concentration of readily available organics. A total of at least 66 plants in Australia, Brazil, China, Denmark, France, Germany, Greece, Hungary, Ireland, Japan, South Korea, the Netherlands, Poland, Romania, Switzerland, Spain, Taiwan, UK and USA have seen improvements in VS destruction and biogas production due to the addition of ultrasound pretreatment ("Ultrawaves," 2015).

2.5. Contributions with Regards to Existing Literature

When sludge treatment is considered, two types of studies are frequent: laboratory scale experimental studies or calculations based on full-scale treatment plants. With this study, results of a series of laboratory experiments will be used to assess different treatment scenarios with respect to their total energy yields. This way, changes in the energy gains when different processes are used in a variety of combinations can be demonstrated. Also, the assessment of ultrasound pretreatment with respect to its energy consumption will also be carried out. Overall, this study aims to fill the gap between lab-scale and full-scale studies, providing a suggested treatment scheme to maximize the energy gain from sludge.

CHAPTER 3

MATERIALS AND METHODS

Following the scope of the study, to demonstrate how fuel characteristics of sludge change with anaerobic digestion including and excluding pretreatment, series of experiments were planned and conducted. To start with, a BMP experiment was prepared to see how different levels of pre-treatment (and lack of) affected digestion performance. Then, a second BMP assay was conducted to verify the initial results. After this point, a single pre-treatment condition was selected, and larger anaerobic reactors were used to see how fuel characteristics changed *during* anaerobic digestion. The chart, given below in Figure 3.1 shows the main steps followed in each of the three experiments. Details regarding the experimental procedures are given throughout this section.

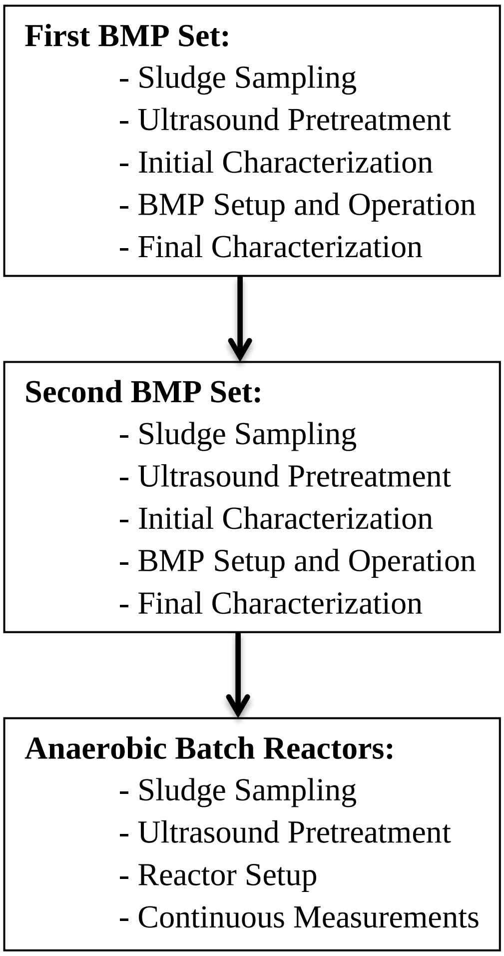


Figure 3.1: Conducted experiments and main steps followed.

3.1. Sludge Samples

Waste activated sludge (WAS) and anaerobic seed sludge that were used in the experiments were taken from Ankara Central Wastewater Treatment Plant. In this plant, a conventional activated sludge system is employed for the wastewater line and sludge from primary and secondary sedimentation tanks are mixed and digested together in a mesophilic anaerobic digester. Average daily flow rate is reported to be 765,000 m^3 and digesters are operated with an SRT of 14 days (ASKI, 2015).

Experimental setups explained in the following sections, where anaerobic digestion takes place, require two types of sludge; a sample of “seed” containing the necessary microorganisms for anaerobic degradation, and a sample of “food” that will be degraded by these microorganisms. The seed samples are taken from inside the mesophilic digesters of the treatment plant, while the food samples are taken from the return activated sludge line following the secondary sedimentation tanks. Once the samples were taken, they were left to settle to increase the solids concentration. After settling was achieved, the water portion above the settled sludge was drained and discarded. Anaerobic sludge was stored at room temperature in order not to inhibit the anaerobic microorganisms, while the activated sludge was stored at 4°C to minimize degradation. All experimental procedures were started within a day of sludge sampling. Sampling was done instantaneously as composite sampling would have led to faster decomposition, especially for the WAS samples.

3.2. Ultrasound Pretreatment

Ultrasonic pretreatment was selected to improve the digestibility and biogas (and methane) yield of the activated sludge. Following settling, the concentrated activated sludge was divided into 350 mL portions and each beaker containing these samples was placed in a large ice bath to minimize the heating effect of sonication. Figure 3.2 depicts the sonication setup.

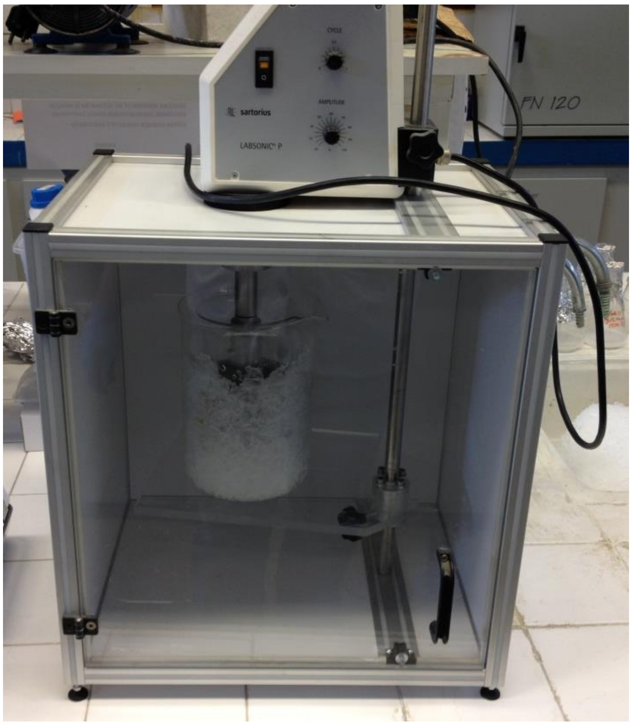


Figure 3.2: Sonication setup, showing the sludge sample, the ice bath and the sonicator.

Sartorius Labsonic P (Sartorius AG, Germany) was the selected sonication equipment. It has a 22 mm probe, specifications of which are given below in Table 3.1. For BMP setups 1 and 2 the only varying parameter was the sonication duration, for the anaerobic batch reactors, a single sonication time was selected, based on the results of the BMP tests. As explained in section 2.4, the effectiveness of sonication is measured by checking the soluble COD (sCOD) concentrations prior to and after sonication. Effects of the ultrasound pretreatment and the increase in sCOD concentrations are given in Chapter 4. Throughout the experiments, sonication was only applied to the waste activated sludge (food) because sonicating the anaerobic seed sludge would kill the microorganisms required for anaerobic digestion.

Table 3.1: Specifications of the sonication procedure

Sonication Frequency	24 kHz
Probe Size	22 mm
Sonication Power	255 W
Sample Volume	350 mL
Sonication Density	0.73 W/mL
Sonication Times (min)	0, 5, 10, 15, 20, 25

3.3. Experimental Setups

The main experimental setups prepared through the course of this study are; the first BMP test lasting 67 days, the second BMP test lasting 61 days and anaerobic batch reactors lasting 71 days. Details regarding the preparation of these experiments are presented in this section.

3.3.1. BMP Set 1

For this experiment, anaerobic seed sludge and WAS were left to settle and afterwards, WAS was partitioned into six parts. Each part was sonicated for 0, 5, 10, 15, 20 and 25 minutes, respectively. Then, TS, TSS, VS and VSS concentrations of these separate sludge samples, as well as the anaerobic seed, were measured to determine the mixing volumes of each sludge sample in accordance with the F/M (g VS/g VSS) ratio of 1. This ratio was selected following the prior studies of Köksoy and Sanin (2010), where it was reported that the highest specific methane yield resulted from an F/M ratio of 0.5. However, in the same study, it was also stated that higher F/M ratios helped better demonstrate the difference in total methane production levels, between sonicated and non-sonicated sludge samples. Thus, keeping the ratio at 1 (g VS/g VSS) enabled a high specific methane yield along with better display of the changes in methane production between sonication levels. Given in Table 3.2 are the solids concentrations of the sludge samples examined in the first BMP test of this study.

Table 3.2: Solids concentrations of the sludge samples, prepared for the first BMP test.

Sludge Type	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	TSS/TS (%)	VSS/VS (%)	VS/TS (%)	VSS/TSS (%)
Anaerobic Seed	18783	15800	11467	9683	84.1	84.4	61.0	61.3
WAS - No Sonic.	16700	13175	13067	10450	78.9	80.0	78.2	79.3
WAS - 5 Min. Sonic.	14967	12325	11667	9725	82.3	83.4	78.0	78.9
WAS - 10 Min. Sonic.	14775	11867	11375	9400	80.3	82.6	77.0	79.2
WAS - 15 Min. Sonic.	14975	11967	11400	9483	79.9	83.2	76.1	79.2
WAS - 20 Min. Sonic.	14850	11150	11433	8800	75.1	77.0	77.0	78.9
WAS - 25 Min. Sonic.	15233	11267	11550	8933	74.0	77.3	75.8	79.3

For the BMP assay, serum bottles of 275 mL in total volume, with an effective volume of 200 mL were used. Also seen on Table 3.2, sonication yielded six different kinds of WAS. Along with the seed control group, a total of seven different mixtures were prepared. To demonstrate repeatability, these seven different sludge mixtures were analyzed in triplicates, yielding a total of 21 bottles. For three replicates of a given sludge mixture, 600 mL of that sludge mixture is required. In addition to this amount, 700 mL more was prepared to conduct analyses depicting the initial conditions of the sludge samples, adding to the total of 1300 mL of each mixture. Given in Table 3.3 are the volumes required of each sample within the mixture. Basal medium was not used as the microorganisms present in the seed were already acclimated to the given type of waste.

Table 3.3: Composition of the mixtures, prepared for the first BMP test.

Mixture	**Label**	Seed Vol. (mL)	Food Vol. (mL)	Distilled Water (mL)	Total Vol. (mL)
Seed	**S**	700.0	0.00	600.0	1300.0
Seed + WAS - No Sonic.	**U0**	700.0	518.8	81.2	1300.0
Seed + WAS - 5 Min. Sonic.	**U5**	700.0	581.0	19.0	1300.0
Seed + WAS - 10 Min. Sonic.	**U10**	700.0	595.9	4.1	1300.0
Seed + WAS - 15 Min. Sonic.	**U15**	700.0	594.6	5.4	1300.0
Seed + WAS - 20 Min. Sonic.	**U20**	700.0	592.9	7.1	1300.0
Seed + WAS - 25 Min. Sonic.	**U25**	700.0	586.9	13.1	1300.0

Once the samples were prepared and bottled, each bottle was purged with nitrogen gas at 99% purity for 10 minutes to lessen the effect of already present oxygen. After purging, bottle caps were sealed and samples were left to incubate at 35°C while shaking at 125 rpm. Figure 3.3 depicts the setup of the BMP bottles inside the incubator. Parameters measured and their measurement frequencies are presented in Table 3.4 below. For the first seventeen days, measurements related to biogas were conducted daily. As the biogas production slowed down, so did the measurement frequency. The final measurement was done on day 67 to ensure that digestion had completely stopped, and this BMP set was terminated subsequently.

Figure 3.3: BMP bottles inside the incubator

Table 3.4: Parameters measured during the first BMP set, along with their measurement frequencies

Parameter	**Frequency**
TS (mg/L)	Before and after anaerobic digestion (days 0 and 67, respectively).
VS (mg/L)	
COD (mg/L)	
Ash (mg/L)	
pH	
CV (cal/g)	
Biogas Volume (mL)	Days 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 19, 22, 30, 40, 67.
Biogas Composition (% CH_4, % CO_2, % N_2)	

3.3.2. BMP Set 2

Results of the first BMP set showed considerable variations among the replicates of the same sludge mixture. To ensure that the results and conclusions following these results were valid and presentable, a second BMP set was prepared and similar experiments were conducted. Similarly, anaerobic seed and waste activated sludge were settled, and WAS was split into 6 parts, each part subjected to different sonication duration (for 0, 5, 10, 15, 20 and 25 minutes). Again, F/M ratio was set to 1 (g VS/g VSS), and the TS, TSS, VS and VSS concentrations were measured to determine the mixing volumes. Given in Table 3.5 are the results of these analyses.

Table 3.5: Solids concentrations of the sludge samples prepared for the second BMP test

Sludge Type	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	TSS/TS (%)	VSS/VS (%)	VS/TS (%)	VSS/TSS (%)
Anaerobic Seed	22527	11633	21800	11388	51.6	52.2	96.8	97.9
WAS - No Sonic.	11453	9033	9151	7254	78.9	79.3	79.9	80.3
WAS - 5 Min. Sonic.	11053	8547	9042	7196	77.3	79.6	81.8	84.2
WAS - 10 Min. Sonic.	11273	8780	9098	7243	77.9	79.6	80.7	82.5
WAS - 15 Min. Sonic.	11073	8573	8947	7150	77.4	79.9	80.8	83.4
WAS - 20 Min. Sonic.	11433	8827	9044	6832	77.2	75.5	79.1	77.4
WAS - 25 Min. Sonic.	11513	8853	9222	6799	76.9	73.7	80.1	76.8

For this BMP set, serum bottles of 275 mL volume, with 200 mL active volume, were used as well. This set also has six different WAS samples after sonication, and the seed control group, a total of seven sludge types. The preparation of the bottles was different this time however. Instead of preparing a large volume then splitting into bottles and using the remainder for the analyses, six bottles were prepared separately, for each sludge type. Of these six bottles, three were used in the BMP assay and the remaining three were used to find the initial calorific values and elemental compositions. Once prepared, each bottle had 217 mL volume of mixture in it. 17 mL of this total volume was taken right away for the determination of the initial TS, VS, ash and COD concentrations. Given in Table 3.6 are the mixing volumes to achieve the designated F/M ratio of 1 (g VS/g VSS).

Table 3.6: Composition of the mixtures, prepared for the second BMP test

Mixture	**Label**	Seed Vol. (mL)	Food Vol. (mL)	Distilled Water (mL)	Total Vol. (mL)
Seed	**S**	93.0	0.0	124.0	217.0
Seed + WAS - No Sonic.	**U0**	93.0	117.2	6.8	217.0
Seed + WAS - 5 Min. Sonic.	**U5**	93.0	123.9	0.1	217.0
Seed + WAS - 10 Min. Sonic.	**U10**	93.0	120.6	3.4	217.0
Seed + WAS - 15 Min. Sonic.	**U15**	93.0	123.5	0.5	217.0
Seed + WAS - 20 Min. Sonic.	**U20**	93.0	120.0	4.0	217.0
Seed + WAS - 25 Min. Sonic.	**U25**	93.0	119.6	4.4	217.0

Same as the first BMP set, after samples were bottled, they were purged for 10 minutes using nitrogen gas at 99% purity. Afterwards, the caps were sealed and bottles were incubated at 35°C, while shaking at 125 rpm. Parameters measured during the second test, and their measurement frequencies are given in Table 3.7. Measurements related to biogas were carried out daily for the first two weeks. From then on, measurement frequency decreased with the decreasing biogas, eventually stopping at day 61, when gas production ceased.

Table 3.7: Parameters measured during the second BMP set along with their measurement frequencies.

Parameter	Frequency
TS (mg/L)	Before and after anaerobic digestion (days 0 and 61 respectively).
VS (mg/L)	
COD (mg/L)	
Ash (mg/L)	
pH	
CV (cal/g)	
Biogas Volume (mL)	Days 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 18, 21, 25, 31, 38, 42, 61.
Biogas Composition (% CH_4, % CO_2, % N_2)	

3.3.3. Anaerobic Batch Reactors

After the completion of the BMP tests, it was decided that bigger scale anaerobic batch reactors should be used to see how the parameters that were measured only before and after anaerobic digestion were changing during treatment. Following the results of the BMP tests, a sonication time of 10 minutes was agreed upon to continue with experiments, as it provided the optimal increase in biogas and methane yield.

Sludge samples acquired for this experiment set were subjected to centrifugation for 5 minutes at 4000 rpm following the settling to increase the solids concentrations further (the liquid portion after settling and centrifugation was discarded). Then, half of the concentrated WAS sample was sonicated for 10 minutes. Solids concentrations for the anaerobic seed, WAS and sonicated WAS are given below in Table 3.8.

Table 3.8: Solids concentrations of the sludge samples, prepared for the anaerobic reactors

Sludge Type	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	TSS/TS (%)	VSS/VS (%)	VS/TS (%)	VSS/TSS (%)
Anaerobic Seed	39090	37810	23760	20625	96.7	86.8	60.8	54.5
WAS - No Sonic.	33810	31255	24870	22430	92.4	90.2	73.6	71.8
WAS - 10 Min. Sonic.	35570	32640	25370	23190	91.8	91.4	71.3	71.0

As reactors, glass bottles of 3 L were used with effective volumes of 2.56 L for non-sonicated sludge, and 2.54 L for sonicated sludge. Following the previous BMP tests, F/M was again set to 1 (g VS/g VSS). To demonstrate the repeatability, two sets of reactors were prepared for each sludge type. This time, anaerobic seed control was not used, yielding a total of four reactors. Given in Table 3.9 are the mixture volumes, satisfying the F/M ratio.

Table 3.9: Composition of the mixtures, prepared for the anaerobic batch reactors.

Mixture	**Label**	Seed Vol. (L)	Food Vol. (L)	Total Vol. (L)
Seed + WAS - No Sonic.	**U0A**	1.40	1.16	2.56
Seed + WAS - No Sonic.	**U0B**	1.40	1.16	2.56
Seed + WAS - 10 Min. Sonic.	**U10A**	1.40	1.14	2.54
Seed + WAS - 10 Min. Sonic.	**U10B**	1.40	1.14	2.54

Through their caps, the glass bottles were connected to graduated cylindrical gas collection units which housed a brine solution consisting of 10% NaCl (w/v) and 2% H_2SO_4 (v/v) to prevent the dissolution of the produced biogas. Magnetic stirrers were placed in bottles to provide mixing during digestion. Figure 3.4 depicts the working reactor setup with the gas collection unit and the stirrer. After the sludge mixtures were prepared, they were placed inside the reactors and purged with nitrogen gas at 99% purity for 10 minutes. Then, the caps were sealed and the reactors were left to incubate in a constant temperature room, at 35°C. Sludge sampling was done through a sampling port at the base of the reactors; a 50 mL syringe was used to suck the desired sample volume out. As biogas was produced, it would push the marked brine level down, showing the difference between then and the previous measurement. After the produced biogas level was recorded, a vacuum pump was used to revert the brine level back to its initial position.

Figure 3.4: The reactor setup including the gas collection unit and the stirrer.

Reactor operation was continued until the gas production became negligible, and then reactors were terminated. These reactors were operated for a total of 71 days, the measured parameters and their measurement frequencies are reported in Table 3.10 below.

Table 3.10: Parameters measured for the anaerobic batch reactors, along with their measurement frequencies

Parameter	Frequency
TS (mg/L) VS (mg/L) Ash (mg/L) pH Biogas Volume (mL) Biogas Composition (% CH_4, % CO_2, % N_2)	Days 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 18, 20, 23, 25, 30, 35, 41, 65, 71
COD (mg/L) CV (cal/g) Elemental Analysis (%C, %H, %N)	Days 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 23, 30, 35, 41, 65, 71

3.4. Evaluation of Energy Potential of Sludge

As the primary purpose of this study is to define and quantify the maximum energy that can be generated by sludge, measuring calorific value, along with other parameters indicating fuel properties, is important. For both of the BMP tests, calorific value was measured before and after anaerobic treatment, whereas, sampling sludge from the larger scale anaerobic reactors during the course of treatment enabled documentation of continuous changes in both calorific value and other parameters as anaerobic degradation progressed.

Energy of the combustion of biogas was also considered, since it constitutes another energy type that can be harvested from sludge. Methane, being the main combustible portion of biogas, has a calorific value 50 MJ/kg. Dividing this value by methane's density at 35°C and 1 atm pressure (conditions of the produced methane, 0.6234 g/L) yields 31.17 J/mL. This value was then used to calculate the total energy from methane, as part of the total energy yield from sludge.

Energy consumptions of the sludge handling processes were calculated along with sludge and methane combustion. Their calculation methods, related assumptions and the complete analyses are given in detail, in Chapter 5.

3.5. Analytical Methods

Throughout the course of the experiments, the following parameters were measured for sludge: TS, VS, TSS, VSS, COD, sCOD, pH, ash content, calorific value and elemental composition. As for the produced biogas, the volume and its composition were tracked.

3.5.1. Solids Characterization

During the experiments, TS, VS, TSS and VSS analyses were conducted frequently. For the former two, Standard Methods 2540B and 2540E were used, respectively, whereas, for the latter two, Standard Methods 2540D and 2540E were used, respectively (APHA, AWWA, and WEF, 2005). Analyses were done in duplicates.

3.5.2. Chemical Oxygen Demand

Both soluble and total COD measurements were done using HACH LCK-514 kits (100-2000 mg/L) and HACH DR 3900 spectrophotometer (Hach Company, Colorado, USA), following the US Environmental Protection Agency approved dichromate method (Jirka and Carter, 1975). For soluble COD, sludge was filtered through Millipore (Merck Millipore, Massachusetts, USA) filter papers with 0.45 µm-pores, then the filtrate was used in the COD experiment. All measurements were done in either duplicates or triplicates.

3.5.3. Ash Content

Ash contents of the sludge samples were found after combusting the samples at 750°C, for two hours, in accordance with ASTM Standard Method D3174-12 (ASTM, 2012).

3.5.4. pH Measurements

pH of the sludge samples were determined using CyberScan PC 510 pH-meter with an EC-PH510/21S probe (Eutech Instruments Pte Ltd., Spain), following Standard Method 4500H (APHA, AWWA, WEF, 2005). Calibration was done using standard solutions with pH values of 4, 7 and 10, before the analyses.

3.5.5. Gas Volume and Composition

For both of the BMP assays, a water displacement unit was used to measure the produced biogas volume. Normally, as biogas is produced inside the serum bottle, the pressure inside of the bottle increases because the sealed bottle has a constant volume. Once it is connected to the water displacement unit via a needle (that does not compromise the integrity of the air-tight seal after it is removed), pressure of the gas decreases to atmospheric pressure, and the volume of the displaced water indicates the produced gas amount. The same principle is used in the gas collection columns of the reactors; produced biogas replaces the water (or brine, for this case), and the water level difference shows the produced amount.

The composition of the biogas was determined using Agilent Technologies 6890N Gas Chromatograph (Agilent Technologies, California, USA) with thermal conductivity detector (TCD). The device was equipped with a HP-Plot Q capillary column with dimensions of 30.0 m x 530 µm x 40.0 µm. Carrier gas was helium with a flow rate of 29 cm/s. Measurement program was set to initiate the measurement at 45°C for the first minute, then, the temperature was increased to 65°C at a rate of 10°C/min. For calibration, compositions of two different calibration standards consisting of 65% methane, 25% carbon dioxide, 10% nitrogen and 25% methane, 55% carbon dioxide, 20% nitrogen, respectively, were measured. The measured gas compositions were corrected daily with the measured standards. The injections were done using a Hamilton Samplelock syringe (Hamilton Company, Nevada, USA) of 500 μL volume. Measurements were done in triplicates.

