Enhancement of Biogas Production from Organic Wastes through Leachate Blending and Co-digestion

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Abstract

Several operational and environmental conditions can result in poor biogas yield during the operation of anaerobic digesters and anaerobic bioreactor landfills. Over time, anaerobic co-digestion and leachate blending have been identified as strategies that can help address some of these challenges to improve biogas production. While co-digestion entails the co-treatment of multiple substrates, leachate blending involves combination of mature and young landfill leachate. Despite the benefits attributed to these strategies, their impact on recirculating bioreactor landfill scenarios and anaerobic digesters requires further investigation.

In the first phase of this thesis, an attempt to assess biogas production improvement from organic fraction of municipal solid waste in simulated bioreactor landfills through recirculation of blended landfill leachate was conducted. Real old and new leachate blends (67%New leachate:33%Old leachate, 33%New leachate:67%Old leachate) as well as 100%New and 100%Old leachate were recirculated through six laboratory-scale bioreactors using open-loop and closed-loops modes. Compared with the control bioreactor where 100% new leachate was recirculated and operated as a closed-loop, cumulative biogas production was improved by as much as 77 to 193% when a leachate blend of 33%New:67%Old was recirculated. Furthermore, comparison of the results from open-loop and closed-loop operated bioreactors indicated that there was approximately 28 to 65% more biogas in open-loop bioreactors. The Gompertz model applied to the methane data produced a better fit (R^2 > 0.99) than first order and logistic function models. Leachate blending reduced the lag phase by almost half and thus helps in alleviating the ensiling during the start-up phase.

In the second phase, a biochemical methane potential (BMP) assay was conducted to investigate the synergistic effect of percentage sewage scum addition; 10%, 20% and 40% (volatile solids basis) on biogas production during mesophilic co-digestion with various organic substrates viz; organic fraction of municipal solid waste, old leachate, new leachate and a leachate blend prepared from 67%old leachate and 33%new leachate under sub-optimal condition. Results show that the net cumulative bio-methane yield was improved with increased sewage scum percentage during co-digestion because of positive synergism. Meanwhile, the addition of 40% sewage scum to the individual co-substrates improved net cumulative bio-methane yield by 28% - 67% when compared to their respective mono-substrate digestion bio-methane yield. Furthermore, reactors containing leachate blends consistently produced more biogas over other sets because of blending. Kinetic modelling applied to the bio-methane production data shows modified Gompertz equation achieved a better fit with up to an R^2 value of 0.999. Finally, co-digestion substantially reduced the lag time encountered during mono-digestion.

In the last phase, the biomethane potential involved in the ACo-D of sewage scum, organic fraction of municipal solid waste was investigated in this phase using either thickened waste activated sludge or leachate blend (67%old leachate and 33%new leachate) as a tertiary component. Compared to the mono-digestion of TWAS, results shows that biomethane yield was enhanced in by as much as 32 - 127% in trinary mixtures with SS and OFMSW mainly due to the effect of positive synergism. Furthermore, LB addition improved biomethane production in trinary mixtures of SS:LB: OFMSW by 38% than in corresponding trinary mixtures of TWAS. Whereas an optimal combination of 40%SS:10%TWAS:50%OFMSW and 20%SS:70%LB:10%OFMSW produced the highest biogas yield of $407 mL.gVS^{-1}$ and $487 mL.gVS^{-1}$ respectively. The application of the first order model showed that lower hydrolysis rates promoted methanogenesis with k = 0.04day^{-1} in both 20%SS:70%LB:10%OFMSW and 20%SS:50%LB:30%OFMSW. Estimations by the modified Gompertz and logistic function were conclusive methane production rate improved by as much a 60% in a trinary mixture over the production rate during mono-digestion of TWAS alone.

The results of the various experiments of this thesis therefore suggest that leachate blending can be used as a strategy to improve biogas production in both bioreactor landfills and anaerobic digesters. Also, sewage scum as an energy-rich substrate can be better utilized during co-digestion with other low-energy substrates.

Co-Authorship

The work presented in this thesis starting from Chapter 2 through Chapter 5 are articles that have either been published, under peer review or under preparation for submission to scientific journals. All work presented herewith were carried out by Adewale Aromolaran, with the assistance of the thesis supervisor Dr. Majid Sartaj, who provided supervision, suggestions, valuable comments, and necessary revisions.