3.5.6. Calorific Value

To determine the calorific value, a Leco AC 500 Bomb Calorimeter (LECO Corporation, Michigan, USA) was used. Collected sludge samples were first dried at 105°C, then sieved through a 60 mesh size sieve to minimize the effect of different particle sizes. Once the samples were ready, they were first weighed, then placed in a sealed vessel, or the bomb, and were pressurized with 99.99% purity oxygen. Calorific value can be found from the temperature rise from the combustion of the sludge and oxygen mixture.

3.5.7. Elemental Analysis

Similar to the determination of the calorific value, sludge samples were first dried at 105°C then sieved using a 60 mesh size sieve. After the preparation of the samples and determination of their weight, they were placed in the auto-sampler of Leco Truspec CHN analyzer (LECO Corporation, Michigan, USA), where the carbon, hydrogen and nitrogen content of the sludge is determined.

CHAPTER 4

RESULTS OF THE EXPERIMENTS

4.1. Results of BMP Set 1

The first set of the BMP experiments were run for 67 days. Measured parameters include biogas volume and composition, TS, VS, COD, pH, calorific value and ash content. Changes in these parameters and the overall results are presented in the sections below.

4.1.1. Effects of Ultrasound Pretreatment on Soluble COD Concentrations

Figure 4.1 shows the changes in the sCOD concentrations of the samples with respect to sonication duration. It can be seen from the graph that sCOD concentrations increase up to 15 minutes of sonication. From then on, the concentrations start to decrease until the 20 minutes mark, and once again increase when the duration is set to 25 minutes. This behavior is consistent with the studies conducted by Show et al. (2006) where sCOD concentrations have increased by 100% after 1 minute of sonication and Apul and Sanin (2010), where a similar decrease in sCOD after 15 minutes mark was observed. This phenomenon was attributed to complex thermal and sono-chemical reactions occurring during sonication, which may lead to recapturing of organics within the floc structure (Apul and Sanin, 2010).

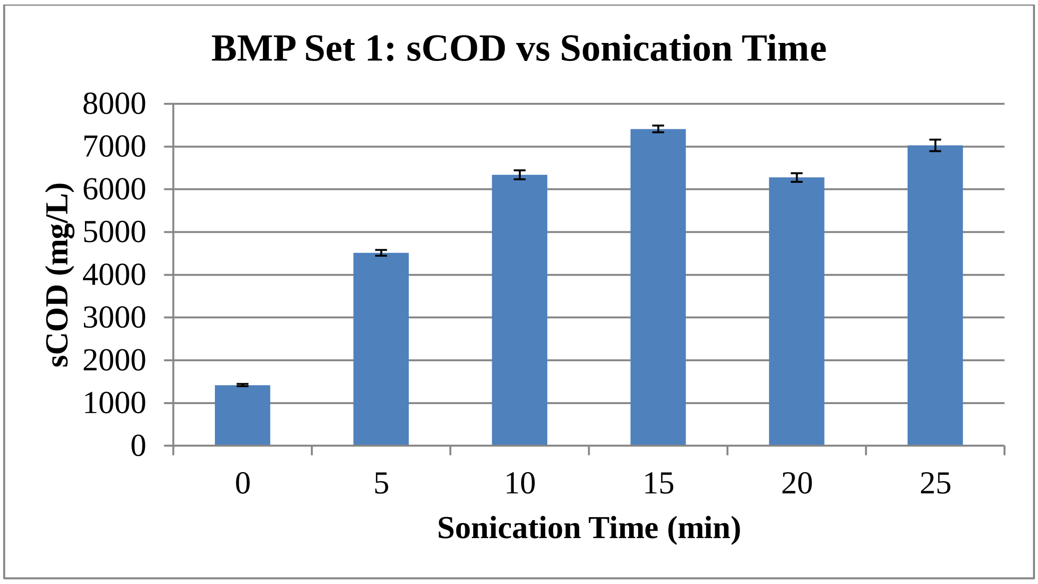


Figure 4.1: Soluble COD concentrations with respect to sonication time for BMP set 1.

4.1.2. Biogas and Methane Productions

For the first 17 days, gas production was measured daily using a water displacement unit. After that point, frequency of measurements was decreased as gas production decreased. Measurements were ceased after the 67th day due to negligible gas production. Figure 4.2 shows the cumulative biogas production, while Figure 4.3 depicts the daily biogas production for the first 17 days. Values shown here are the averages of three replicates, for the given sludge mixture.

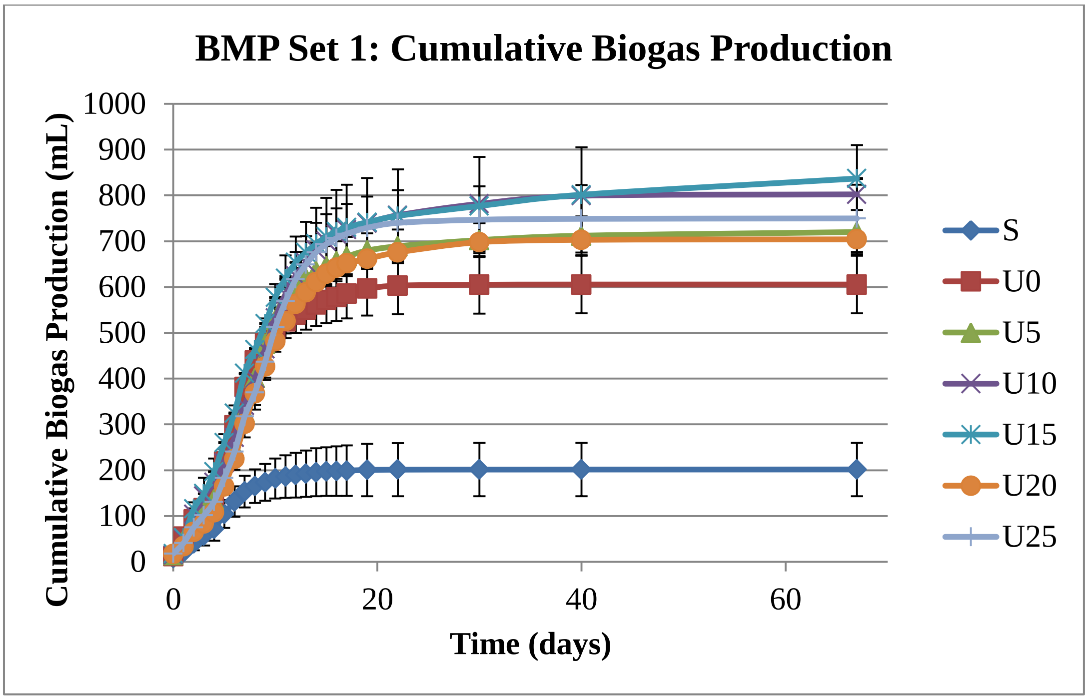


Figure 4.2: Cumulative biogas production of different sludge mixtures from BMP Set 1.

Comparing the total biogas production amounts, all of the samples containing pretreated sludge yielded more biogas than non-sonicated sludge. At reactor termination highest production was from the sample that was sonicated for 15 minutes (U15) (836.9 mL) which was 38% higher than that of the non-pretreated sample. It was closely followed by 10 minutes sonicated sludge (U10) (802.3 mL), which produced 33% more than the control group. Rest of the samples were as follows; 749.7 mL from 25 minutes (U25), 720.0 mL from 5 minutes (U5), 704.1 mL from 20 minutes (U20) of sonication and 605.4 mL from the control group (U0), which did not have a pretreatment procedure applied to it. Results indicate that 10 minutes of sonication seems optimal; while it yields less biogas than 15 minutes of sonication, it needs only two thirds of the energy required for sonication. It should also be noted that the error boundaries of these two times are overlapping with each other. As for the most inefficient sonication duration, 20 minutes and 25 minutes actually show a lower yield compared to lower sonication durations, making them obsolete and impractical to use.

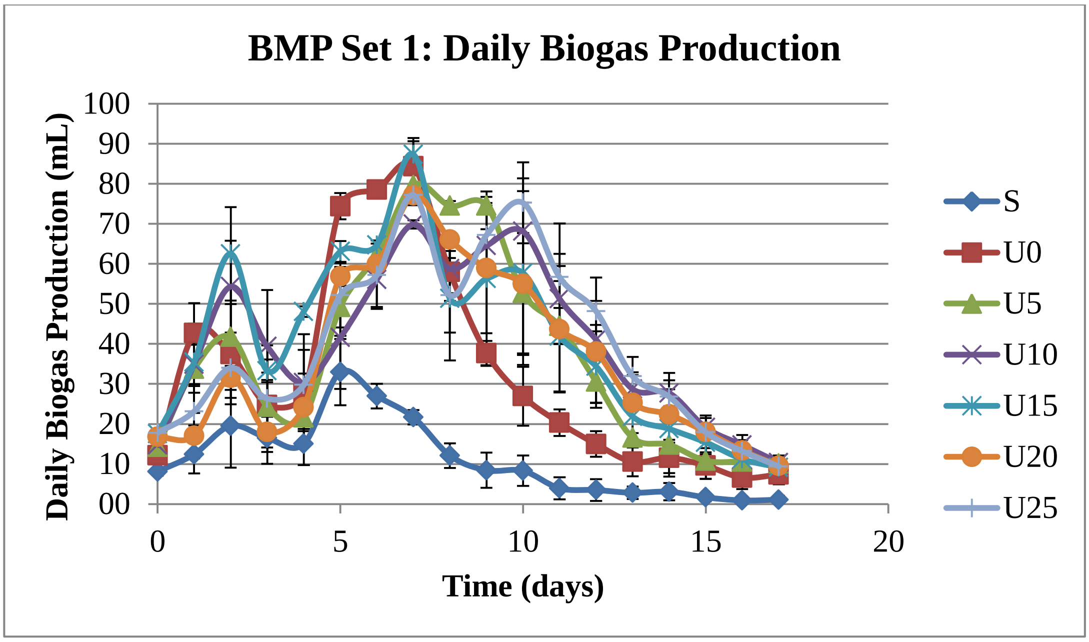


Figure 4.3: Daily biogas production of different sludge mixtures from BMP Set 1.

It can be seen from Figure 4.3 that, for most of the samples, peaks are occurring around the same time; days 2 and 7. Also, similar shapes of the curves representing different mixtures indicate that none of the samples had problems with acclimation. Because of sonication and the increased sCOD concentration, sonicated samples show bigger peaks on day 2 and following day 7, their biogas production are higher.

Apart from the total volume of biogas produced, composition of the gas was also determined using gas chromatography. Then separate share of methane was calculated. Figure 4.4 shows the cumulative methane production over the total period of 67 days, while Figure 4.5 depicts daily methane production for the first 17 days. Similar to total biogas production, the values shown here are the averages of the three replicates of the same sludge mixture. On the whole, about 68% of the produced biogas was methane, for all sludge samples.

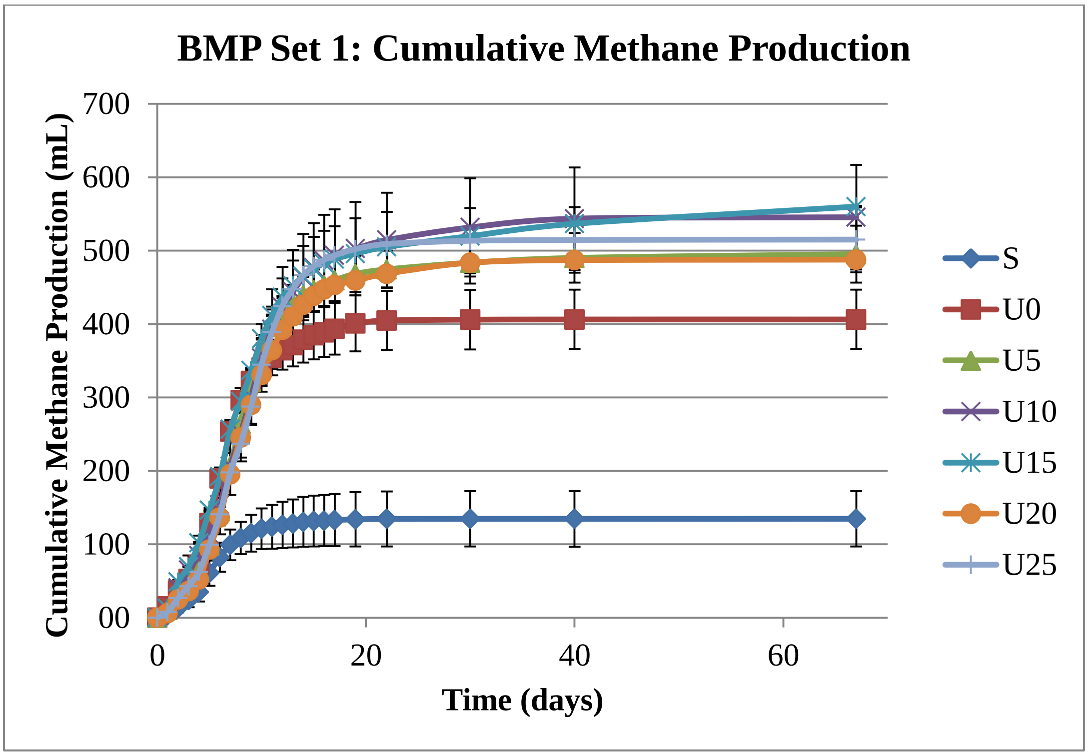


Figure 4.4: Cumulative methane production of different sludge mixtures from BMP Set 1.

For cumulative methane production, results indicate that the highest yield was from sludge sonicated for 15 minutes (560.0 mL), being 38% more than the control group. It was followed by 10 minutes of sonication time (545.5 mL) which was 34% higher than the non-pretreated sample. After these two, 25 minutes of ultrasound pretreatment yielded 515.1 mL, 5 minutes 495.3 mL, and 20 minutes sonicated reactors yielded 487.8 mL. The non-sonicated control group showed a production of 406.3 mL. Reactor including only the seed sludge produced much smaller quantity of methane which was about 30% of the non-sonicated reactor.

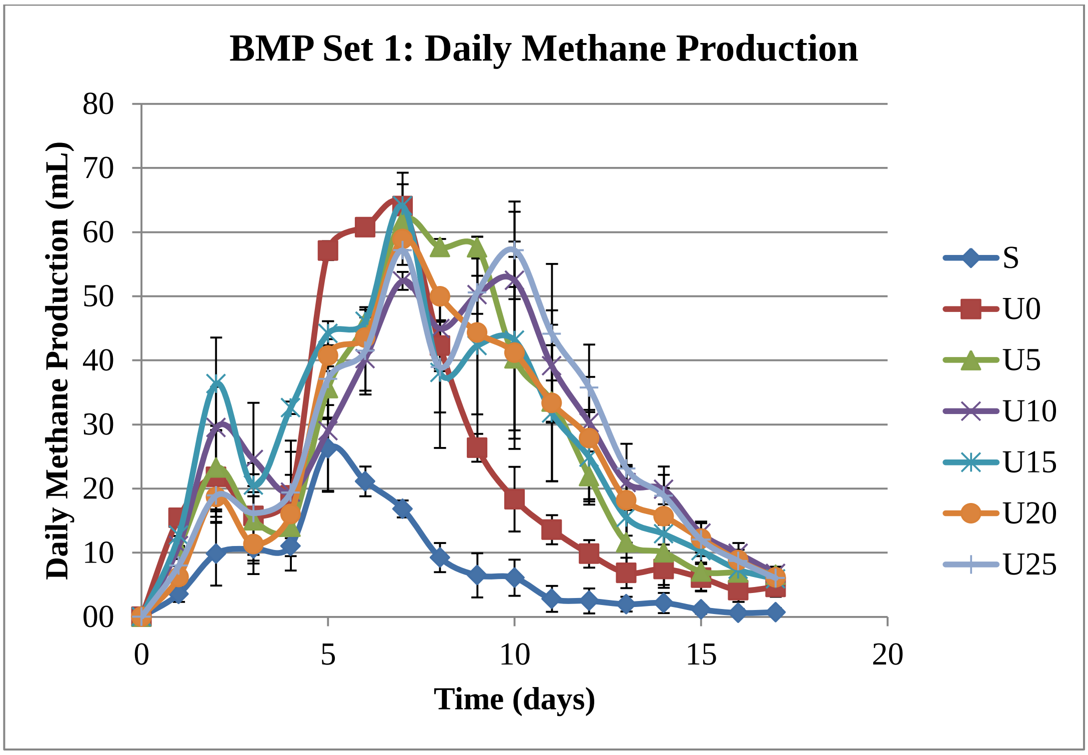


Figure 4.5: Daily methane production of different sludge mixtures from BMP Set 1.

Similar to the daily biogas production, main peaks on Figure 4.5 seem to be occurring on days 2 and 7. Sonicated sludge is known to have more of its organics solubilized (S. I. Pérez-Elvira et al., 2006). This effect is visible on Figures 4.3 and 4.5; sonicated samples – especially for 10 and 15 minutes – show a higher peak on day 2, indicating that the higher initial sCOD concentration had begun converting into biogas (and methane). Consequently, the control group shows a lower peak during day 2. However, once hydrolysis begins to show its effects starting with day 5, the control group shows a higher methane production than sonicated samples. They even out after day 7, and begin to steadily decrease towards the end of the measurements. This result shows that ultrasound pretreatment made more of the organics available for digestion, increasing the total biogas and methane productions.

The decrease of methane production when sonication time is increased beyond 15 minutes may have been caused by the decrease in soluble organics after that point. This is also reflected in the differences in sCOD concentrations following the pretreatment, presented in Figure 4.1. A possible reason for this phenomenon may be attributed to the way ultrasound treatment affects the organics in the sludge. The identified mechanisms like hydro-mechanical shearing effect, production of radicals, thermal decomposition of organics and increase in temperature (Wang, Wang, and Ji, 2005) may take part at different rates changing the final result depending on the sonication duration.

4.1.3. Post-Digestion Characterization and Fuel Properties

Shown in Table 4.1 are the initial and final TS and VS concentrations and their removal rates (as averages of three replicates). For all the samples, a TS removal of 41% was observed on the average. VS removal rates were between 57.3% for the non-pretreated control group and 53.5% for the sample that was sonicated for 25 minutes. Initial TS and VS concentrations were calculated using the measurements conducted for the determination of the F/M ratio. This fact seems to have affected the results, as the expectations were that removal rates would vary in accordance with methane production. As a result, for the second BMP set, this approach was abandoned, and direct measurements were conducted. On Figure 4.6, biogas produced per gram of volatile solids destroyed is shown. A trend similar to sCOD concentrations following sonication can be seen; produced biogas amount increases up to 15 minutes of sonication then starts decreasing with increased sonication duration. The typical yield valid primarily for already established full-scale digesters (with no pretreatment) is 0.8 L biogas/ g VS destroyed (WEF and ASCE/EWRI, 2009). For all samples, yields were below this baseline, which can be expected due to differences in operating conditions.

Table 4.1: Initial and final TS and VS concentrations and their removal rates during digestion, BMP Set 1. Subscripts “i” and “f” denote initial and final conditions, respectively.

Label	TS_i (mg/L)	TS_f (mg/L)	TS Removal (%)	VS_i (mg/L)	VS_f (mg/L)	VS Removal (%)
U0	16778	9450	43.7	11388	4867	57.3
U5	16803	9803	41.7	11388	5077	55.4
U10	16887	9877	41.5	11388	5077	55.4
U15	16963	10083	40.6	11388	5260	53.8
U20	16886	10157	39.9	11388	5167	54.6
U25	16991	10233	39.8	11388	5290	53.5
S	10114	6473	36.0	6174	3100	49.8

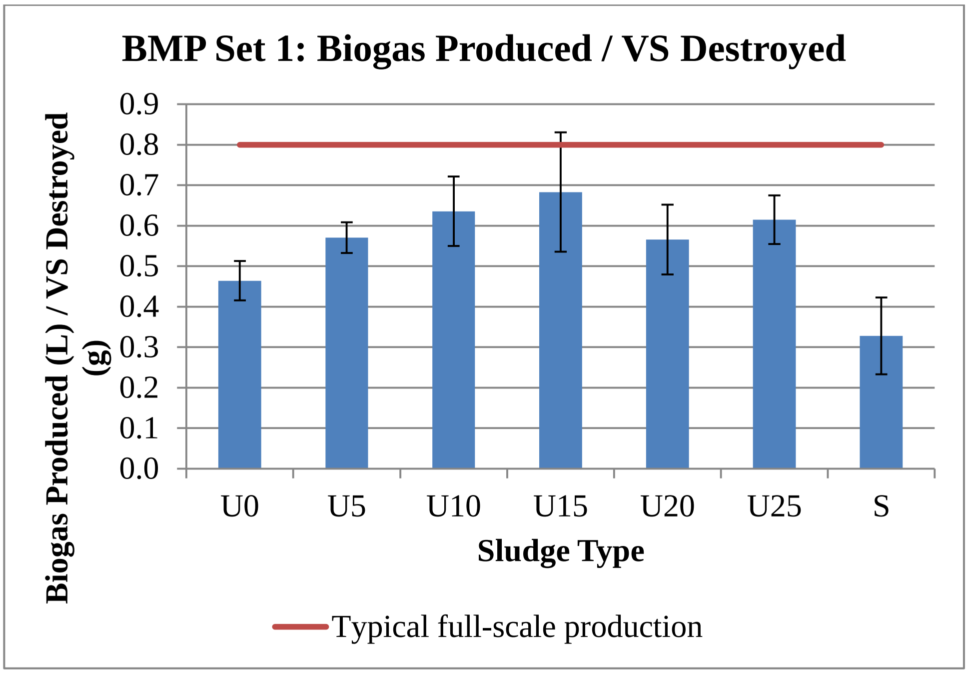


Figure 4.6: Biogas yield in liters per gram VS destroyed from BMP Set 1, compared to typical production in full-scale digesters.

COD concentrations were measured before and after anaerobic digestion. Given in Table 4.2 are the initial and final concentrations along with removal rates. On the average, a COD removal of 38% was observed, however, this amount varied significantly between different samples. 15 minutes of sonication which yielded the highest methane production, showed the lowest COD removal, while the non-pretreated control had over 35% removal. This discrepancy is thought to have resulted from using COD kits that were prepared as a part of the experiments, and for the second BMP set, kits bought directly from the supplier were used instead. Depicted in Figure 4.7 are the produced methane amounts per gram of COD destroyed as averages of the triplicate BMP reactors. 5 and 15 minutes of sonication yielded more than the theoretical maximum of 0.395 L/g COD destroyed at 35 °C and 1 atm (Speece, 1996). This also may have resulted from the inaccuracies of using COD kits. As for the other samples, being below this theoretical yield is expected, as it represents the absolute maximum, assuming that all the COD present is converted to methane.

Table 4.2: Initial and final COD concentrations and removal rates during digestion, BMP Set 1

Label	COD_i (mg/L)	COD_f (mg/L)	COD Removal (%)
U0	17550	11308	35.6
U5	17250	11483	33.4
U10	19950	11033	44.7
U15	17967	13000	27.6
U20	18767	11958	36.3
U25	22833	11333	50.4
S	9700	7550	22.2

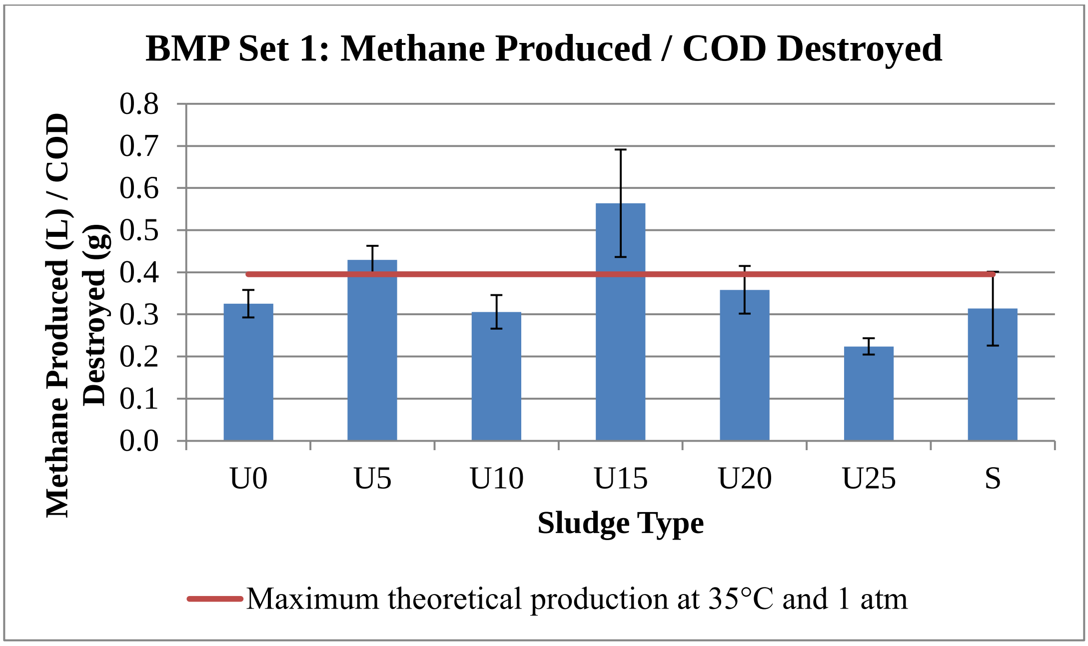


Figure 4.7: Methane yield in liters per gram COD destroyed from BMP Set 1, compared to maximum theoretical production.

Table 4.3 shows the changes in ash content of the sludge samples. The actual amount of ash within each sample did not seem to change significantly. The average ash concentration change was less than 1%. However, because of the reduction in total solids content, ash percent in the remaining solids increased from 26% to 44% of total dry solids.

Table 4.3: Initial and final ash concentrations as mg/L and % of dry solids, BMP Set 1

Label	Ash_i (mg/L)	Ash_i (%)	Ash_f (mg/L)	Ash_f (%)
U0	4240	25.3	4180	44.2
U5	4570	27.2	4313	44.2
U10	4380	25.9	4400	44.5
U15	4350	25.6	4430	43.9
U20	4480	26.5	4543	44.7
U25	4310	25.4	4540	44.4
S	3460	34.2	2990	46.2

In order to quantify the change in the energy potential of the sludge, calorific values of the sludge in each BMP bottle were measured before and after anaerobic digestion. Their average was taken and the results of these analyses are given in Table 4.4. Initially, samples could provide 16300 J/g, and digestion reduced this value by 28% on the average. In addition, because of the loss in total solids content, the loss in energy potential is magnified. In other words, both the calorific value and the combustible solids amount are reduced. The last column (lost energy) in Table 4.4 indicates this overall loss. A trend based on sonication duration was not observed.

Table 4.4: Initial and final calorific values of the samples along with the loss in the energy potential, BMP Set 1.

Label	CV_i (J/g)	CV_f (J/g)	CV Reduction (%)	TS Removal (%)	Lost Energy (%)
U0	16435	11757	28.5	43.7	59.7
U5	16113	11615	27.9	41.7	57.9
U10	16284	11711	28.1	41.5	57.9
U15	16355	11799	27.9	40.6	57.1
U20	16238	11765	27.5	39.9	56.4
U25	16175	11665	27.9	39.8	56.6
S	14853	10862	26.9	36.0	53.2

Results of the first BMP set indicate that sonication beyond 15 minutes does not produce any additional benefit, but rather reduce the biogas and methane yield while increasing the energy requirement of the pretreatment process. For biogas and methane productions, while the best results were seen for 15 minutes of sonication, 10 minutes of sonication time also showed comparable increase in gas production over the control group while consuming only two thirds of the energy.

Another point to be made about the first BMP set is that, the variability between the samples was not negligible, also indicated by the error bars that can be seen in Figures 4.2, 4.3, 4.4 and 4.5. To verify that 10 minutes of sonication is the optimum pretreatment level, and better display the differences in VS and COD reductions resulting from different sonication durations, this BMP experiment was repeated using the same WAS and anaerobic seed samples and the F/M ratio.

4.2. Results of BMP Set 2

The second set of the BMP experiments were run for 61 days, and were terminated as biogas productions ceased. Same as the first set, measured parameters include biogas volume and composition, TS, VS, COD, pH, calorific value, ash content and additionally, elemental composition. Changes in these parameters and the overall results are presented in the sections below.

4.2.1. Effects of Ultrasound Pretreatment on Soluble COD Concentrations

Figure 4.8 shows the changes in the sCOD concentrations of the samples of the second BMP test, with respect to sonication duration. Reflecting the results of the first BMP set, sCOD concentrations increase rapidly, up to 15 minutes of sonication, then decrease until 20 minutes and increase once again up to 25 minutes. This behavior was observed for other measured parameters such as VS and COD reductions and biogas and methane productions.

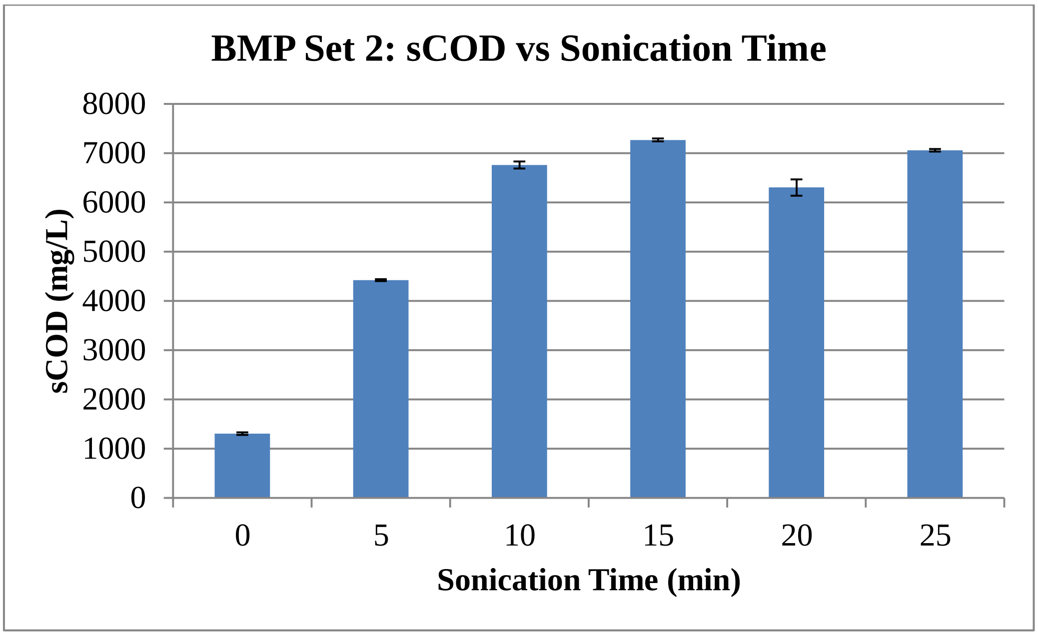


Figure 4.8: Soluble COD concentrations with respect to sonication time for BMP set 2.

4.2.2. Biogas and Methane Productions

For the first 14 days, gas production (and its composition) was measured daily. Then, frequency of the measurements were decreased and the experiment was terminated on day 61. Figure 4.9 shows the cumulative biogas production, while Figure 4.10 depicts the daily biogas production for the first 14 days. Values shown here are the averages of three replicates, for the given sludge mixture.

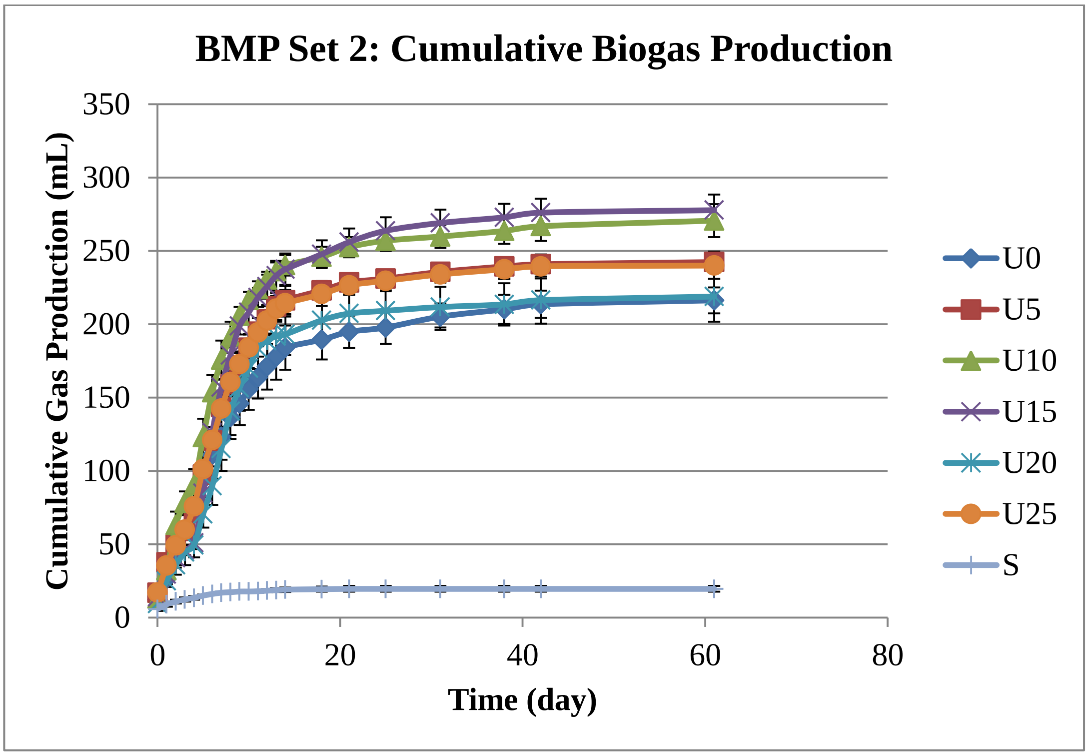


Figure 4.9: Cumulative biogas production of different sludge mixtures from BMP Set 2.

Comparison of total gas production amounts indicated that all pretreated sludge samples yielded more biogas than the non-sonicated sludge as expected. Highest production was from the sample that was sonicated for 15 minutes (U15) (277.7

mL). This was closely followed by the 10 minutes sonicated sludge (U10) (270.6 mL). Gas productions for the rest of the samples were as follows; 242.4 mL from 5 minutes of sonication (U5), 240.0 mL from 25 minutes (U25), and 218.8 mL from 20 minutes (U20). Lastly, 216.3 mL gas was produced in the control group (U0) which did not receive pretreatment. Examining these values, it seemed like 10 minutes of sonication was once again the optimal, showing a 25% increase in gas production. Although 10 minutes of sonication did not yield more biogas than 15 minutes of sonication, it required only two thirds of the energy in comparison. Similar to the results from the first set, 20 and 25 minutes of sonication resulted in lower biogas yield. A significant improvement over the first set was achieved on the variability of the results. For this set, standard deviations indicated on Figure 4.9 were less than 10% of the averages of the three replicates.

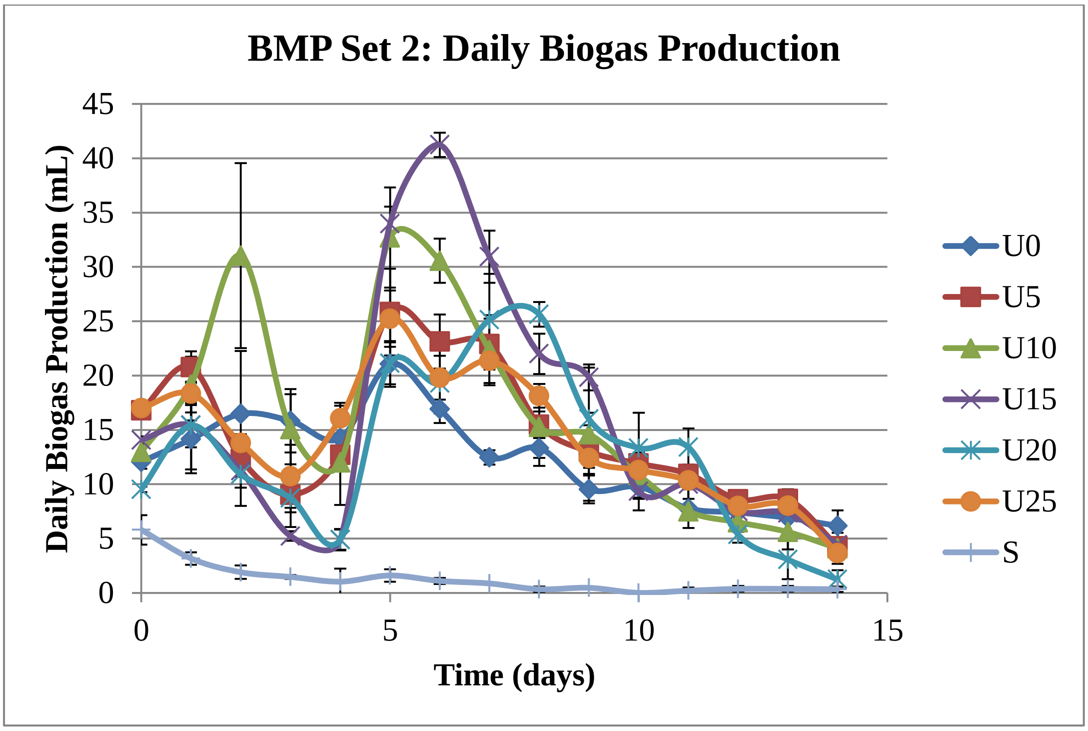


Figure 4.10: Daily biogas production of different sludge mixtures from BMP Set 2.

As seen on Figure 4.10, local maximums have been observed on days 1-2 and 5-6. First set of the peaks indicate the conversion of soluble organics into biogas. The following reduction on days 3 and 4 may have resulted from that hydrolysis step is in progress and once a sufficient hydrolysis level is reached, the second set of peaks is seen on days 5 and 6. This behavior is similar to the first BMP set, further showing that the seed was acclimated to this WAS.

Gas chromatography was used to determine the composition of the produced biogas. Figure 4.11 shows the cumulative methane production over the total period of 61 days, while Figure 4.12 depicts daily methane production for the first 14 days. Similar to biogas production, the values shown here are the averages of the three replicates. On the average, from all the WAS samples, 65% of the produced biogas was methane.

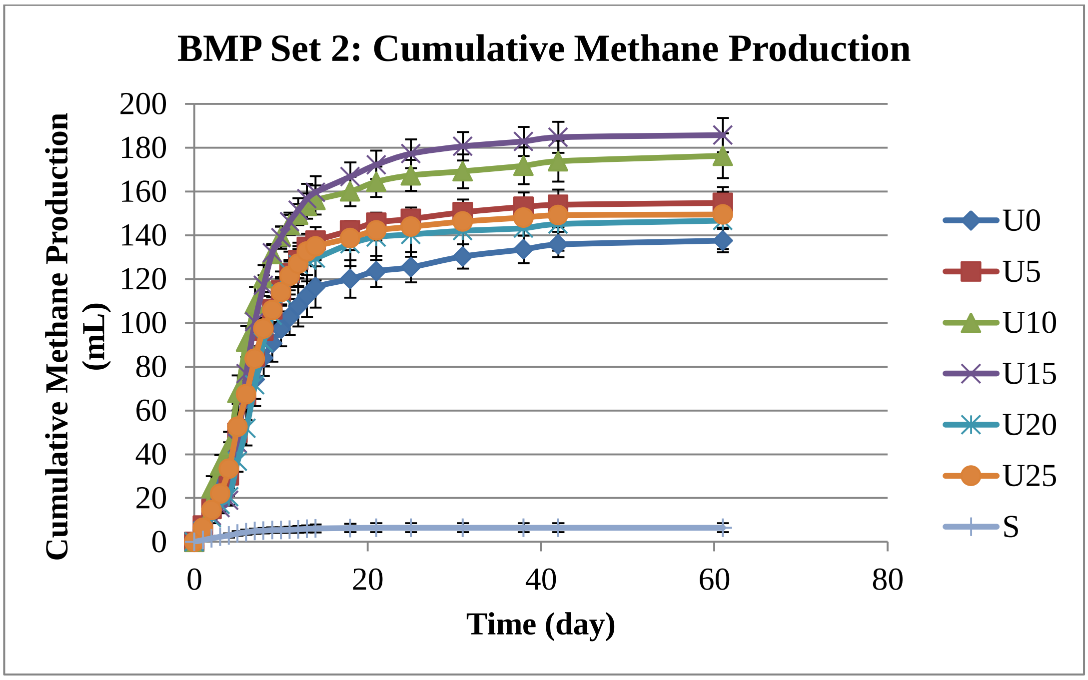


Figure 4.11: Cumulative methane production of different sludge mixtures from BMP Set 2.

For cumulative methane production, the highest yield was from the sludge sonicated for 15 minutes (185.7 mL), followed by 10 minutes of sonication time (176.3 mL). After these two, 5 minutes of ultrasound pretreatment yielded 154.8 mL. 25 and 20 minutes of sonication resulted in 149.5 mL, and 146.7 mL gas production, respectively. The control group (no pretreatment) showed a production of 137.6 mL. This situation is quite similar to the total gas production results, further proving that 10 minutes of sonication was the optimal application with regards to consumed energy and produced methane. The decrease in biogas and methane production after 15 minutes of sonication time is observed once again, reflecting the decrease in sCOD concentration, depicted in Figure 4.10. Reactor with only seed sludge produced methane of about 5% of that in control reactors, indicating that the seed contributed to the produced gas minimally.

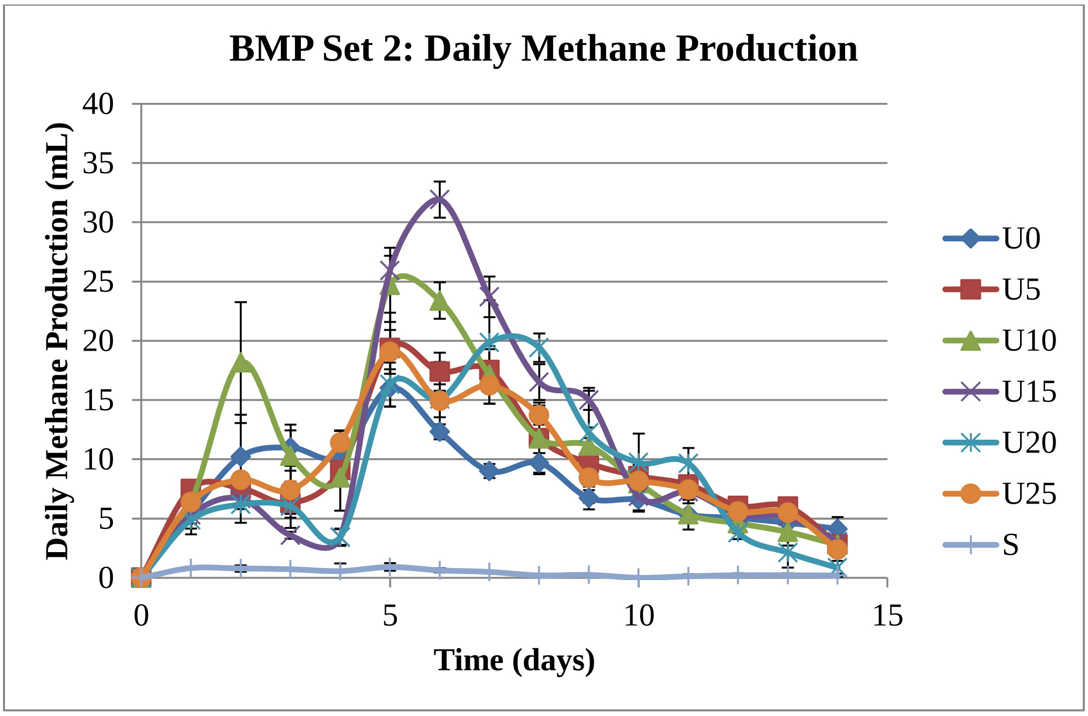


Figure 4.12: Daily methane production of different sludge mixtures from BMP Set 1.

Similar to the daily biogas production, main peaks on Figure 4.12 seem to be occurring on days 1-2 and 5-6. As demonstrated before in the first BMP set, sonicated samples show bigger peaks, indicating the solubilization of organics. First peak on days 1 and 2 are resulting from the consumption of the sCOD, while the higher peaks on days 5 and 6 are caused by the near completion of hydrolysis of complex organics. After this point, methane production steadily decreases towards the end of the measurements.

4.2.3. Post-Digestion Characterization and Fuel Properties

Shown in Table 4.5 are the initial and final TS and VS concentrations as averages of three replicates. For all the samples, a TS removal of 25% was observed on the average. This value was consistent with the ones reported in literature (Apul and Sanin, 2010). Different from the first set, VS removal rates seemed to vary in accordance with the biogas and methane production of corresponding sonication duration. In other words, 15 minutes of sonication which yielded the highest gas production values also showed the best VS destruction rate at 45.0%. Other samples displayed similar VS removal rates; 10 minutes of sonication showed a 43.9% reduction, 5 and 25 minutes followed with 43.1%, and 20 minutes of sonication yielded 42.4% removal. Samples that were not subjected to pretreatment displayed 41.0% VS removal, the lowest of them all. On Figure 4.13, biogas produced per gram of volatile solids destroyed is shown. A trend similar to sCOD concentrations is seen in biogas and methane productions and VS removals; produced biogas amount increases up to 15 minutes of sonication then starts to decrease with increased sonication duration. In comparison to the typical value of 0.8 L / g VS destroyed (WEF and ASCE/EWRI, 2009), the yields of all the samples were significantly lower, more than that was observed in the first set. This is expected as the typical yield is calculated from the averages of full-scale digesters, and the initial solids amount was lower than that of the first set. However, while the yield is lower than the full-scale value, it changes according to the sonication durations and the corresponding sCOD concentrations. Because of this, a comparison between different sludge types can be made. Supporting the previous BMP set's results, 10 and 15 minutes of sonication showed the highest yield, with 10 minutes being slightly ahead this time.

Table 4.5: Initial and final TS and VS concentrations and their removal rates during digestion, BMP Set 2.