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Abbreviations

ACo-D	Anaerobic co-digestion
AD	Anaerobic digestion
BMP	Biochemical methane potential
BRL	Bioreactor landfill
C:N	Carbon to nitrogen ratio
COD	Chemical oxygen demand
ET	Elevated temperature
FOG	Fat, oil and grease
ISR	Inoculum to substrate ratio
LB	Leachate blend
LCFAs	Long chain fatty acids
LF	Logistic Function
MG	Modified Gompertz model
MSW	Municipal solid waste
OFMSW	Organic fraction of municipal solid waste
SS	Sewage scum
TA	Total alkalinity
TAN	Total ammonia nitrogen
TS	Total solids
TVFA	Total volatile fatty acids
TWAS	Thickened waste activated sludge
VFA	Volatile fatty acids
VS	Volatile solids
WAS	Waste activate sludge
WWTPs	Wastewater treatment plants

Chapter 1-Introduction

1.1 Background

The consequence of global development, urbanization and industrialization in cities and towns has been a concomitant increase in population density and waste generation (Hoornweg et al., 2013; Papargyropoulou et al., 2014; Kaza, 2018). In Canada, approximately 34 million tonnes of municipal solid waste (MSW) is generated annually (Statistics Canada 2012; Conference Board of Canada, 2013). Available data also indicates that an annual estimate of 660,000 dry metrics tonnes of sewage sludge is generated from Canadian wastewater treatment plants (WWTPs) (Canadian Council, 2012). 4% of the total solids from WWTPs has been reported to contain sewage scum (Young, 2012). As it stands, solid waste has been suggested to be generated faster than any other environmental pollutant (Hoornweg et al., 2013).

MSW composition varies considerably but typically consists of organic and inorganic fractions such as food waste, paper, wood, vegetable and yard waste, plastic, glass, and other inert materials (Li et al., 2011; Panigrahi and Dubey, 2019; Kumar and Samadder, 2020). The biodegradable portion referred to as organic content, known as the organic fraction of municipal solid waste (OFMSW) constitutes the highest percentage with about 46% worldwide, varying about 64% in developing countries and approximately 28% in developed countries (Li et al., 2011; Hoornweg and Bhada-Tata., 2012; Mata-Alvarez et al., 2014; Hussain et al., 2017). Sewage sludge is the main by-product from physical, chemical, and biological processes in conventional WWTPs. It typically consists of primary sludge and waste activated sludge (WAS) made of organic and inorganic components, heavy metals, and pathogens. (Ruffino et al., 2015; Zhen et al., 2017; Pan et al., 2019). When it comes to sewage scum, it is usually collected from the surface of primary and secondary tanks of WWTPs and it contains fat, oil and grease (FOG), gas, plastic material, soaps, waxes or other impurities (Martín-González et al., 2010; Young, 2012; Salama et al., 2019).

Appropriate waste management of these wastes is fundamental to sustainable development and environmental protection (Sartaj et al., 2010; Mata-Alvarez et al., 2014). The natural tendency is for most of these wastes to be landfilled. However, with stringent regulations and in tandem with sustainable resource management and circular economy, these wastes have been recognized as valuable resources which can be converted into useful products through various energy recovery pathways such as biological, chemical, physical or a combination of these methods prior to final disposal (Khalid et al., 2011). Biological processes are more commonly investigated due to their cost-effectiveness, environmental friendliness and ability for treatment and energy generation from a vast number of organics (Bouallagui et al., 2003; Khalid et al., 2011; Ara et al., 2015; Kumar and Samadder, 2020). Amongst the available biological processes, anaerobic digestion (AD) or biological gasification represents one of the most attractive, economic, and stabilization methods for OFMSW, sewage sludge, sewage scum and even other feedstocks such as agriculture wastes, slaughterhouse waste, including liquid organic streams such as landfill leachate and wastewater (Angelidaki and Bastone, 2010; Bouallagui et al., 2003; Jingura and Matengaifa, 2009; Mao et al., 2015; Ara et al., 2015; Alqaralleh et al., 2016; Nair et al., 2014; Hagos et al., 2017) .

AD is a mature technology, and it involves a complex process whereby a consortium of syntrophic micro-organisms breaks down organic matter in 4 major steps (hydrolysis, acidogenesis, acetogenesis and methanogenesis) in an oxygen-free environment (Jingura and Matengaifa, 2009; Angelidaki and Bastone, 2010; Mao et al., 2015; Ren et al., 2018; Bajpai, 2017). Although a slow process in natural ecosystem, anaerobic biodegradation of organic waste can be optimized and enhanced, controlled and contained in anaerobic digesters and in well operated anaerobic bioreactor landfills (Chan et al., 2002; San and Onay, 2001; Bilgili et al., 2007; Ahmadifar et al., 2016). Anaerobic bioreactor landfills are a variant of the bioreactor landfill concept which utilize certain operational procedures to stimulate the microbial stabilization and treatment of organic waste under anaerobic conditions (Pohland, 1996; San and Onay, 2001; Nair et al., 2014; Nwaokorie et al., 2018). In fact, the main process in anaerobic bioreactor landfills is AD (Reinhart et al., 2002; Themelis and Ulloa, 2007; Pohland, 1996).

It has however been regularly reported that the global demand for renewable energy is currently on the rise due to depleting fossil fuel reserves and greenhouse gas emission (Cesaro and Belgiorno, 2014; Papargyropoulou et al., 2014; Mao et al., 2015). One of the benefits of methanation of organic waste during AD is the production of biogas (Angelidaki and Bastone, 2010). Biogas collected from anaerobic digesters and anaerobic landfill bioreactors (landfill gas) are approved alternative renewable energy sources (Bouallagui et al., 2003; Alqaralleh et al., 2016). The action of the methanogenic bacteria on organic waste leads to formation of biogas by breaking down the acids to methane and carbon dioxide, or by reducing carbon dioxide with hydrogen (Jingura and Matengaifa, 2009). Biogas typically contains mainly methane (55–65%) and carbon dioxide (35–45%) and other trace gases (Balat and Balat, 2009). The composition of biogas varies depending on the anaerobic system, the stabilization stage and characteristics of the organic waste at a given time (Jingura and Matengaifa, 2009). What makes biogas distinct from other renewable energy sources is its elevated methane which makes it useful for heating and electricity generation. Biogas has a heat value of approximately 537–700Btu/ft^3 (Balat and Balat, 2009). It is affordable and on a lower sale cost when compared to diesel and petrol (Mao et al., 2015). Besides, stabilized wastes from digesters are referred to as digestate represents a rich source of nutrient that can be applied to land (Angelidaki and Bastone, 2010; Papargyropoulou et al., 2014).

Although the biogas technology through anaerobic fermentation of organic waste is a well-established and attractive process in the production of renewable energy (Bouallagui et al., 2003; Ponsá et al., 2011), technical and scientific interests have recently been diverted towards process optimization with the aim of maximizing the process yields; mainly biogas collected during the treatment and stabilization of waste (Cesaro and Belgiorno, 2014). This is necessary because the microbial population, most especially methanogens involved in biogas generation in an anaerobic environment are very sensitive and often negatively affected by several conditions which may involve mass transfer limitations of substrates to microbes, nutritional imbalance, lack of diversified microorganism, accumulation of toxic compounds, ammonia toxicity, acidic conditions and ensiling (ensiling is a state of inhibited microbial activity and stalled waste stabilization and biogas production in landfills) (Hagos et al., 2017; Mao et al., 2015 Khalid et al., 2011; Ara et al., 2015; Akindele and Sartaj, 2018; O'Keefe and Chynoweth, 2000). For instance, high number of soluble organics in food waste has been reported to lead to VFA accumulation during the early-stage digestion which causes a drastic drop in digester pH thereby inhibiting methanogenesis (Behera et al., 2010; Li et al., 2011; Khalid et al., 2011; Hussain et al., 2017; Ren et al., 2018). In the digestion of fatty substances, methanogenesis maybe disturbed and inhibited by the accumulation of long chain fatty acid (LCFAs) produced during the acidogenesis (Long et al., 2012; Salama et al., 2019). Similar disruptions are also prevalent in young landfills recirculating VFA-rich leachate which creates an imbalance between acidogenesis and methanogenesis and ultimately cause the failure of the methanogenesis (Chynoweth et al., 1992; O'Keefe and Chynoweth, 2000;

Yuen, 2001; Erses and Onay, 2003; Behera et al., 2010). The failure of methanogenesis is tantamount to biogas inhibition and or low biogas yield (Jain et al., 2015).

Depending on the anaerobic system, substrate characteristics and environmental conditions, several strategies exist for preventing process dysfunction and inhibition in order to boost biogas production from organic waste treatment. For instance, one of the commonly used strategies for accelerating waste stabilization and promoting higher calorific biogas production in anaerobic bioreactor landfills is moisture control through leachate recirculation (Pohland, 1996; San and Onay, 2001; Yuen, 2001; Warith, 2002; Reinhart et al., 2002; Nwaokorie et al., 2018; Pearse et al., 2018). This basically involves the reintroduction of collected leachate back into the landfill. To avoid acidic conditions and ensiling which may occur during leachate recirculation in young/new landfills, leachate recirculation is recommended to be combined with pH control, buffer addition, sewage sludge addition and old leachate addition (leachate blending) (Warith et al., 2002; Yuen 2001; Nair et al., 2014; Pearse et al., 2018). No known landfill currently practices recirculation of blended leachate.