Label	TS_i (mg/L)	TS_f (mg/L)	TS Removal (%)	VS_i (mg/L)	VS_f (mg/L)	VS Removal (%)
U0	15853	11982	24.4	9631	5684	41.0
U5	15996	11871	25.8	9849	5607	43.1
U10	15893	11633	26.8	9851	5529	43.9
U15	15982	11571	27.6	9953	5478	45.0
U20	15709	11602	26.1	9720	5596	42.4
U25	16118	11864	26.4	9973	5671	43.1
S	9876	8671	12.2	5058	3847	23.9

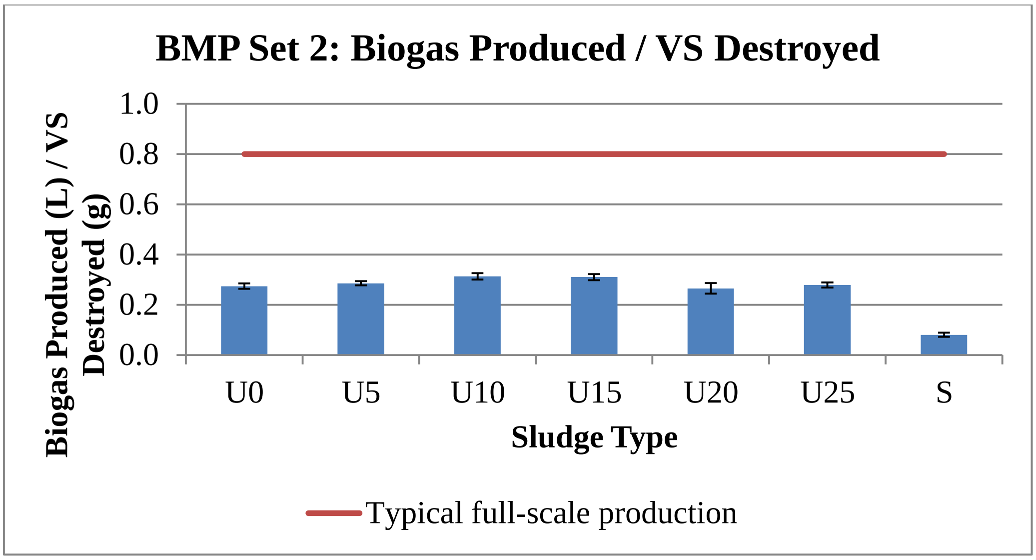


Figure 4.13: Biogas yield in liters per gram VS destroyed from BMP Set 2, compared to typical production.

Given in table 4.6 are the initial and final COD concentrations and removal rates for the second BMP set. On the average, COD removal rates ranged between 31.6% and 36.6%, similar to those that were reported in previous studies conducted by Köksoy and Sanin, (2010). Again reflecting the level of gas productions and VS removals, 15 minutes of sonication provided the highest removal rate, 10 minutes of sonication followed that with 36.0% removal, along with 5 minutes at 34.6% and 25 minutes at 33.7%. Different from VS removals and gas productions, however, COD removal in the non-pretreated WAS surpassed that of the pretreated for 20 minutes. This is another indication that increased sonication times may not necessarily yield more desirable results. In Figure 4.14, methane productions per gram of COD destroyed from the samples are given as averages of three replicates. Similar to the specific biogas yield, the results are less than the maximum yield of 0.395 L methane/g COD destroyed (Speece, 1996). This is expected as the theoretical maximum value is calculated assuming all the available COD is converted to methane, and this is not achievable with sewage sludge (Speece, 1996). When compared to one another, it can be seen that, once again, the highest specific yield was achieved for 15 minutes of sonication, followed closely by 10 minutes.

Table 4.6: Initial and final COD concentrations and removal rates during digestion, BMP Set 2.

Label	COD_i (mg/L)	COD_f (mg/L)	COD Removal (%)
U0	15200	10242	32.6
U5	15675	10250	34.6
U10	15942	10208	36.0
U15	16200	10275	36.6
U20	15783	10792	31.6
U25	16067	10658	33.7
S	8208	7317	10.9

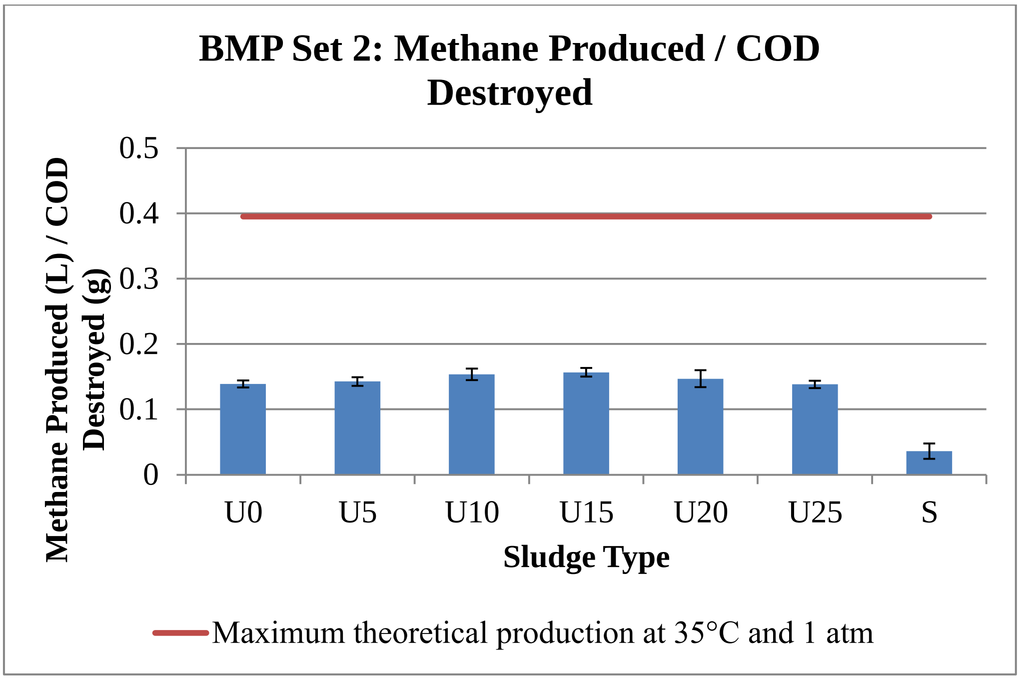


Figure 4.14: Methane yield in liters per gram COD destroyed from BMP Set 2, compared to maximum theoretical production.

Ash contents of the samples were measured before and after digestion, the change in between remained less than 2%. However, as the TS concentrations decreased, ash portion relative to the remaining solids increased. Given in Table 4.7 are the initial and final ash contents in both mg/L and % of TS. Since both BMP tests show the same result, it can be concluded that anaerobic digestion, regardless of sonication duration, does not change the ash content inherently present in the sludge. Additionally, for this BMP set, carbon, nitrogen and hydrogen content of the sludge samples pre- and post-digestion were measured, results of which are given in Table 4.8. Even though the carbon content seems to have increased by a minuscule amount for most of the samples, when the reduction in total solids is considered, there actually is a loss, part of which was converted into the components of the biogas. Alongside the loss in total solids, hydrogen content of the sludge was reduced as well as a part of the stoichiometry of anaerobic digestion. Nitrogen content of the sludge remained more or less constant and was affected only by the reduction in total solids.

Table 4.7: Initial and final ash concentrations as mg/L and % of dry solids, BMP Set 2.

Label	Ash_i (mg/L)	Ash_i (%)	Ash_f (mg/L)	Ash_f (%)
U0	5342	33.7	5547	46.3
U5	5387	33.7	5576	47.0
U10	5371	33.8	5509	47.4
U15	5369	33.6	5536	47.8
U20	5427	34.5	5491	47.3
U25	5522	34.3	5649	47.6
S	4196	42.5	4256	49.1

Table 4.8: Initial and final C, H and N contents as % of dry solids, BMP Set 2.

Label	C_i (%)	C_f (%)	H_i (%)	H_f (%)	N_i (%)	N_f (%)
U0	26.04	27.21	5.13	3.42	3.10	3.11
U5	26.45	27.39	5.21	3.34	2.99	3.04
U10	26.15	27.71	5.16	3.38	3.03	2.95
U15	26.03	27.53	5.16	3.37	2.99	3.02
U20	27.84	26.41	4.54	3.18	2.94	2.76
U25	26.68	26.51	4.97	3.21	3.00	2.80
S	24.99	26.76	4.84	3.14	2.89	2.66

For the second BMP set as well, calorific values of the sludge within the bottles were measured both before and after anaerobic digestion. Results of the analyses as averages of the three replicates are given in Table 4.9. Initially, measurements indicate an average of 13400 J/g, followed by an 18% reduction by digestion. In addition, as mentioned before with the results of BMP set 1, as both the total combustible solids and their calorific value is reduced, the loss in energy potential is magnified (column titled as "lost energy" in Table 4.9 indicates the total energy loss). Highest loss in the calorific value was observed for U25 as 19.4%, followed by U5 with 19.3%. When the removed TS was taken into account, the trend shifted to what can be observed from other parameters: an increase in energy loss up to 15 minutes of sonication, then a decrease afterwards. Similar to the results of TS, VS and COD analyses, all the sonicated samples showed a bigger overall energy loss than the non-pretreated control group.

Table 4.9: Initial and final calorific values of the samples along with the loss in the energy potential, BMP Set 2.

Label	CV_i (J/g)	CV_f (J/g)	CV Reduction (%)	TS Removal (%)	Lost Energy (%)
U0	13426	11029	17.9	24.4	37.9
U5	13401	10883	18.8	25.8	39.7
U10	13393	10807	19.3	26.8	40.9
U15	13502	10970	18.7	27.6	41.2
U20	13414	10945	18.4	26.1	39.7
U25	13468	10849	19.4	26.4	40.7
S	11527	10016	13.1	12.2	23.7

Results of the second BMP set further prove the point that sonication beyond 15 minutes does not produce any additional benefit, but rather reduce the biogas and methane yield, and VS and COD removal rate, while increasing the energy requirement of the pretreatment process. Examining the overall results, although 15 minutes of sonication showed the peak for all the examined parameters, 10 minutes sonication was significantly close. For methane production, U15 produced 185.7 mL while U10 had 176.3 mL. When VS and COD are concerned, U15 showed 45.0% VS removal and 36.6% COD removal, while U10 had 43.9% VS removal and 36.0% COD removal. Clearly, spending 50% more energy for longer sonication did not yield a significant benefit. Thus, verified with the results from both of the BMP sets, 10 minutes of ultrasound pretreatment was deemed optimal, and was chosen for the next step of the experiments.

4.3. Results of Anaerobic Batch Reactors

After the optimal sonication duration was determined as 10 minutes, a new experiment set was prepared. This time, the sizes of the reactors were increased from 0.2 L active volume to 2.5 L, allowing sampling as digestion progressed, primarily to quantify the changes in parameters during digestion. The same WAS and anaerobic seed samples were used to sustain consistency and this set of experiments was run until the biogas production ceased, on day 71. Measured parameters include biogas volume and composition, TS, VS, COD, pH, ash content, elemental composition and calorific value. Changes in these parameters and the overall results are presented in the sections below.

4.3.1. Effects of Ultrasound Pretreatment on Soluble COD Concentrations

Depicted in Figure 4.15 are the sCOD concentrations of the WAS samples used in anaerobic batch reactors. It can be seen that 10 minutes of ultrasound pretreatment increased the concentration by 340%, from 3000 mg/L to 13200 mg/L.

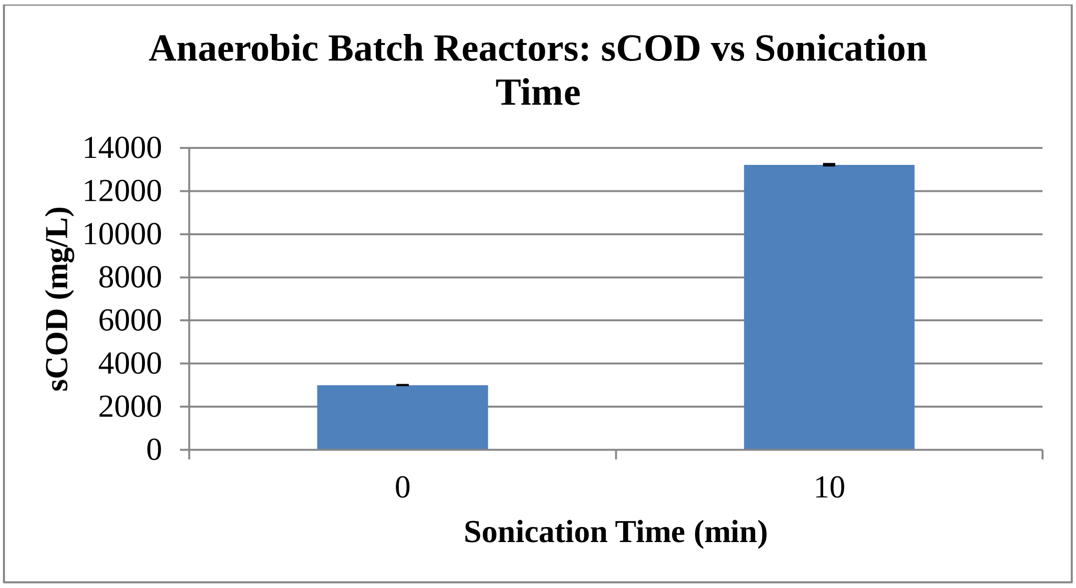


Figure 4.15: Soluble COD concentrations with respect to sonication time for anaerobic batch reactors.

4.3.2. Biogas and Methane Productions

Biogas generated from the reactors were collected in gas collection units, filled with a brine solution to prevent gas dissolution. For the first 16 days, samples from both the biogas and the sludge itself were taken daily for analyses, following this point, the frequency of sampling decreased as the daily changes became insignificant. Given in Figure 4.16 is the cumulative biogas generation from the four reactors over the duration of the experiment. On Figure 4.17, daily biogas production for the first 16 days is depicted.

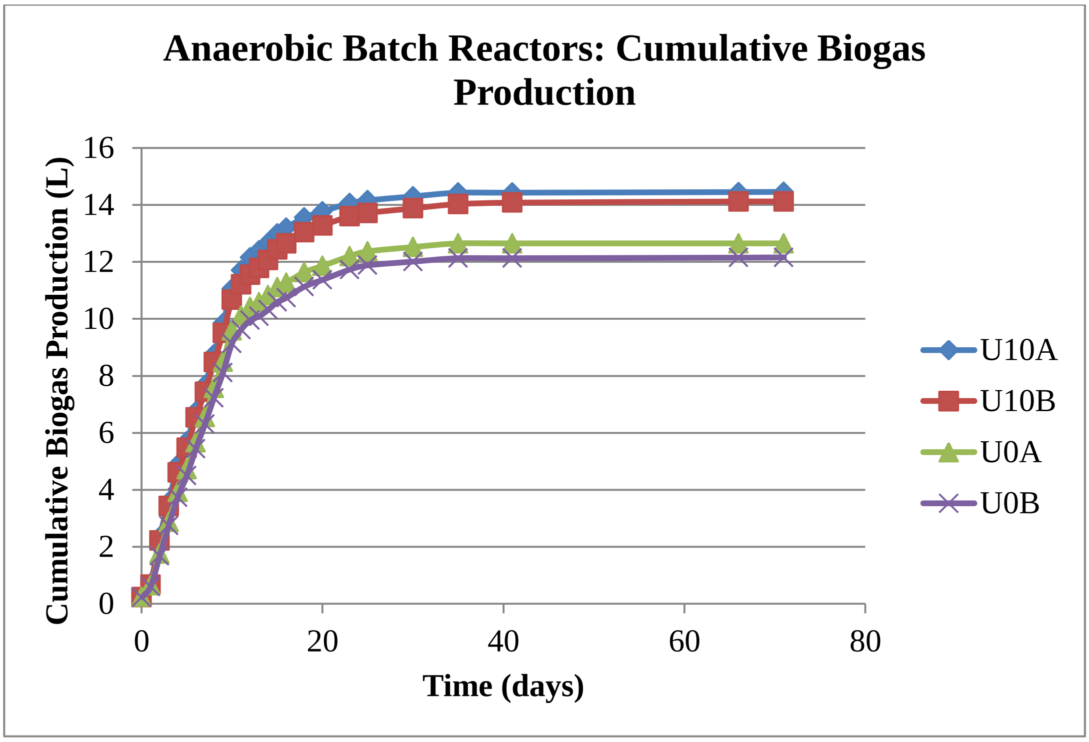


Figure 4.16: Cumulative biogas productions of sonicated and non-sonicated sludges from Anaerobic Batch Reactors.

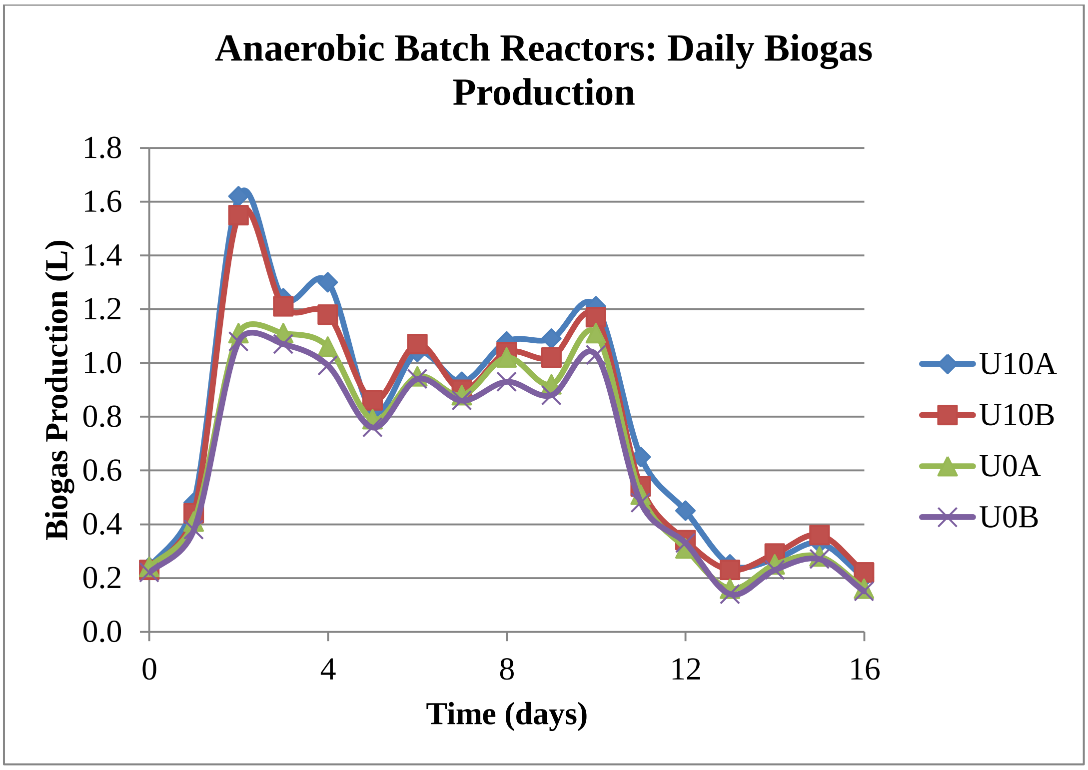


Figure 4.17: Daily biogas productions of sonicated and non-sonicated sludges from Anaerobic Batch Reactors.

As demonstrated before by the BMP sets, and once again visible in Figure 4.16, 10 minutes of sonication provided more biogas than the case of no sonication. Throughout the duration of the experiment, U10A and U10B which are the duplicate sonicated reactors produced 14.46 L and 14.12 L, respectively, compared to 12.65 L from U0A and 12.16 L from U0B, which were the duplicate control reactors. Compared to control reactors, reactors containing sonicated sludge exhibited an average increase of 15.2% in gas production. By day 16, more than 90% of the total biogas to be produced had been produced, indicating that the digestible portion of the sludge was almost fully consumed at this point. The daily production graph, presented in Figure 4.17 shows that the increase in sCOD because of sonication boosted the biogas produced on day 2 from 1.10 L to 1.59 L, a 44.5%

increase on the average. From then on, the daily productions from all four reactors followed a similar pattern, with sonicated reactors always producing slightly more biogas.

Similar to the biogas production, also agreeing with the results of the BMP tests, after 10 minutes of sonication, cumulative methane production increased by 32.1%; from U0A’s 6.74 L and U0B’s 6.31 L to 8.81 L for U10A and 8.43 L for U10B, as depicted in Figure 4.18. This increase is higher than the increase in biogas production, indicating that more of the produced biogas is methane when sonicated sludge is digested. By day 16, about 90% of the potential methane was produced; Figure 4.19 shows the daily production up to this point. As mentioned before, high sCOD concentrations promoted an increased production (Pérez-Elvira et al., 2006; Xu et al., 2011), especially in the first few days of digestion. Starting with day 2, sonicated reactors show a consistently higher yield. On the daily biogas graph (Figure 4.17), after the fourth day reactors had a similar production value. However, on the daily methane graph (Figure 4.19), it is clear that even after this point sonicated reactors show more production, supporting the fact that more of the biogas consisted of methane. Other than the differences between sonicated and non-sonicated reactors, duplicate reactors of the same kind of sludge showed consistent results, displaying the repeatability.

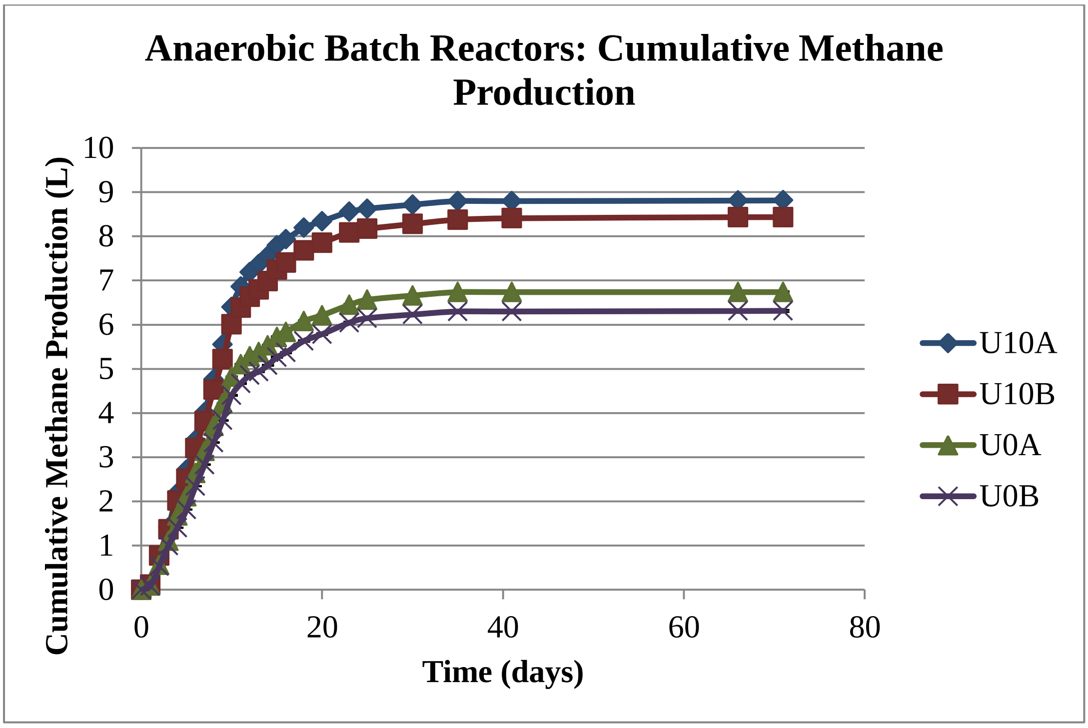


Figure 4.18: Cumulative methane productions of sonicated and non-sonicated sludges from Anaerobic Batch Reactors.