On the other hand, several options have been suggested for the dual purpose of alleviating inhibition and promoting biogas production in anaerobic digesters as well. In order to achieve these objectives, strategies such as waste pre-treatment, addition of additives, digester design and anaerobic co-digestion (ACo-D) or co-fermentation have been commonly prescribed and applied to organic waste (Kim et al., 2003; Koupaie et al., 2014; Ara et al., 2015; Shah et al., 2015; Mao et al., 2015; Montecchio et al., 2019). The proper application of these strategies in an anaerobic system can help boost and accelerate the overall biogas production and at the same time curb possible inhibitions to the biological process. Of all these alternatives, ACo-D has been recognized as one of the most effective and a low-cost alternative to improve biogas yields and minimize process instabilities (Ara et al., 2015; Li et al., 2014).

ACo-D is the fundamental practice of co-digesting complimentary liquid or solid organic substrates with the aim of improving biogas yield through nutrient balancing and positive synergism (Li et al., 2014; Ara et al., 2015; Nielfa et al., 2015). Asides the benefit of improving biogas yield over mono-digestion of substrates, ACo-D has been reported to improve buffering capacity and dilute inhibitory and toxic compounds even during increased loading of degradable organic matter (Khalid et al., 2011; Ara et al., 2015). The success of ACo-D is dependent on the substrate characteristics since antagonistic or neutral outcomes may occur when incompatible substrates are co-digested (Nielfa et al., 2015).

Consequently, this work considers the application of leachate blending and anerobic co-digestion to a number of organic substrates as a means of alleviating process imbalances and bottlenecks in order to aid process optimization and recovery of the highest amount of biogas during treatment and stabilization of waste in anaerobic systems.

1.2 Study Rationale and Objectives

The rationale for this study is based on several previous research works;

1. Numerous works on laboratory, pilot and large-scale studies have documented the several benefits of leachate recirculation most especially the enhancement of biogas production from OFMSW (Pohland, 1996; San and Onay, 2001; Reinhart, 2002; Sponza and Agdad, 2004; Yuen 2001, Warith, 2002; Ahmadifar et al., 2016; Grossule et al., 2018). The full benefits of recirculation may however be hampered by ensiling, acidification and ammonia accumulation leading to low biogas yield especially in young landfills (<5years old) (San and Onay, 2001; Akindele and Sartaj, 2018). While no known bioreactor landfill currently practices recirculation of blended leachate, the effect of recirculating blended leachate on biogas production during the treatment of MSW in bioreactor landfills has not been investigated by researchers. In fact, nothing has been discussed so far in the open literature about how leachate blending affects ensiling in bioreactor landfills. Therefore, the novel intent of the first part of this study is to explore recirculation of blended leachate as a tool for alleviating ensiling as well as improving biogas production in simulated continuous landfill columns treating OFMSW.
2. Some of the challenges of mono-digestion of substrates involves low conversion efficiency, nutritional imbalance, ammonia toxicity and early acidification leading to methanogenic inhibition and retarded biogas production (Li et al., 2014; Mata-Alvarez et al., 2014; Ara et al., 2015; Akindele and Sartaj, 2018). Research over time has also suggested that strategies such as leachate blending (Nair et al., 2014) and ACo-D can reduce process inhibition and improve biogas yield over mono-digestion (Ara et al., 2015; Chan et al., 2002; Martín-González et al., 2010). Of recent however, lipidic waste such as fat oil and grease (FOG) has been identified as a highly desirable co-substrate due to their

high theoretical biogas potential (Martín-González et al., 2010; Loustarinen et al., 2009; Long et al*.,* 2012; Alqaralleh et al., 2016; Salama et al., 2019). Sewage Scum (SS), a FOG-rich substrate with an appropriate C:N ratio accounts for up to 4% total solids (TS) at most wastewater treatment plant (Young, 2012). Till date, SS has not received much attention as a potential substrate for biogas production during digestion AD or ACo-D. Currently, there is limited information on ACo-D of SS with biodegradable wastes such as OFMSW. Moreover, the effect of leachate blending during ACo-D with SS remains unknown. Consequently, the second study investigates process stability and biogas production from SS during ACo-D with OFMSW and leachate blend addition.