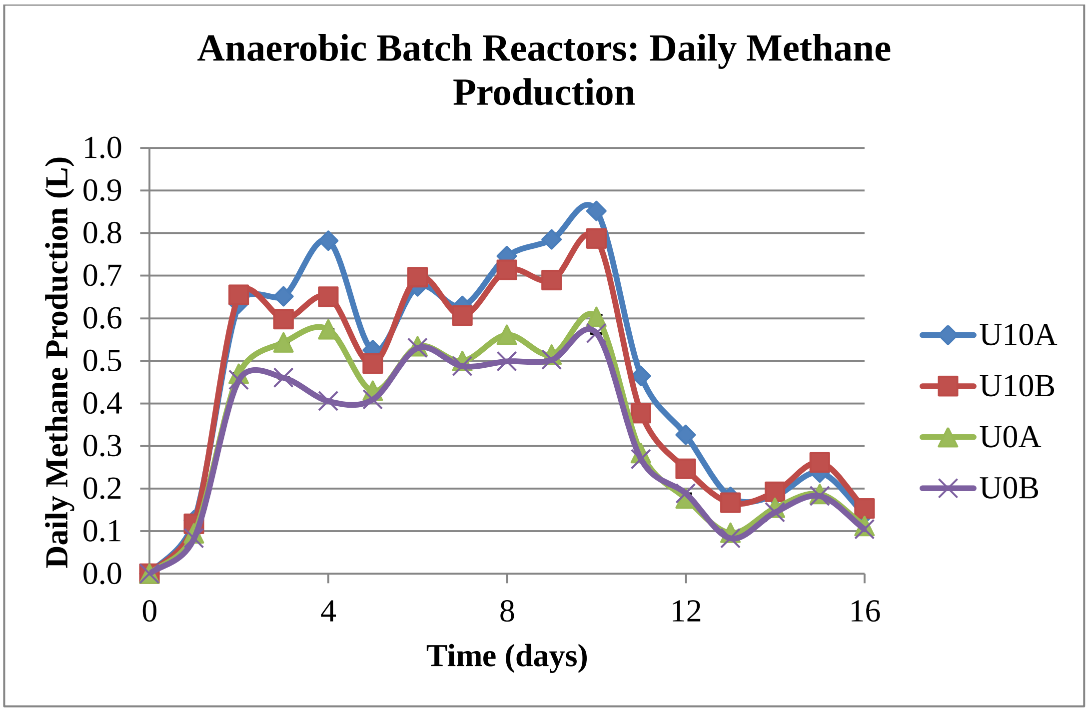


Figure 4.19: Daily methane productions of sonicated and non-sonicated sludges from Anaerobic Batch Reactors.

4.3.3. Characterization and Changes in Fuel Properties during Anaerobic Digestion

Figure 4.20 depicts the TS concentrations of the reactors throughout the digestion duration. First of the sonicated reactors, U10A showed a 28.1% TS reduction, from 36517 mg/L to 26267 mg/L. The second sonicated reactor, U10B showed a 27.8% reduction, from 36333 mg/L to 26233 mg/L. First of the control reactors had its TS reduced by 29.5%, from 37483 mg/L to 26417 mg/L. And finally, the second control reactor showed a 28.0% reduction, from 36783 mg/L to 26500 mg/L. Also mentioned before, most of these reductions are achieved within the first two weeks of anaerobic digestion.

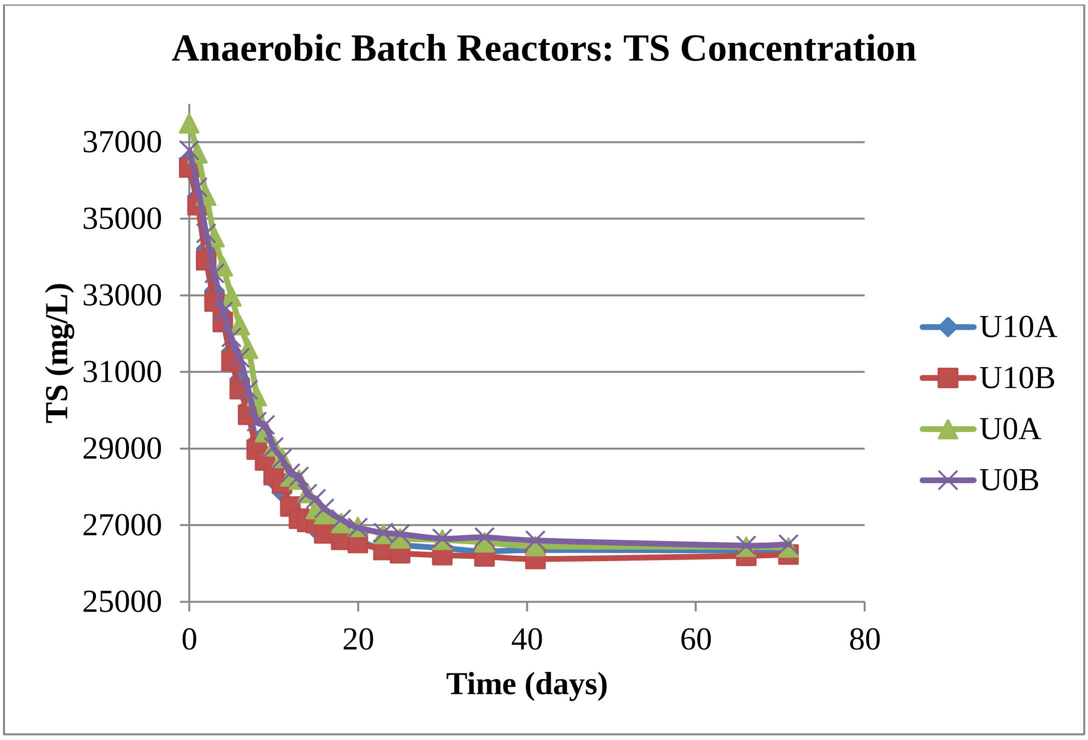


Figure 4.20: Changes in TS concentrations of the anaerobic batch reactors.

Shown in Figure 4.21 is the change in VS concentrations in the reactors with time. All four reactors showed a similar pattern, with sonicated reactors being one or two days ahead of the non-pretreated reactors, in terms of the progression of digestion, especially during the first two weeks. U10A, the first of the sonicated reactors had a VS concentration of 21583 mg/L which is reduced to 10817 mg/L, showing a 49.9% removal. U10B had 21267 mg/L initially and 10717 mg/L after the digestion, totaling to 49.6% removal in VS. U0A, the first of the control group started with a VS concentration of 21717 mg/L and it was reduced to 11150 mg/L, displaying a removal rate of 48.7%. Finally, U0B had its VS concentration reduced from 21633 mg/L to 11100 mg/L, a 48.7% reduction overall. Cumulative VS destruction was also tracked and specific biogas yield per gram of VS destroyed is plotted in Figure 4.22. The given typical production for full-scale anaerobic digesters for a combination of WAS and primary sludge is 0.8 L/g VS destroyed (WEF and ASCE/EWRI, 2009). As visible on the plot, the yield of the sonicated reactors is higher. Sonicated reactor duplicates show almost identical results. Common for all four reactors, initially the high VS destruction in the first few days do no produce much biogas. In the following days, the yield increases up to day 16, finally reaching 0.59 g/L for sonicated reactors and 0.53 g/L for non-sonicated reactors. These values respectively correspond to about 75% and 65% of the full-scale data reported.

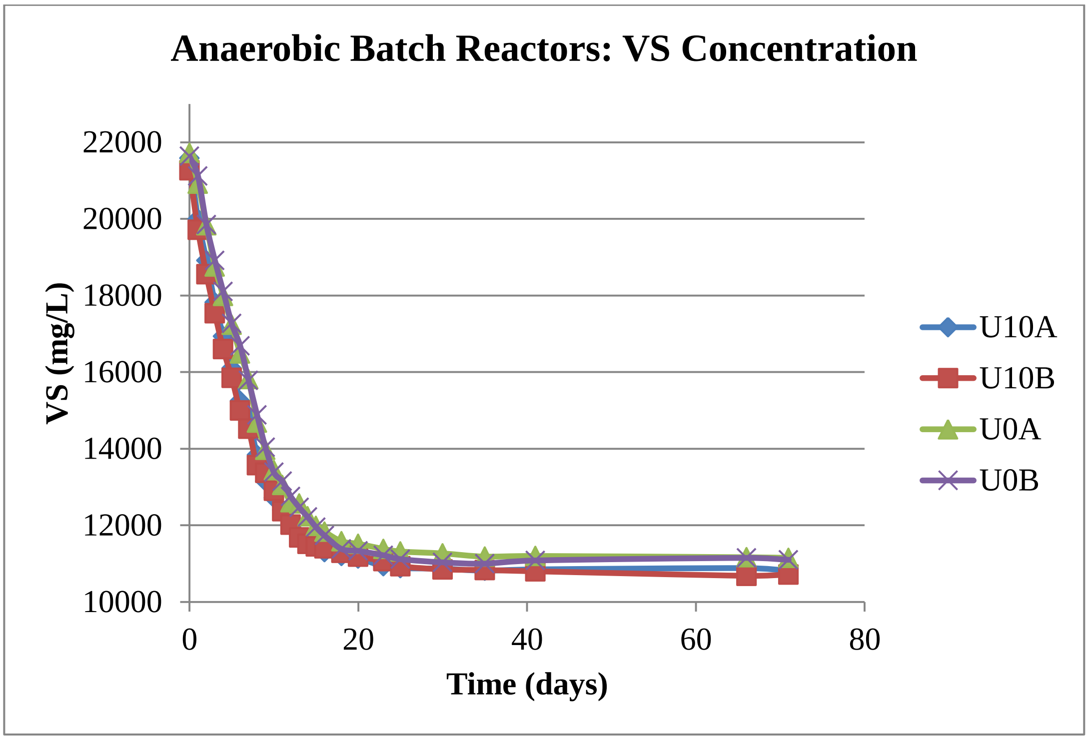


Figure 4.21: Changes in VS concentrations of the anaerobic batch reactors.

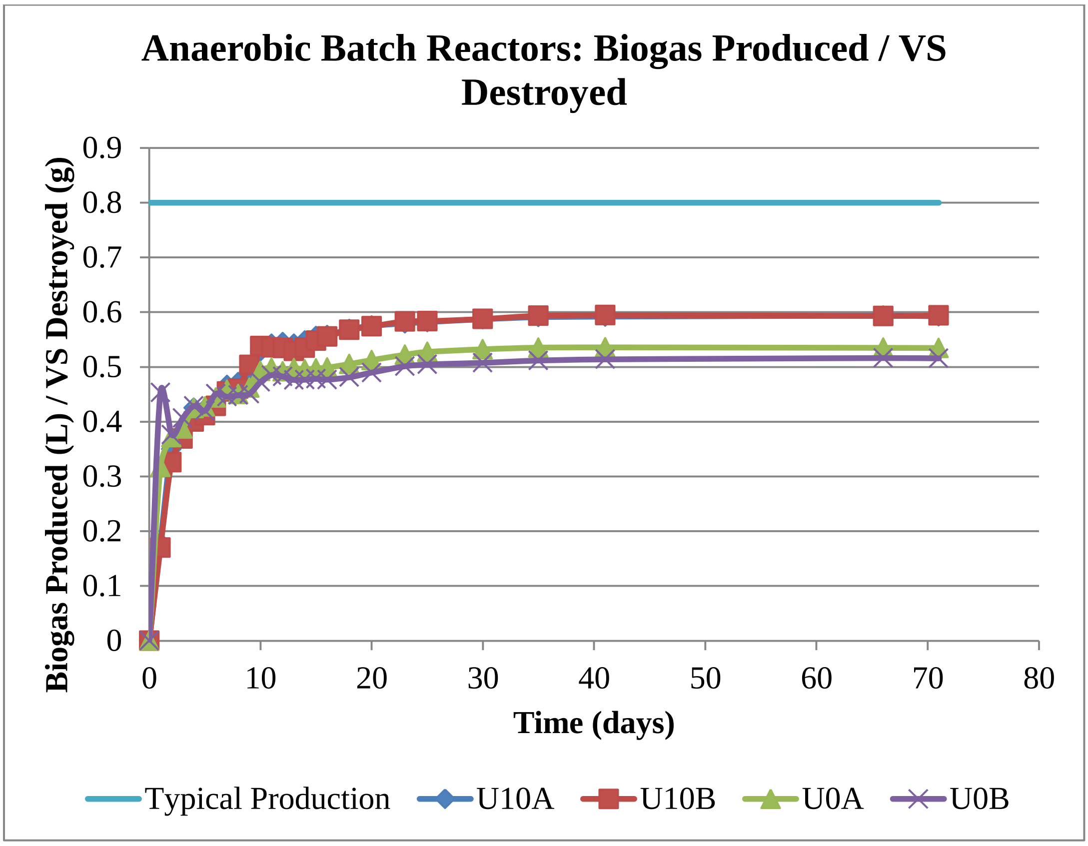


Figure 4.22: Cumulative biogas yield in liters per cumulative grams of VS destroyed in the anaerobic batch reactors compared to the typical yield.

Figure 4.23 shows the changes in COD concentrations of the reactors. U10A had its COD reduced from 42025 mg/L to 25950 mg/L, with a 38.3% reduction. The other sonicated reactor, U10B, showed a 39.0% decrease from 41800 mg/L to 25000 mg/L. As was the case in the BMP sets and VS reductions, sonicated samples showed more COD removal. Control groups of U0A and U0B exhibited 37.9% (from 43275 mg/L to 26875 mg/L) and 37.5% (from 43650 mg/L to 27300 mg/L) reduction, respectively. In Figure 4.24, cumulative methane produced per cumulative gram of COD destroyed is shown along with the maximum theoretical yield of 0.395 L/g at 35°C and 1 atm (Speece, 1996). Resembling the case with biogas production per unit amount of VS destroyed, the destroyed COD did not yield that much methane in the beginning. However, as the experiment progressed, the specific yield kept increasing, producing peaks on day 14 for U10A at 0.32 L/g COD destroyed, day 10 for U10B at 0.29 L/g COD destroyed, day 10 for U0A at 0.25 L/g COD destroyed and lastly, day 10 for U0B at 0.24 L/g COD destroyed. Following these peaks, the yield decreased, indicating that COD destroyed during this period until the end yielded less methane. Overall, the yield values were higher than that of the second BMP set, but still below the theoretical maximum as expected.

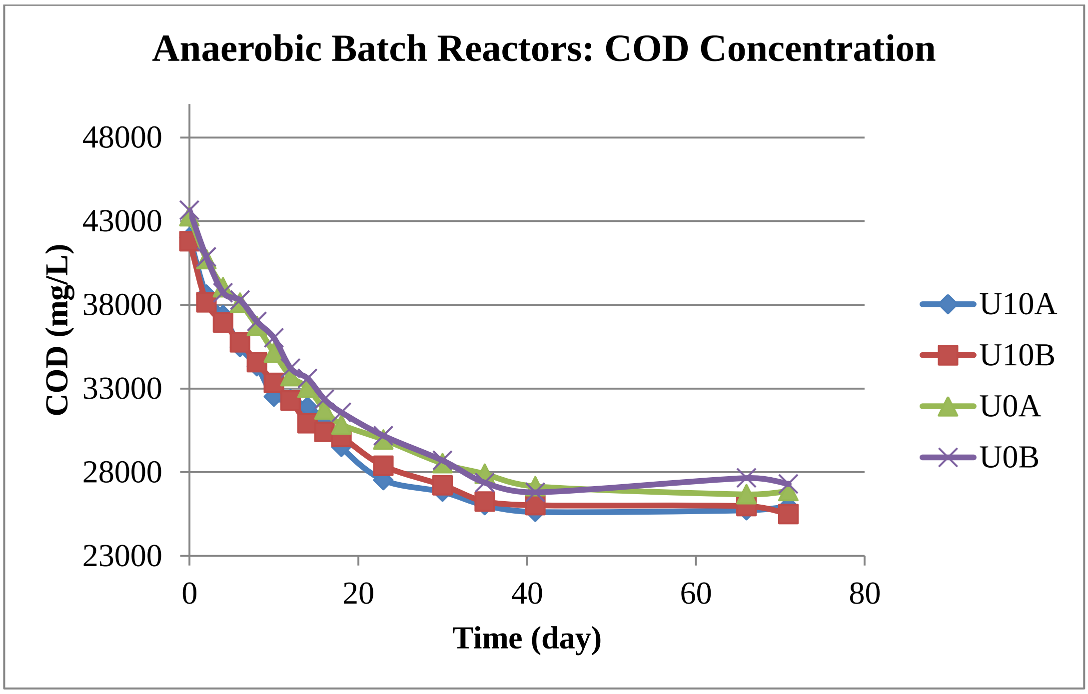


Figure 4.23: Changes in COD concentrations of the anaerobic batch reactors.

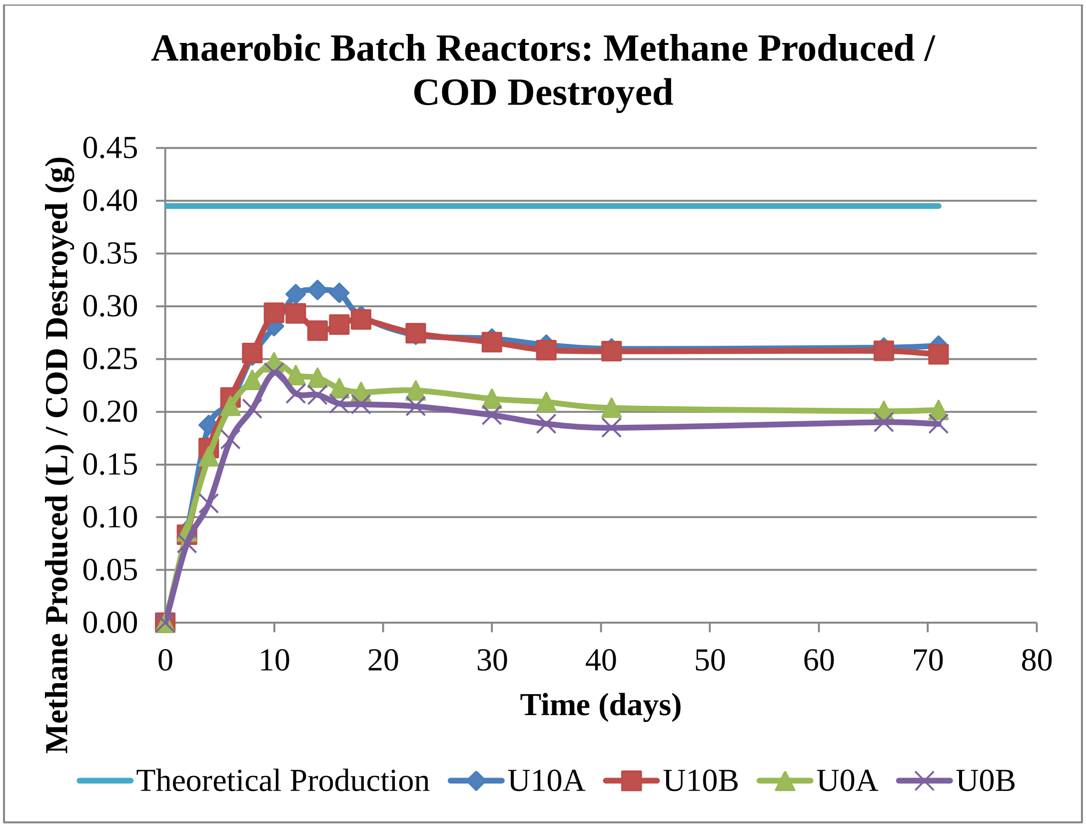


Figure 4.24: Cumulative methane yield in liters per cumulative grams of COD destroyed in the anaerobic batch reactors, compared to the theoretical maximum.

Ash concentrations of the reactors were tracked in both mg/L and percent of dry solids. In Figure 4.25 it can be seen that ash concentrations fluctuate between 13000 mg/L and 14000 mg/L for the sonicated reactors and 12500 mg/L and 13000 mg/L for the non-sonicated reactors. Judging by this figure and the results of the previous experiments, it can be said that the absolute amount of ash does not change during digestion and this fluctuation is caused by the lack of sensitivity of the measurement method, specifically, combusting minuscule amount of the sludge sample. On the other hand, the relative amount of ash within the sludge was again found to increase as the total solids amount decreased. Depicted in Figure 4.26 is the ash content as a part of dry solids. The initial ash contents which were 36.5% of U10A, 37.6% of

U10B, 34.2% of U0A and 34.3% of U0B were found to increase to 52.3% for U10A, 52.2% for U10B, 49.0% for U0A and 49.0% for U0B. In other words, by day 16 where daily measurements were stopped, about half the sludge consisted of incombustible and inert ash for both sonicated and non-pretreated sludge. At this point, combustion would only reduce the sludge amount by 50%, with ash remaining thereafter.

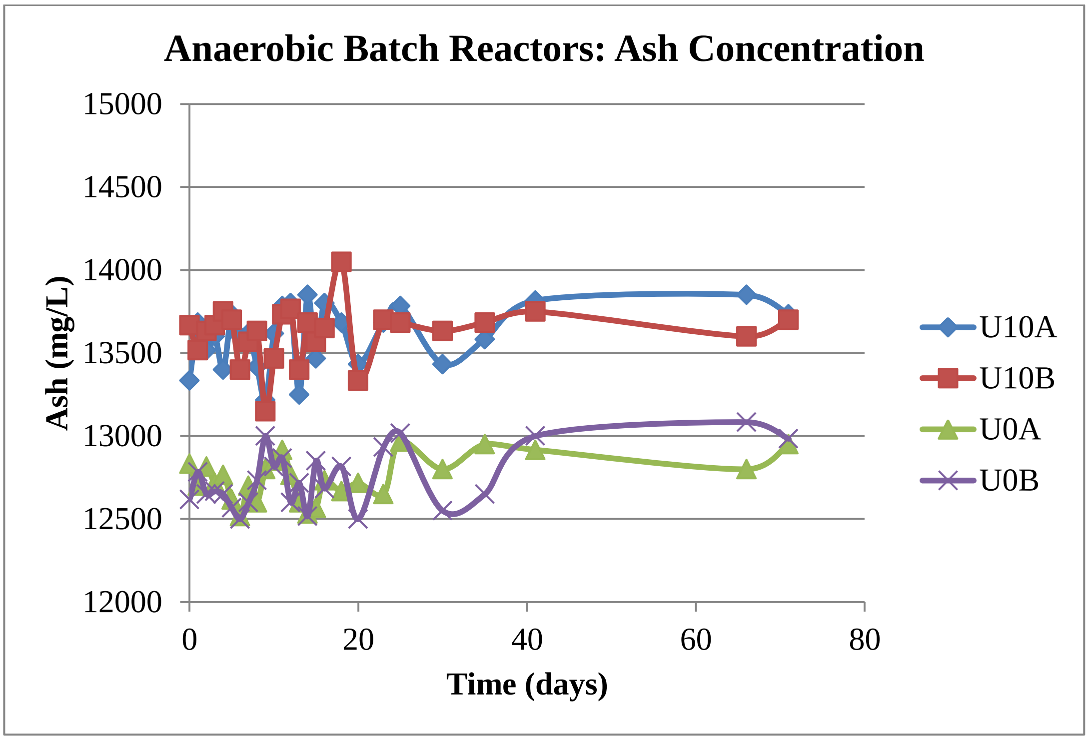


Figure 4.25: Changes in ash contents of the anaerobic batch reactors.

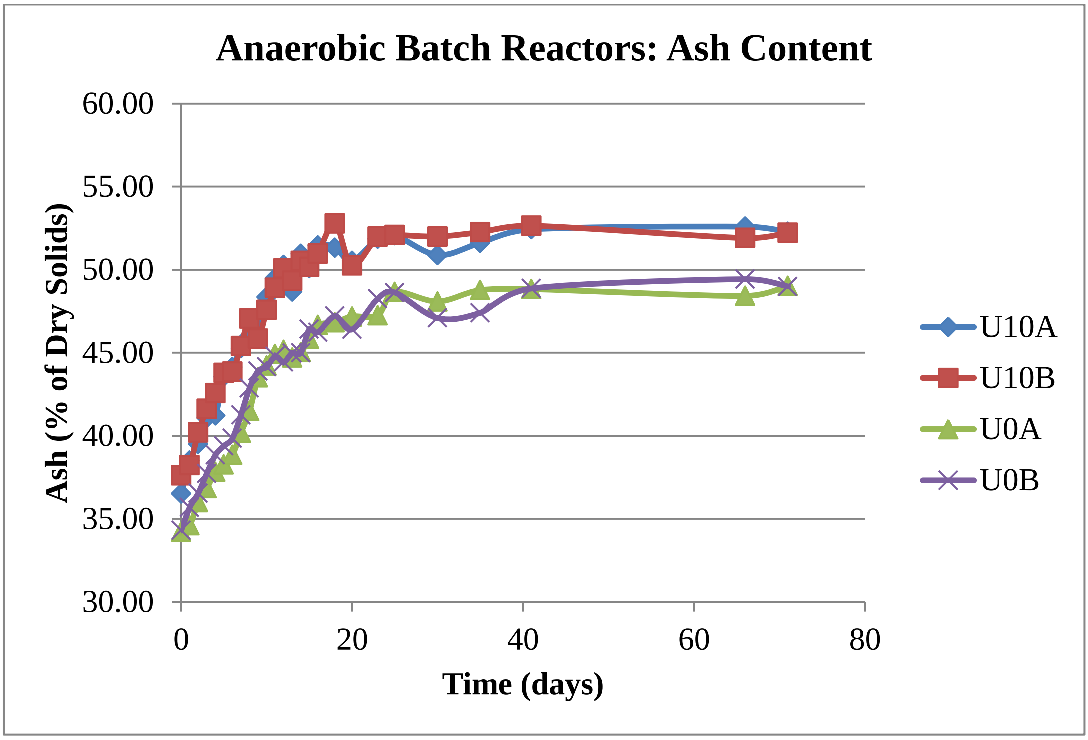


Figure 4.26: Changes in ash content of the anaerobic batch reactors as percent of dry solids.

Elemental analysis was done throughout the digestion duration to quantify the changes in carbon, hydrogen and nitrogen contents of the sludge. Figures 4.27, 4.28 and 4.29 show C, H and N content (as percent of dry solids) of the sludge, respectively. On the average, sludge from all four reactors started with 31.9% carbon, the non-sonicated reactors ended up both with 24.7%. Sonication reduced this further to 22.7% for U10A and 23.5% for U10B. Reason for this additional loss can be attributed to the increase in biogas production due to sonication. As demonstrated before with BMP set 2, hydrogen levels decrease as digestion progresses, as it takes part in methane yielding reactions during digestion. Initially, samples contained 4.7% hydrogen, and this value decreased while showing some fluctuations, towards 3.4% finally. Nitrogen content remained between 1.8% and

2.7% throughout digestion, without showing any significant changes. In this sense, there is an agreement with the results shown previously for the second BMP set.

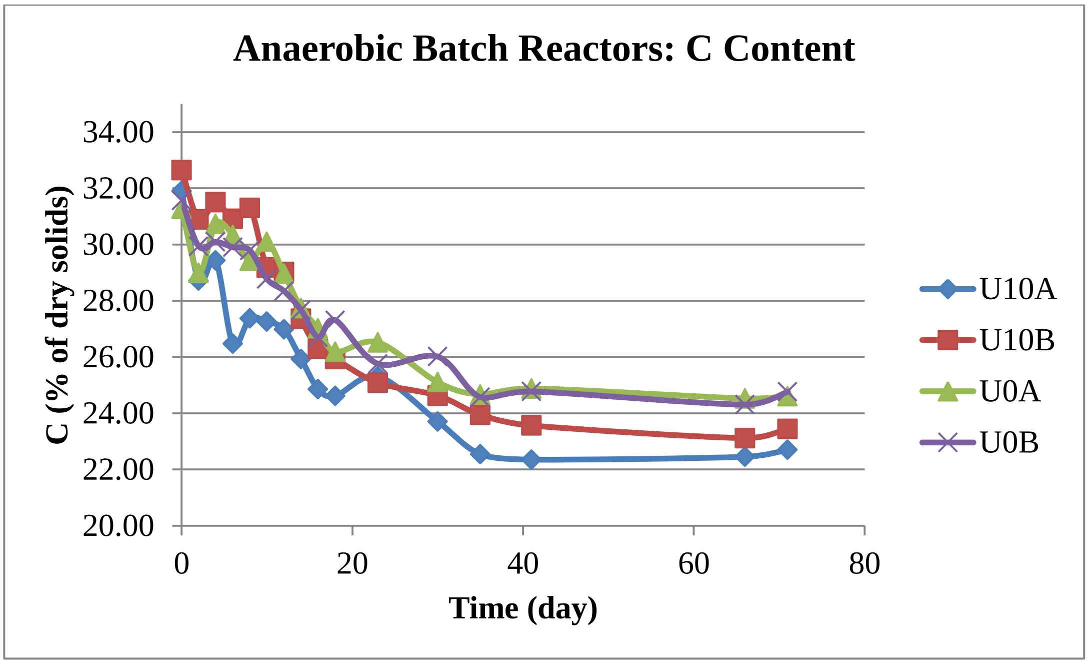


Figure 4.27: Changes in the carbon content of the anaerobic batch reactors as percent of dry solids.

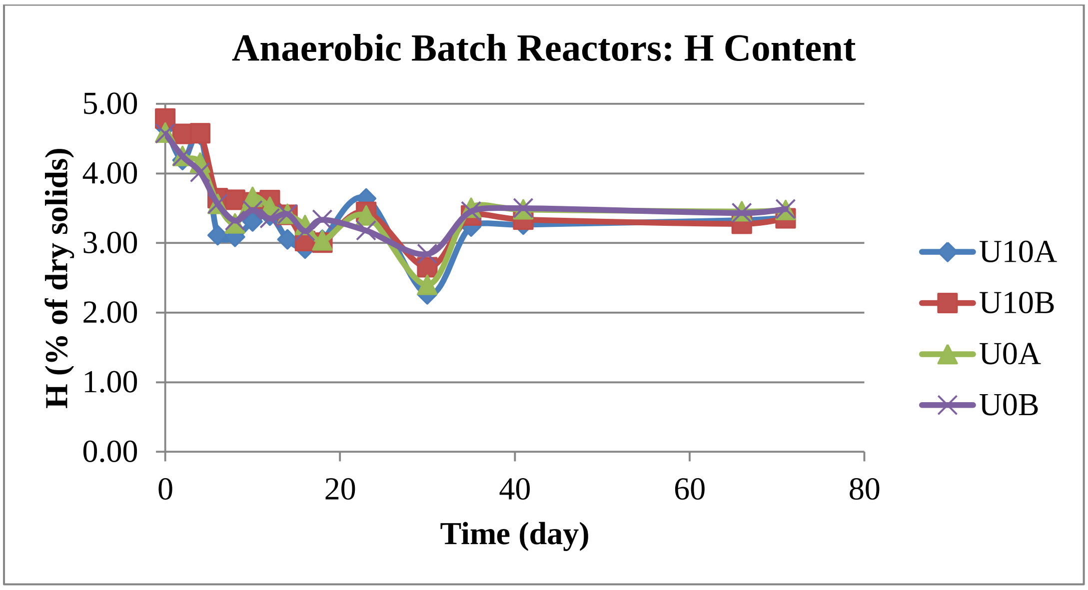


Figure 4.28: Changes in the hydrogen content of the anaerobic batch reactors as percent of dry solids.

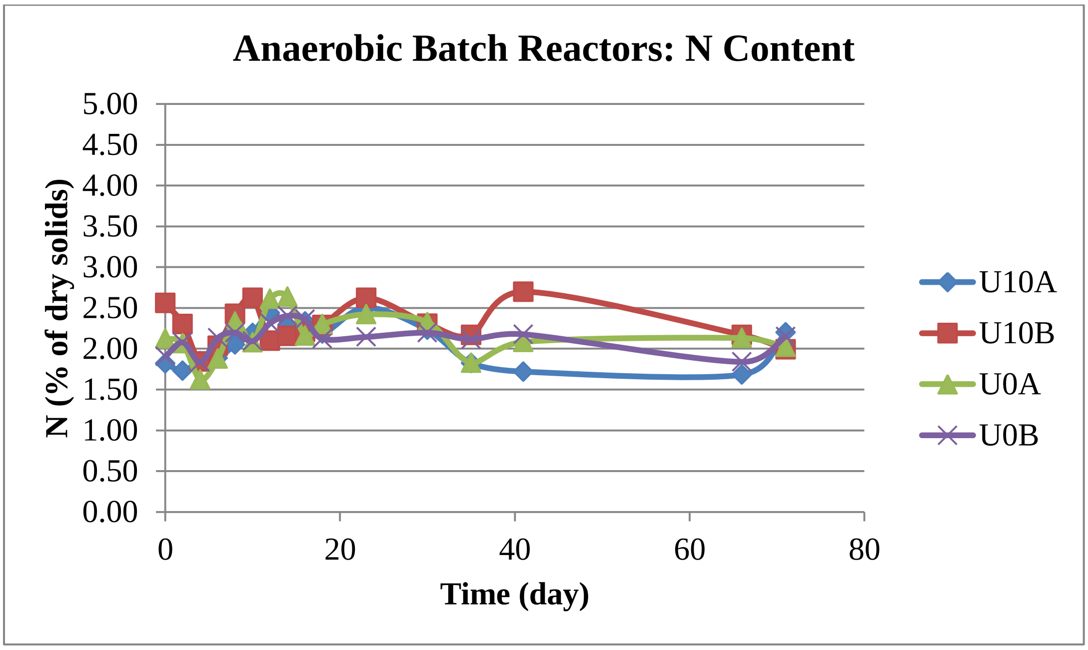


Figure 4.29: Changes in the nitrogen content of the anaerobic batch reactors as percent of dry solids.

As displayed in Figure 4.30, calorific values of sludge from each of the reactors were measured during anaerobic digestion to show how it changes with respect to time. Prior to digestion, the first of the sonicated reactors, U10A, had 14730 J/g, while the second one, U10B, had 14680 J/g. Control reactor U0A had 15552 J/g and the second control reactor U0B had 15550 J/g. On the very first day, the initial calorific values were reduced by about 10%. From this point forward, the decrease showed a declining pattern up to day 30. During this time, sonicated reactors displayed a lower calorific value, as more of the carbon was converted to biogas (and methane). After the 30 day mark, calorific values were stabilized and final values were 9845 J/g for U10A (33.1% decrease), 9950 J/g for U10B (32.2% decrease), 10183 J/g for U0A (30.0% decrease) and finally 10108 J/g for U0B (30.4% decrease). Following the same pattern for biogas and methane productions, and VS and COD removal, sonication reduced the calorific value further compared to the case with no pretreatment. Mentioned alongside the results of the BMP sets, the impact of the reduction of calorific value on the total energy potential of sludge is increased when the reduction in total solids is also taken into account.

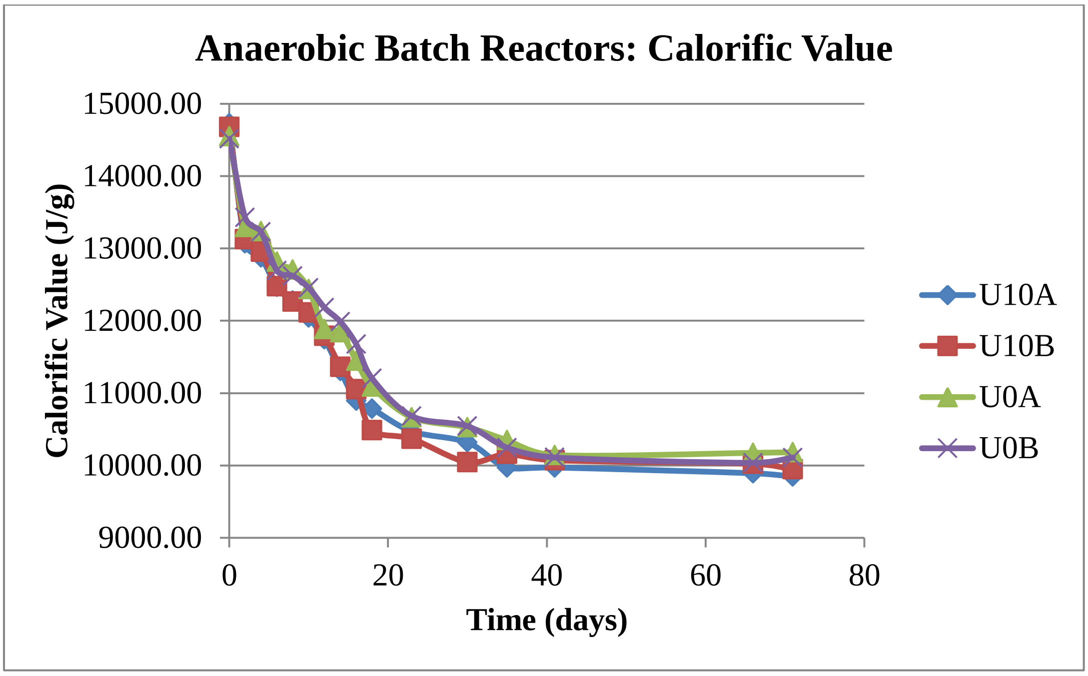


Figure 4.30: Changes in the calorific values of the anaerobic batch reactors.

Overall results of the reactors further prove that, 10 minutes of ultrasound pretreatment at 0.73 W/mL density has improved the anaerobic digestion compared to no pre-treatment case, showing better VS and COD removal and higher biogas and methane production. However, as sonication consumes a significant amount of energy, its actual benefit can only be realized through a detailed energy analysis. In the next section, several scenarios involving different treatment schemes have been developed to assess the overall energy consumption and production using the results obtained from the anaerobic batch reactor experiments.

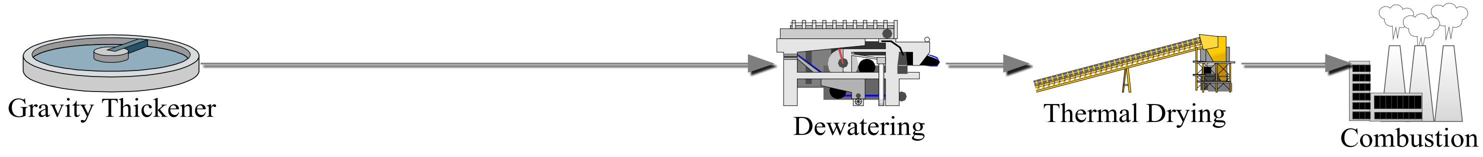
CHAPTER 5

ENERGY ANALYSIS

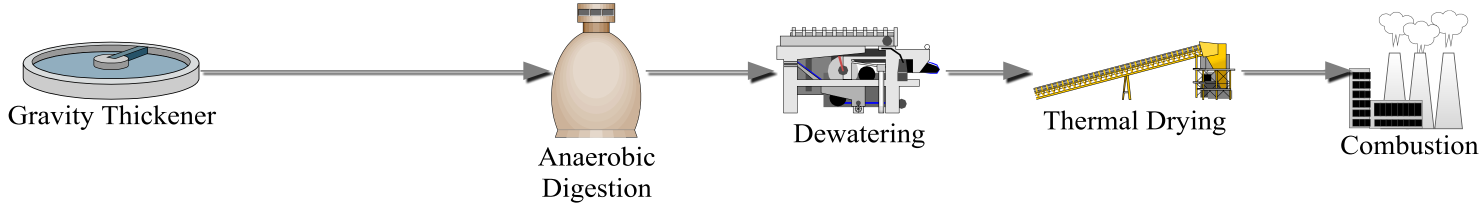
The primary purpose of this stage of the study was to find the optimal sludge management method to maximize energy gain. For this purpose, several scenarios consisting of different sludge handling methods are considered. Besides ultrasound pretreatment, anaerobic digestion and combustion which were experimented on, dewatering, thermal drying, solar drying and preparation for land application were included in the analyses. Various combinations of these processes are presented below as different scenarios. For each of them, energy gains and losses caused by selected handling method will be calculated.

5.1. Scenarios

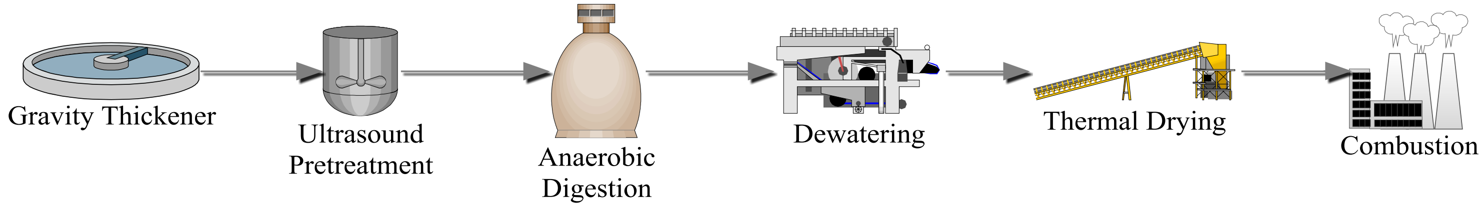
A total of six scenarios have been developed including a series of sludge handling methods, starting from thickening and then combining some or all of the following units: ultrasound pretreatment, anaerobic digestion, dewatering, thermal drying, solar drying, combustion and land application. All these scenarios are presented in Figures 5.1 and 5.2. The first scenario consists of dewatering, drying and combustion. This scenario will set the baseline for comparison to other alternatives (second and third scenarios) which consider sludge combustion as the final disposal. The second scenario includes mesophilic anaerobic digestion before dewatering. In the third scenario, ultrasound pretreatment is added to increase the level of treatment during anaerobic digestion, increasing the biogas yield. In the last two scenarios, the only energy exploitation method from sludge is assumed to be anaerobic digestion. In these scenarios, combustion is skipped and the final use is assumed to be by land application of sludge. So the fourth scenario shows the base case when land application is the final disposal method. In order, it follows as anaerobic digestion, dewatering and land application. The fifth scenario adds thermal drying before land application as treatment plants serving to an equivalent population of more than 1,000,000 are required to dry their sludge up to 90% dry solids by law (Regulation on the Use of Domestic and Municipal Wastewater Treatment Sludge in Land Application). The final scenario replaces thermal drying with solar drying to reduce the required energy by the drying process.



Scenario 1: Sludge is thickened, dewatered, dried and sent to a combustion facility.

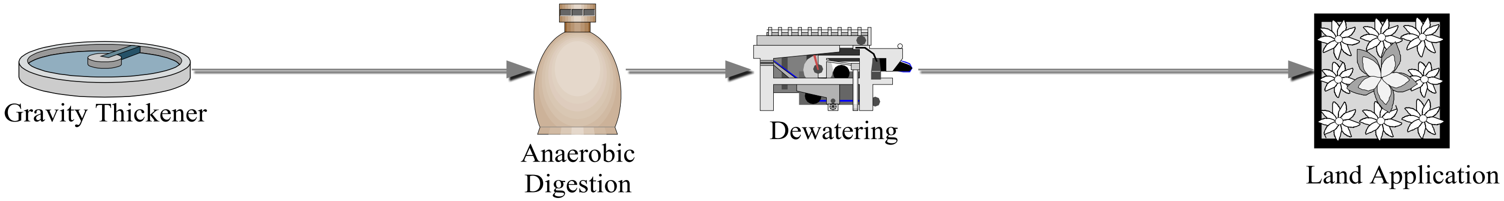


Scenario 2: Includes anaerobic digestion before dewatering.

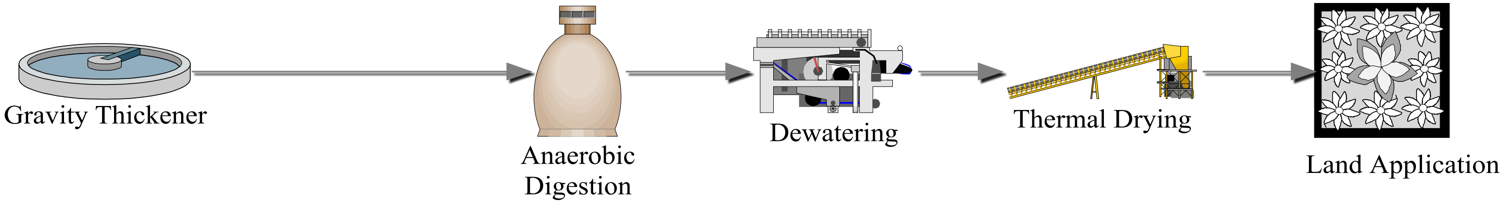


Scenario 3: Includes both ultrasound pretreatment and anaerobic digestion before dewatering.

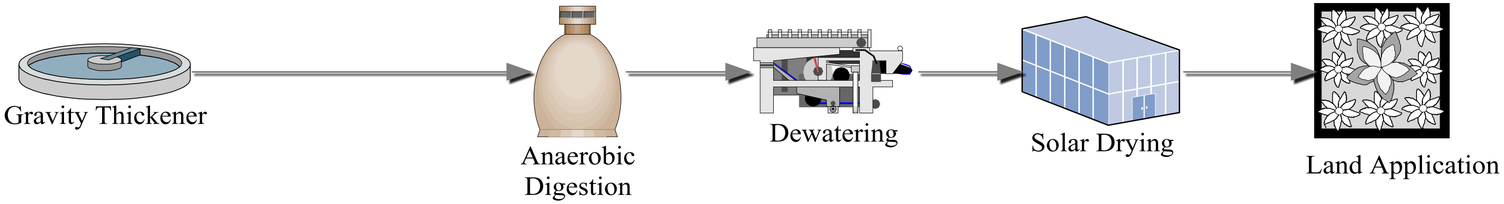
Figure 5.1: Schematic representation of scenarios 1, 2 and 3.



Scenario 4: Sludge is thickened, digested, dewatered and used in land application.



Scenario 5: Includes thermal drying before land application.



Scenario 6: Thermal drying is replaced with solar drying.

Figure 5.2: Schematic representation of scenarios 4, 5 and 6.

5.2. Assumptions

After the determination of scenarios, several assumptions were required in order to proceed with the calculations. The list of assumptions valid throughout the treatment schemes can be found below.

1. Energy balance was constructed based on the larger scale anaerobic batch reactors. Experimental data were used, particularly for methane production and calorific values of the sludge samples. In the scenarios that included digestion, digestion duration was also taken into consideration. For scenario 2, as an example, the total energy that can be harvested was calculated for every measurement day that included calorific value. In this case, total solids amount, cumulative methane production, calorific value were all that of the sludge in the reactors on a specific day.

2. Calculations of the energy requirements and gains for each unit in the sludge handling scheme of a given scenario were done based on constants, relatable to the amount of sludge that represents the full-scale processes. Ultrasound pretreatment's requirement was based on sonication density which is in turn, based on the volume of the sludge. Energies necessary for the heating and mixing part of the anaerobic digestion, dewatering, drying were calculated using the unit energy (mass or volume based) required by the sludge. Calculations of the gains from combusting methane and sludge involved their calorific values and the amount usable as they change with digestion duration. Table 5.1 shows the scenarios and the energy intense processes that were included in the energy analyses.

Table 5.1: Processes that were used in the energy analyses for each of the scenarios

Process	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6
Ultrasound Pretreatment						
Sonication			✓			
Anaerobic Digestion						
Heating to 35 °C		✓	✓	✓	✓	✓
Mechanical mixing		✓	✓	✓	✓	✓
Combustion of methane		✓	✓	✓	✓	✓
Dewatering						
Centrifugation	✓	✓	✓	✓	✓	✓
Thermal Drying						
Heating of sludge to 100 °C	✓	✓	✓		✓	
Solar Drying						
Ventilation						✓
Internal Air Mixing						✓
Sludge Mixing						✓
Combustion						
Combustion of the sludge	✓	✓	✓			
Land Application				✓	✓	✓

3. Calculated energy requirements and gains are all based on sludge itself. For ultrasound pretreatment, the calculated energy was the amount that needs to be imparted on the sludge, the efficiency of the sonicator was not taken into consideration. Similarly, for anaerobic digestion, calculations included the energy needed to heat the sludge, and not the exterior or other parts of the digester. Energy required to mix the sludge during anaerobic digestion was

again, that of the sludge and not the mixing equipment. For the combustion of methane and sludge, gains of energy were 100% of the heat released during combustion, disregarding losses and inefficiencies. The only exception to this method was the dewatering unit, where a manufacturer's data on energy consumption was used. It was multiplied with an efficiency factor to simulate the energy required by the sludge (Chu, Lee, and Chang, 2005). On the whole, this approach negates the differences from using different equipment for the same purpose and helps retain focus on the potential of sludge itself. Also, efficiencies can easily be plugged into the equations, to make a case specific estimation when needed.

4. As all six of the scenarios share the same thickening operation at the start, it is excluded from the calculations.

5. The differences in energy consumed during pumping or conveying of sludge were assumed to be negligible among the scenarios, and were excluded from the calculations.

6. All the processes mentioned in the scenarios are assumed to be on-site, not requiring any transportation, as this may result in differences in energy requirement that are completely unrelated to characteristics of the sludge itself.

5.3. Calculations for each of the Treatment Processes

5.3.1. Ultrasound Pretreatment

Energy required for sonication was calculated by Equation 5.1.

$$E_{sonication} = D_S * t_S * V_S * 60\frac{s}{min} \tag{5.1}$$

where,

$E_{sonication}$: Energy required for sonication (J),

D_S: Sonication density (0.73 W/mL),

t_S: Sonication duration (10 min),

V_S: Sonicated sludge volume (1140 mL).

In above equation D_s, t_s and V_s are set as 0.73 W/mL, 10 minutes, and 1140 mL (calculated from the F/M ratio), respectively.

5.3.2. Anaerobic Digestion

Energy requirements and gains from anaerobic digestion are separated into three sections: digester heating, mechanical mixing and combustion of methane.

Digester heating was calculated using Equation 5.2, where sludge is separated into three parts: water, volatile solids and non-volatile solids. Each of these parts is initially heated to 35°C (308 K) from 15°C (288 K) which was the assumed as the initial temperature of the sludge. Then, a daily temperature loss of 0.56 °C (0.56 K/d) was assumed (Braguglia, Gianico, and Mininni, 2011), which presented the base for daily heating loss.

$$E_{digester\ heating} = \left[m_{water} * c_{p,water} * (T_2 - T_1) + c_{p,water} * T_{LD} * \sum_{i=1}^{t} m_{water,i}\right] + \left[m_{NVS} * c_{p,NVS} * (T_2 - T_1) + c_{p,NVS} * T_{LD} * \sum_{i=1}^{t} m_{NVS,i}\right] + \left[m_{VS} * c_{p,VS} * (T_2 - T_1) + c_{p,VS} * T_{LD} * \sum_{i=1}^{t} m_{VS,i}\right] \tag{5.2}$$

Where;

$E_{digester\ heating}$: Energy required for digester heating (J),

m_{water}: Initial mass of water present in the sludge to be digested (g),

$c_{p,\ water}$: Heat capacity of water (4.1855 J/g-K) (Sandler, 2006),

T_2: Temperature of digestion (308 K),

T_1: Initial temperature (288 K),

T_{LD}: Daily temperature loss (0.56 K/d) (Braguglia et al., 2011),

t: Digestion duration (d),

$m_{water,i}$: Mass of water present in the sludge on day “i” of digestion (g),

m_{NVS}: Initial mass of non-volatile solids present in the sludge to be digested (g),

$c_{p,\ NVS}$: Heat capacity of non-volatile solids (0.88 J/g-K) (Schwarz, 1988),

$m_{NVS,i}$: Mass of non-volatile solids present in the sludge on day “i” of digestion (g),

m_{VS}: Initial mass of volatile solids present in the sludge to be digested (g),

$c_{p,\,VS}$: Heat capacity of volatile solids (1.34 J/g-K) (Schwarz, 1988).

$m_{VS,i}$: Mass of volatile solids present in the sludge on day “i” of digestion (g),

Energy required for digester mixing is calculated using Equation 5.3. The mixing requirement of sludge is given as 0.0226 W/L, on the average (WEF and ASCE/EWRI, 2009). Effective reactor volumes were 2.54 L for sonicated sludge and 2.56 L for non-sonicated sludge, and they were assumed to be constant throughout digestion.

$$E_{digester\ mixing} = R_M * V_D * t * 86400\frac{s}{d} \tag{5.3}$$

where,

$E_{digester\ mixing}$: Energy required for digester mixing (J),

R_M: Mixing rate (0.0226 W/L),

V_D: Digested sludge volume (L)

t: Digestion duration (d).

Energy gain from the combustion of methane was calculated using the volume-based calorific value of methane and the cumulative methane production from the anaerobic batch reactors. Methane has a calorific value of 50 MJ/kg. Multiplying it with the density of methane at 35°C and 1 atm (conditions that methane was produced), which is 0.6234 kg/m^3 (Sandler, 2006), yields 31.17 J/mL. Equation 5.4 is for calculation of the energy gain from methane.

$$E_{methane} = CMP * CV_{Methane} * 1000\frac{mL}{L} \tag{5.4}$$

where,

$E_{digester\ mixing}$: Energy gained from the combustion of methane (J),

CMP: Cumulative methane produced during digestion (L),

$CV_{Methane}$: Volume based calorific value of methane (31.17 J/mL).

5.3.3. Dewatering

Energy required for centrifugation was taken to be 165.14 J/g dry solids, based on the solids loading rate of a suggested equipment (HUBER Rotamat Screw Press RoS 3Q) after personal contact with Huber (HUBER SE, Berching, Germany). This value however, was the result of the energy consumed by the centrifuge unit, thus, to base it on the sludge instead, an efficiency value was assumed (Chu et al., 2005). Equation 5.5 shows the exact calculation.

$$E_{dewatering} = m_{TS} * C_c * \eta_d * 4.184 \frac{J}{cal} \tag{5.5}$$

where,

$E_{dewatering}$: Energy consumed for centrifugation (J),

m_{TS}: Mass of total solids to be dewatered at the end of digestion (g),

C_c: Unit energy required for centrifugation (39.47 cal/g),

η_d: Efficiency of the dewatering equipment (60%).

5.3.4. Thermal Drying

Thermal drying consists of heating the sludge to 100 °C and maintaining this temperature, in order to evaporate the excess water. The total energy requirement was calculated similar to that of the anaerobic digester heating, where sludge is considered to be consisting of three parts: volatile solids, non-volatile solids and water. Each of these parts is heated from 35°C (308 K) to 100°C (373 K) and water to be removed to reach the designated dry solids concentration of 90% is evaporated. Equation 5.6 was used to calculate this step.

$$E_{thermal\,drying} = \left[m_{water-d} * c_{p,water} * (T_3 - T_2)\right] + \left[m_{evap.water-td} * \left(H_{steam,100} - H_{water,100}\right)\right] + \left[m_{NVS-d} * c_{p,NVS} * (T_3 - T_2)\right] + \left[m_{VS-d} * c_{p,VS} * (T_3 - T_2)\right] \quad (5.6)$$

where,

$E_{thermal\ drying}$: Energy required for thermal drying (J),

$m_{water\text{-}d}$: Mass of water present in the sludge after dewatering (g),

$c_{p,\ water}$: Heat capacity of water (4.1855 J/g-K) (Sandler, 2006),

T_3: Temperature of drying (373 K),

T_2: Temperature after dewatering, assumed to remain the same after digestion (308 K),

$m_{evap.water\text{-}td}$: Amount of water to be evaporated by thermal drying (g),

$H_{steam,100}$: Enthalpy of steam at 100°C (2676 J/g) (Sandler, 2006),

$H_{water,100}$: Enthalpy of water at 100 °C (419.06 J/g) (Sandler, 2006),

$m_{NVS\text{-}d}$: Amount of non-volatile solids present in the sludge after dewatering (g),

$c_{p,\ NVS}$: Heat capacity of non-volatile solids (0.88 J/g-K) (Schwarz, 1988),

$m_{VS\text{-}d}$: Amount of volatile solids present in the sludge after dewatering (g),

$c_{p,\ VS}$: Heat capacity of volatile solids (1.34 J/g-K) (Schwarz, 1988).

5.3.5. Solar Drying

Solar drying consists of a greenhouse system where sludge is laid to dry with the energy of radiation of the sun. Most of the systems involve a mechanized mixer, internal air mixer and a ventilation unit (Seginer, Ioslovich, and Bux, 2007). The total amount of energy required by this process is calculated using Equation 5.7. Unit energy consumed per mass of evaporated water was taken to be 20 kWh/ton (Kurt et al., 2015).

$$E_{solar\ drying} = m_{evap.water-sd} * C_{sd} * \frac{ton}{10^6 g} * 3600000 \frac{J}{kWh} \tag{5.7}$$

where,

$E_{solar\ drying}$: Energy required for solar drying (J),

$m_{evap.water-sd}$: Mass of water to be evaporated by solar drying (g),

C_{sd}: Unit energy consumed for solar drying (20 kWh/ton evaporated water) (Kurt et al., 2015).

5.3.6. Combustion

Calorific values of the sludge samples were measured frequently, this value and the total solids amount was used to find the output of combustion, as demonstrated in Equation 5.8.

$$E_{combustion} = m_{TS-c} * CV_{TS-c} \tag{5.8}$$

where,

$E_{combustion}$: Energy gained from sludge combustion (J),

m_{TS-c}: Mass of total solids to be combusted (g),

CV_{TS-c}: Calorific value of sludge (J/g),

5.3.7. Land Application

In this study, land application was regarded to be an energy neutral process. The assumptions of neglecting pumping and conveying of sludge and omitting transportation are also supporting this stance. In other words, once the treatment processes are completed, sludge is ready to be used on land and does not require any additional energy input.

5.4. Results

Using the equations given above, the net amount of energy that can be provided by each scenario, as a function of digestion duration, where applicable, is calculated and presented in Figure 5.3 below. Scenario 1, which excluded pretreatment and anaerobic digestion, appeared to be the best with regards to final energy acquired. Addition of anaerobic digestion with scenario 2 initially reduced the total gain by almost 50% and with increased digestion duration, it was reduced further, reaching negative values after day 32. When sonication was added with scenario 3, despite the gains from increased methane production, the net energy was always negative with short or long digestion times; and the energy gain decreases with longer digestion times. For both these scenarios, the decrease slows down around days 10 to 14 and progresses downward thereafter. Scenarios 4 and 6 showed almost identical patterns, with the only difference being the addition of solar drying in scenario 6, which did not have a significant energy requirement. Although they remain on the negative side of the chart, the energy required decreases around day 10, and starts increasing again after that point. Of all the scenarios, subjecting sludge to digestion, dewatering and thermal drying before land application yielded the worst result, being entirely energy negative, and well below the results other scenarios.

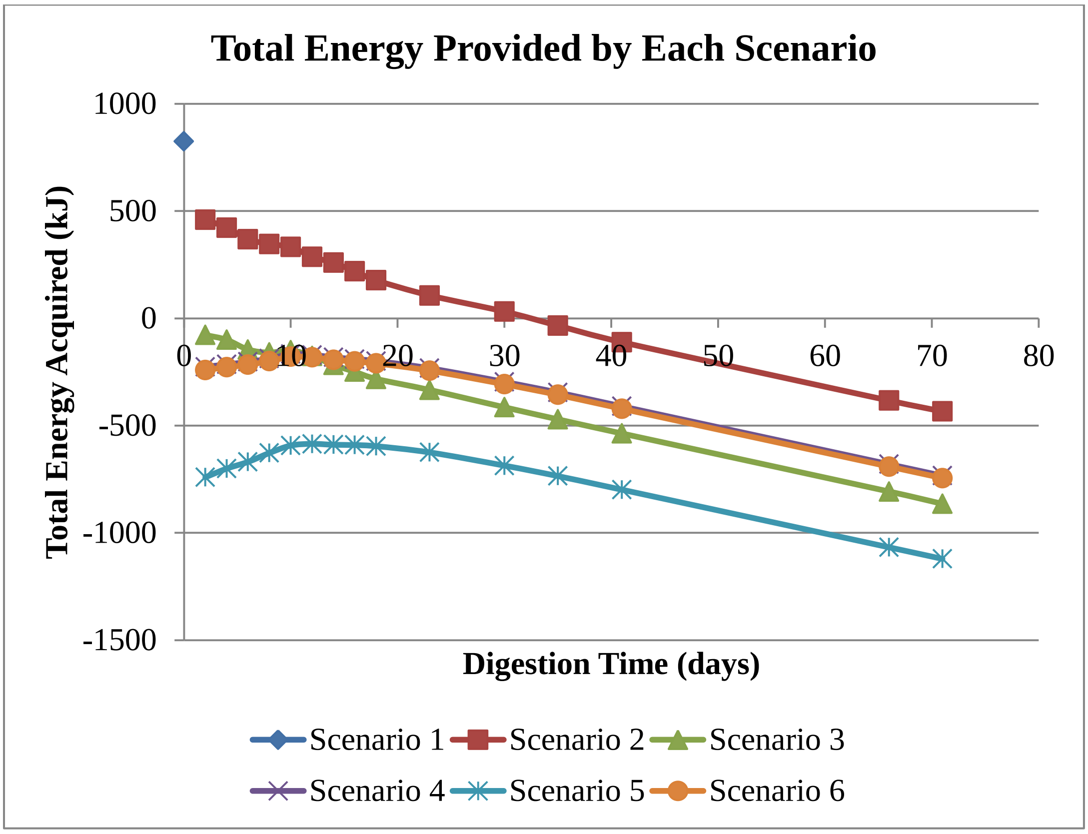


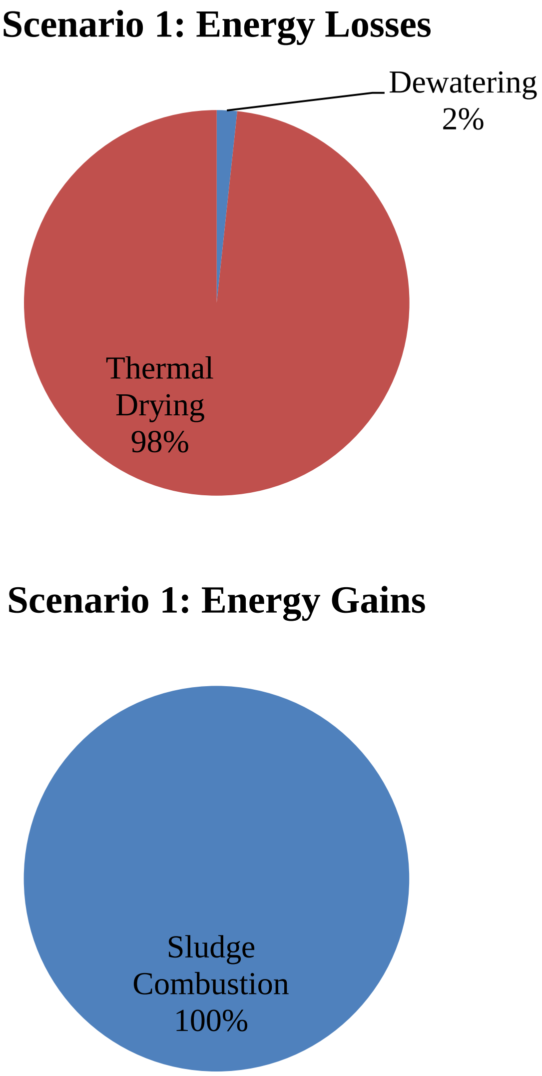
Figure 5.3: Total energy provided by each scenario, with respect to digestion duration.

In order to further analyze the results, a digestion duration of 14 days was selected, taking both the increase in overall acquired energy and the SRT of the digesters of Ankara Central Wastewater Treatment Plant into account. Detailed evaluation of each scenario is given below.

5.4.1. Scenario 1

Total energy that can be acquired by scenario 1 was calculated from Equation 5.9. The percentage breakdown of energy gains and losses are presented in Figure 5.4. Results indicate that energy required by thermal drying was much higher than that of dewatering, however, energy gain from combustion was enough to overcome their sum, and increase the gains to positive numbers. Overall, 60% of the energy produced by combustion is available for other uses after the consumption of dewatering and drying are satisfied.

$$\begin{aligned} E_1 &= E_{dewatering} + E_{thermal\ drying} + E_{combustion} \\ &= -9.3\ kJ - 536.9\ kJ + 1371.0\ kJ = 824.8\ kJ \end{aligned} \tag{5.9}$$


Scenario 1: Energy Losses

Scenario 1: Energy Gains

Figure 5.4: Energy losses and gains as percentage breakdown, Scenario 1.

5.4.2. Scenario 2

Total energy that can be acquired by scenario 2 was calculated using Equation 5.10. The percentage breakdown of energy gains and losses are presented in Figure 5.5. Compared to scenario 1, it can be seen that anaerobic digestion, as expected, reduced the energy required for dewatering and drying, along with the final amount that can be acquired after sludge combustion. However, as compensation, the produced methane also provided some energy. Of the total produced energy within the 14 days, 25% of it is excess and can be used in other energy consuming processes.

$$\begin{aligned} E_2 = E_{digester\ mixing} + E_{digester\ heating} + E_{methane} + E_{dewatering} \\ + E_{thermal\ drying} + E_{combustion} \\ = -75.0\ kJ - 289.8\ kJ + 190.0\ kJ - 7.1\ kJ - 407.5\ kJ \\ + 848.7\ kJ = 259.3\ kJ \end{aligned} \tag{5.10}$$

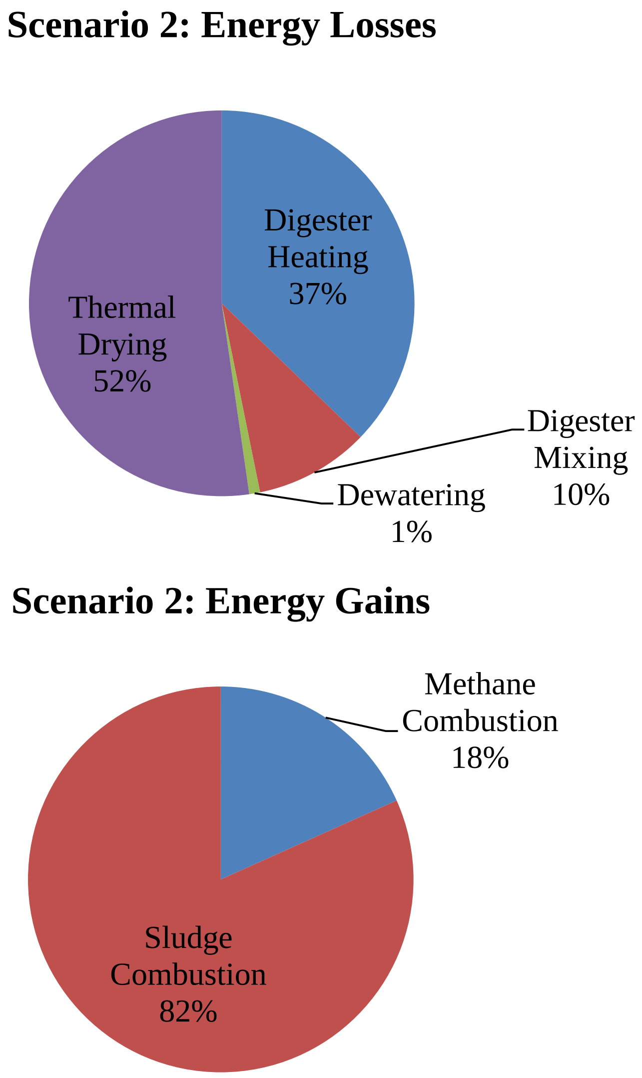


Figure 5.5: Energy losses and gains as percentage breakdown, scenario 2.

5.4.3. Scenario 3

Total energy that can be acquired by scenario 3 was calculated using Equation 5.11. The percentage breakdown of energy gains and losses are presented in Figure 5.6. Addition of sonication to the treatment stream reduced the net energy gain totally to the negative side, meaning that sludge treatment requires more energy than what it can generate by itself. Compared to scenario 2, ultrasound pretreatment increased the gains from methane and decreased the energy requirement of dewatering and drying, and the energy from sludge combustion.

$$\begin{aligned} E_3 = {} & E_{sonication} + E_{digester\ mixing} + E_{digester\ heating} + E_{methane} \\ & + E_{dewatering} + E_{thermal\ drying} + E_{combustion} \\ & = -498.3\ kJ - 74.4\ kJ - 287.7\ kJ + 263.5\ kJ - 6.8\ kJ \\ & - 394.2\ kJ + 781.2\ kJ = -216.9\ kJ \end{aligned} \tag{5.11}$$

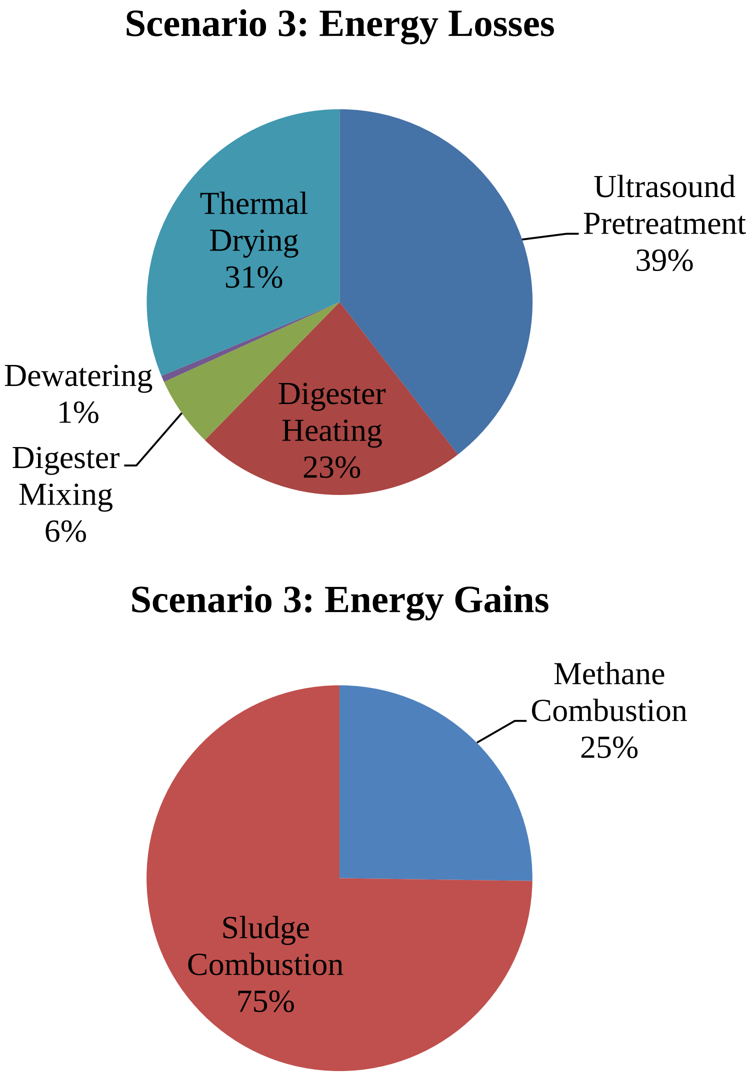


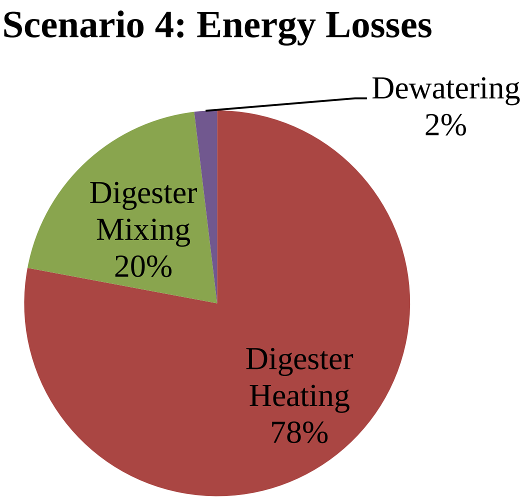
Figure 5.6: Energy losses and gains as percentage breakdown, scenario 3.

5.4.4. Scenario 4

Total energy that can be acquired by scenario 4 was calculated using Equation 5.12. The percentage breakdown of energy gains and losses are presented in Figure 5.7. Changing the final disposal method to land application robs the system of the energy of sludge combustion, which was proven to be the major contributor to the gains. Results of this scenario also indicate that the conventional treatment scheme of thickening, anaerobic digestion and dewatering was an energy intensive system, requiring additional input for its sustenance. This may be caused by the fact that results of the experiments, particularly methane production which was below the full-scale yield, were used in the calculations. Overall, combustion of methane was not enough to fulfill the requirements of the processes, and additional energy is needed.

$$E_4 = E_{digester\ mixing} + E_{digester\ heating} + E_{methane} + E_{dewatering} \tag{5.12}$$
$$= -75.0\ kJ - 289.8\ kJ + 190.0\ kJ - 7.1\ kJ = -181.9\ kJ$$

This scenario has another aspect that results in further evaluation. Since land application is assumed to be energy neutral for this study, scenario 4 also represents the common sludge handling scheme of thickening, digestion and dewatering. Clearly, experimental results show that the combustion of the produced methane is not enough to power digestion. Although personal communications with Ankara Central Wastewater Treatment Plant indicate that this is not the case when a full-scale digester is concerned, several published studies also show that laboratory scale digestion cannot produce the required energy (Braguglia et al., 2011; S. Pérez-Elvira, Fdz-Polanco, Plaza, Garralón, and Fdz-Polanco, 2009).



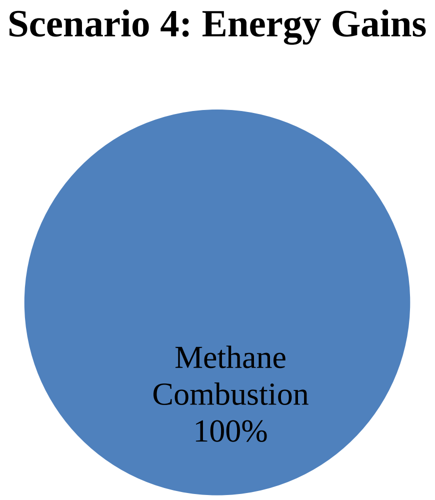
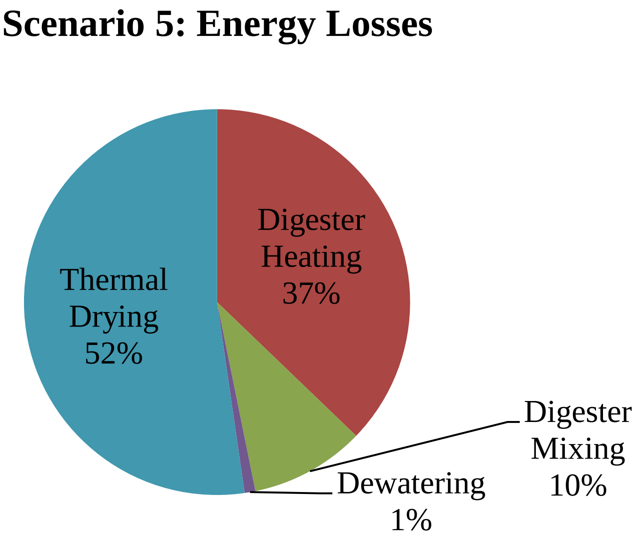


Figure 5.7: Energy losses and gains as percentage breakdown, scenario 4.

5.4.5. Scenario 5

Total energy that can be acquired by scenario 5 was calculated using Equation 5.13. The percentage breakdown of energy gains and losses are presented in Figure 5.8. It can be seen that if thermal drying is needed for land application, total energy requirement increases by over 200%, compared to scenario 4. Once again, methane is not enough by itself, to supply the needed energy. As indicated previously, this scenario yielded the worst results.

$$\begin{aligned} E_5 = {} & E_{digester\ mixing} + E_{digester\ heating} + E_{methane} + E_{dewatering} \\ & + E_{thermal\ drying} \\ & = -75.0\ kJ - 289.8\ kJ + 190.0\ kJ - 7.1\ kJ \\ & - 407.5\ kJ = -589.4\ kJ \end{aligned} \tag{5.13}$$



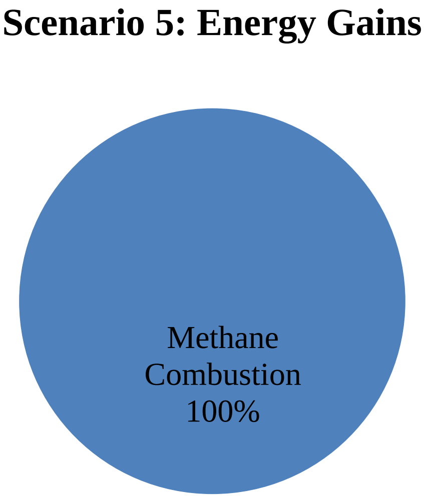
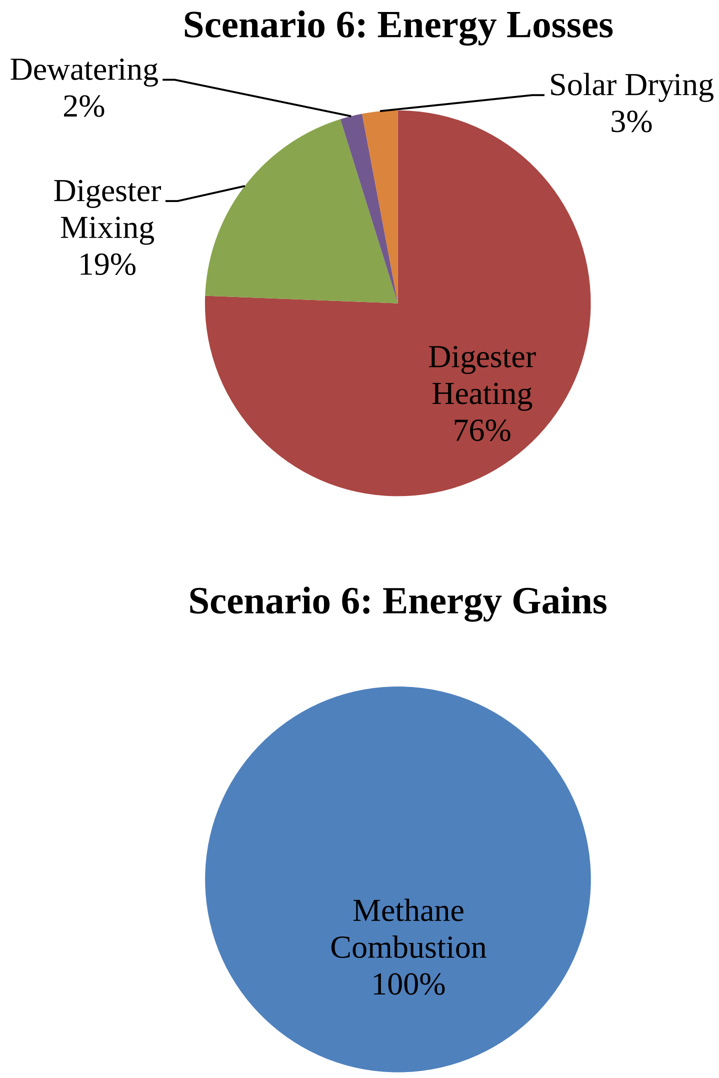


Figure 5.8: Energy losses and gains as percentage breakdown, scenario 5.

5.4.6. Scenario 6

Total energy that can be acquired by scenario 6 was calculated using Equation 5.14. The percentage breakdown of energy gains and losses are presented in Figure 5.9. Switching the fifth scenario's thermal drying with solar drying reverts the massive increase in energy need, lowering it back to the level of scenario 4. However, it should be noted that, not every treatment plant is in an appropriate climate zone to provide the necessary conditions for 90% dry solids, in which case, an external source of energy may be required.

$$\begin{aligned} E_6 = E_{digester\,mixing} + E_{digester\,heating} + E_{methane} + E_{dewatering} \\ + E_{solar\,drying} \\ = -75.0\,kJ - 289.8\,kJ + 190.0\,kJ - 7.1\,kJ - 11.4\,kJ \\ = -193.3\,kJ \end{aligned} \tag{5.14}$$



Scenario 6: Energy Losses

Scenario 6: Energy Gains

Figure 5.9: Energy losses and gains as percentage breakdown, scenario 6.

5.5. Overall Evaluation

The optimal sludge treatment scheme that maximizes the energy gain is found to be scenario 1, consisting of thickening, dewatering, thermal drying and combustion. This way, energy content of the sludge is wholly preserved from the reduction due to digestion, and is available to be used later. Inserting anaerobic digestion between thickening and dewatering shifts some of the potential energy from sludge combustion to methane, however, experimental results show that this is an overall loss, this loss is more pronounced when ultrasound pretreatment is coupled with digestion, with sonication consuming a significant amount of energy by itself, and further reducing the calorific value and the amount of combustible solids. When the final disposal method is determined to be land application, the most energy efficient way is to use the sludge right after dewatering, without adding any further treatment. However, if necessary, solar drying may also be added, as its energy consumption is negligible, especially when compared to thermal drying. Of course, these results only represent the experimental data and are limited with the validity of the assumptions, designing the sludge treatment part of a plant cannot be based solely on a study of this scale. Also, it needs to be mentioned that, these results are representing the total energy that can be acquired from the sludge and are limited with the system boundaries of this study.

CHAPTER 6

CONCLUSION

The purpose of this study was to find the optimal sludge management strategy that maximizes the energy gain. Assessed processes included six different combinations of ultrasound pretreatment, mesophilic anaerobic digestion, solar and thermal drying and land application and combustion as the final disposal methods. Necessary data was acquired from laboratory experiments where sludge was pretreated and digested, and subsequently had its fuel properties analyzed.

First part of the laboratory experiments included two identical BMP experiments to assess the optimal ultrasound pretreatment level. Once it was determined as 10 minutes of sonication at 0.73 W/mL density, the second part of experiments involved bigger anaerobic batch reactors, this time to see how fuel properties of the sludge changed with the progress of anaerobic digestion. Sonication proved to be useful in increasing the sCOD concentration by 340% and biogas and methane production levels by 15% and 32%, respectively. VS and COD removal ratios were also positively affected by sonication, indicating an overall improvement of anaerobic digestion, as expected.

It was known beforehand that anaerobic digestion would reduce the calorific value of the sludge, and this was observed in all three experimental sets. After the completion of digestion in anaerobic batch reactors, an overall reduction of over 30% was documented. With all the necessary data acquired, an energy analysis was conducted on the treatment options.

Results of the energy analysis showed that, when the purpose is to maximize the overall energy gain from sludge treatment, the scheme of thickening, dewatering, thermal drying and sludge combustion was the optimal. This method provided more than any of the other methods, all of which were actually found to be requiring energy rather than producing, with the exception of one: addition of anaerobic digestion. The worst case was when sludge was thickened, digested, dewatered and thermally dried before used in land application. On the whole, land application reduced the energy gains by a significant margin as it replaced combustion, which reversely, provided most of the energy.

It should be noted that the results of this study depend on the results of the laboratory analyses and the assumptions. If the methane production amounts and the calorific values were to change, new results may show that anaerobic digestion, even coupled with a pretreatment method may be more favourable. In addition, a cost based comparison including transportation and capital costs may indicate a different scenario, where land application dominates over sludge combustion.

As the final suggestion, combusting the sludge without applying stabilization provides the most energy. However, this suggestion can only serve as a guideline and decisions for full-scale treatment plant should always be done after conducting detailed feasibility analyses.

CHAPTER 7

RECOMMENDATIONS FOR FUTURE STUDIES

While many studies have been conducted on the combustion of sludge, the effects of different wastewater or sludge treatment processes on the fuel properties of sludge have not been investigated. Parallel to this study, different pretreatment methods like ozonation, microwave or chemical pretreatment may be applied in conjunction with other stabilization methods like thermophilic anaerobic digestion or aerobic digestion to see how fuel properties are affected.

Other than ash content and calorific value, there are parameters important to combustion like the characteristics of combustion, determined by thermogravimetric analysis. Changes in this property with respect to pretreatment methods and digestion duration may prove to be useful for full-scale combustion applications. Emissions from the combustion are also of concern. Different emission characteristics may be observed with the application of different treatment processes. This input, along with the already present data on the carbon footprint of sludge management can be used to find the most optimal method.

A number of full-scale treatment plants can be screened for the necessary data instead of laboratory experiments to conduct feasibility studies focusing on a single treatment plant or to produce guidelines for new treatment plants. While energy is of great importance, it is mainly the cost of a treatment option that determines whether it will be implemented or not. Cost functions along with other important parameters can be devised to provide suggestions based on the location of and the source of wastewater for treatment plants.

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APPENDIX

Sample Calculations for Each of the Treatment Processes

Ultrasound Pretreatment

Energy required for sonication was calculated using Equation 5.1.

$$E_{sonication} = D_S * t_S * V_S * 60\frac{s}{min} \tag{5.1}$$

where,

$E_{sonication}$: Energy required for sonication (J),

D_S: Sonication density (0.73 W/mL),

t_S: Sonication duration (10 min),

V_S: Sonicated sludge volume (1140 mL).

$$E_{sonication} = 0.73\frac{W}{mL} * 10\ min * 1140\ mL * 60\frac{s}{min} = 499320\ J \tag{5.1}$$

Anaerobic Digestion

Energy required for digester heating was calculated using Equation 5.2. Assuming a digestion duration of 2 days, calculations are as follows.

$$E_{digester\ heating} = \left[m_{water} * c_{p,water} * (T_2 - T_1) + c_{p,water} * T_{LD} * \sum_{i=1}^{t} m_{water,i}\right] + \left[m_{NVS} * c_{p,NVS} * (T_2 - T_1) + c_{p,NVS} * T_{LD} * \sum_{i=1}^{t} m_{NVS,i}\right] + \left[m_{VS} * c_{p,VS} * (T_2 - T_1) + c_{p,VS} * T_{LD} * \sum_{i=1}^{t} m_{VS,i}\right] \tag{5.2}$$

Where;

$E_{digester\ heating}$: Energy required for digester heating (J),

m_{water}: Initial mass of water present in the sludge to be digested (963 g),

$c_{p,\ water}$: Heat capacity of water (4.1855 J/g-K) (Sandler, 2006),

T_2: Temperature of digestion (308 K),

T_1: Initial temperature (288 K),

T_{LD}: Daily temperature loss (0.56 K/d) (Braguglia et al., 2011),

t: Digestion duration (2 d),

$m_{water,i}$: Mass of water present in the sludge on day “i” of digestion (g),

m_{NVS}: Initial mass of non-volatile solids present in the sludge to be digested (37.93 g),

$c_{p,\ NVS}$: Heat capacity of non-volatile solids (0.88 J/g-K) (Schwarz, 1988),

$m_{NVS,i}$: Mass of non-volatile solids present in the sludge on day “i” of digestion (g),

m_{VS}: Initial mass of volatile solids present in the sludge to be digested (54.82 g),

$c_{p,\,VS}$: Heat capacity of volatile solids (1.34 J/g-K) (Schwarz, 1988).

$m_{VS,i}$: Mass of volatile solids present in the sludge on day "i" of digestion (g),

$$E_{digester\ heating} = \left[963\ g * 4.1855 \frac{\mathrm{J}}{\mathrm{g} * \mathrm{K}} * (308\ K - 288\ K) + 4.1855 \frac{\mathrm{J}}{\mathrm{g} * \mathrm{K}} * 0.56\ K * (963\ g + 963\ g)\right] + \left[37.93\ \mathrm{g} * 0.88\ \frac{\mathrm{J}}{\mathrm{g} * \mathrm{K}} * (308\ K - 288\ K) + 0.88\ \frac{\mathrm{J}}{\mathrm{g} * \mathrm{K}} * 0.56\ K * (39.45\ g + 38.86\ g)\right] + \left[54.82 * 1.34\ \frac{\mathrm{J}}{\mathrm{g} * \mathrm{K}} * (308\ K - 288\ K) + 1.34\ \frac{\mathrm{J}}{\mathrm{g} * \mathrm{K}} * 0.56\ K * (50.80 g + 48.05\ g)\right] = 87377\ J \tag{5.2}$$

Energy required for digester mixing was calculated using Equation 5.3.

$$E_{digester\ mixing} = R_M * V_D * t * 86400 \frac{s}{d} \tag{5.3}$$

where,

$E_{digester\ mixing}$: Energy required for digester mixing (J),

R_M: Mixing rate (0.0226 W/L),

V_D: Digested sludge volume (1.185 L)

t: Digestion duration (2 d).

$$E_{digester\ mixing} = 0.0226 \frac{W}{L} * 1.185\ L * 2\ d * 86400 \frac{s}{d} = 4628\ J \tag{5.3}$$

Energy gain from methane combustion was calculated using Equation 5.4.

$$E_{methane} = CMP * CV_{Methane} * 1000\frac{mL}{L} \tag{5.4}$$

where,

$E_{digester\ mixing}$: Energy gained from the combustion of methane (J),

CMP: Cumulative methane produced during digestion (L),

$CV_{Methane}$: Volume based calorific value of methane (31.17 J/mL).

$$E_{methane} = 0.76\,L * 31.17\frac{J}{mL} * 1000\frac{mL}{L} = 23689\,J \tag{5.4}$$

Dewatering

Energy required for dewatering was calculated using Equation 5.5.

$$E_{dewatering} = m_{TS} * C_c * \eta_d * 4.184\frac{J}{cal} \tag{5.5}$$

where,

$E_{dewatering}$: Energy consumed for centrifugation (J),

m_{TS}: Mass of total solids to be dewatered at the end of digestion (86.91 g),

C_c: Unit energy required for centrifugation (39.47 cal/g),

η_d: Efficiency of the dewatering equipment (60%).

$$E_{dewatering} = 86.91\,g * 39.47\frac{cal}{g} * 0.6 * 4.184\frac{J}{cal} = 8612\,J \tag{5.5}$$

Thermal Drying

Energy required for thermal drying was calculated using Equation 5.6.

$$E_{thermal\,drying} = \left[m_{water-d} * c_{p,water} * (T_3 - T_2)\right] + \left[m_{evap.water-td} * \left(H_{steam,100} - H_{water,100}\right)\right] + \left[m_{NVS-d} * c_{p,NVS} * (T_3 - T_2)\right] + \left[m_{VS-d} * c_{p,VS} * (T_3 - T_2)\right] \tag{5.6}$$

where,

$E_{thermal\ drying}$: Energy required for thermal drying (J),

$m_{water\text{-}d}$: Mass of water present in the sludge after dewatering (202.79 g),

$c_{p,\ water}$: Heat capacity of water (4.1855 J/g-K) (Sandler, 2006),

T_3: Temperature of drying (373 K),

T_2: Temperature after dewatering, assumed to remain the same after digestion (308 K),

$m_{evap.water\text{-}td}$: Amount of water to be evaporated by thermal drying (193.13 g),

$H_{steam,100}$: Enthalpy of steam at 100°C (2676 J/g) (Sandler, 2006),

$H_{water,100}$: Enthalpy of water at 100 °C (419.06 J/g) (Sandler, 2006),

$m_{NVS\text{-}d}$: Amount of non-volatile solids present in the sludge after dewatering (38.86 g),

$c_{p,\ NVS}$: Heat capacity of non-volatile solids (0.88 J/g-K) (Schwarz, 1988),

$m_{VS\text{-}d}$: Amount of volatile solids present in the sludge after dewatering (48.05 g),

$c_{p,\ VS}$: Heat capacity of volatile solids (1.34 J/g-K) (Schwarz, 1988).

$$E_{thermal\ drying} = \left[202.79\ g * 4.1855 \frac{\mathrm{J}}{\mathrm{g} * \mathrm{K}} * (373\ K - 308\ K)\right] + \left[193.13\ g * \left(2676 \frac{\mathrm{J}}{\mathrm{g}} - 419.06 \frac{J}{g}\right)\right] + \left[38.86\ g * 0.88 \frac{\mathrm{J}}{\mathrm{g} * \mathrm{K}} * (373\ K - 308\ K)\right] + \left[48.05\ g * 1.34 \frac{\mathrm{J}}{\mathrm{g} * \mathrm{K}} * (373\ K - 308\ K)\right] = 491461\ J \tag{5.6}$$

Solar Drying

Energy required for solar drying was calculated using Equation 5.7.

$$E_{solar\ drying} = m_{evap.water-sd} * C_{sd} * \frac{ton}{10^6 g} * 3600000 \frac{J}{kWh} \tag{5.7}$$

where,

$E_{solar\ drying}$: Energy required for solar drying (J),

$m_{evap.water-sd}$: Mass of water to be evaporated by solar drying (202.79 g),

C_{sd}: Unit energy consumed for solar drying (20 kWh/ton evaporated water)

$$E_{solar\ drying} = 202.79\ g * 20 \frac{kWh}{ton} * \frac{ton}{10^6 g} * 3600000 \frac{J}{kWh} = 14601\ J \tag{5.7}$$

Combustion

Energy gain from sludge combustion was calculated using Equation 5.8.

$$E_{combustion} = m_{TS-c} * CV_{TS-c} \tag{5.8}$$

where,

$E_{combustion}$: Energy gained from sludge combustion (J),

m_{TS-c}: Mass of total solids to be combusted (86.91 g),

$CV_{TS\text{-}c}$: Calorific value of sludge (13068.16 J/g),

$$E_{combustion} = 86.91\ g * 13068.16 \frac{\mathrm{J}}{\mathrm{g}} = 1135754\ J \tag{5.8}$$

Land Application

Land application was assumed to be energy neutral, and the energy gains and losses were assumed to be negligible.