3. Several challenges including slow and poor degradation, nutritional imbalance and acid accumulation has led to poor biogas yield during mono-digestion of FOG-rich wastes (Long et al., 2012; Salama et al., 2019). Recent studies have however tested and concluded that co-digesting sewage scum (a FOG rich waste) with other organics such as OFMSW or landfill leachate are promising alternatives to improve biogas production. While co-digestion mixtures involving other FOG-rich wastes have been studied extensively in the open literature (Martín-González et al., 2010; Wan et al., 2011; Ponsà et al., 2011; Mata-Alvarez et al., 2014; Alqaralleh et al., 2016), trinary mixtures involving FOG waste are generally scanty in the literature (Grosser, 2018). To fill this knowledge void, a trinary co-digestion mixture of SS, OFMSW and TWAS will be considered on a WWTP scenario and compared with a trinary mixture of SS, OFMSW and landfill leachate blend will be investigated and considered on a landfill scenario. This study will allow the comparison of the two co-digestion alternatives.

1.3 Chapter Organization

This thesis contains seven chapters, and it is organized in a paper format.

Chapter 1 is a general introduction that contains thesis background information, study rationale, objectives, and chapter organization.

Chapter 2 contains a general literature review relevant to the topic.

Chapters three to five include three separate manuscripts that have either been published, under peer-review or been prepared for publication in peer-reviewed scientific journals. Chapters 3 through 5 are organized as follows;

Chapter 3

Enhancing biogas production from municipal solid waste through recirculation of blended leachate in simulated bioreactor landfills.

Aromolaran, Adewale, Majid Sartaj.

Manuscript published in *Biomass Conversion and Biorefinery* (2021), pp.1-16. Springer Nature.

Chapter 4

Biogas production from sewage scum through anaerobic co-digestion: The effect of organic fraction of municipal solid waste and landfill leachate blend addition.

Aromolaran, Adewale, Majid Sartaj.

A revised version of this manuscript was submitted to *Waste Management & Research*, Sage Publishing.

Chapter 5

Enhancing biomethane production through trinary co-digestion of sewage scum and municipal solid waste with thickened waste activated sludge and leachate blend addition

Aromolaran, Adewale, Majid Sartaj.

This manuscript is currently being prepared for submission to a scientific journal.

Chapter 6

Synthesis, integration and general discussion of all the various phases contained in this thesis.

Chapter 7

Chapter 7 contains conclusions from the entire thesis and recommendations for future work.

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Chapter 2- Literature Review

2.1 Anaerobic digestion

The biological conversion of organic matter to methane without the use of oxygen as an external electron acceptor is known as anaerobic digestion (Jingura and Matengaifa, 2009; Angelidaki and Bastone, 2010; Khalid et al., 2011; Ara et al., 2015; Bajpai, 2017). AD is a mature process, and it has been described as a complex biochemical and symbiotic process comprising of various microorganisms with unique functions and growth rates with the aim of producing a stable end product (Kumar and Samadder, 2020; Jingura and Matengaifa, 2009).

Although there are other microbially mediated methods for treating organic rich wastes, one of the reasons for the treatment of organic waste by AD is due to possibility of energy recovery from the waste (Balat and Balat, 2009: Mata-Alvarez et al., 2014; Bajpai, 2017). A major by-product in anaerobic digestion is biogas which consists of methane (55–65%) and carbon dioxide (35–45%) nitrogen (0–3%), hydrogen (0–1%), hydrogen sulfide (0–1%) and other trace gases (Balat and Balat, 2009). Methane is the same as natural gas. It can be collected and used in dryers and boilers for heat generation. It can also be used in internal combustion engines and turbines for electricity generation. Although the processes are similar, anaerobic digesters produce biogas faster than in bioreactor landfills because the environmental conditions in anaerobic digesters are optimized for biogas production in contrast to the heterogenous conditions in landfills (San and Onay, 2001; Sponza and Agdad, 2004). The quality of biogas generated in AD plants depends on factors such as process design, volatile solids present in the feedstock (or composition) and the C:N ratio (Mata-Alvarez et al., 2014; Mao et al., 2015). In addition to the biogas, a nutrient rich digestate is obtained which can be used as a fertilizer or used as soil conditioner (Angelidaki and Bastone, 2010).

AD is also advantageous over aerobic process due to low energy requirement and low biomass production (Ara et al., 2015; Khalid et al., 2011; Mata-Alvarez et al., 2014; Ponsá et al., 2011). Despite the advantages of AD, the process is complicated and sensitive and involves numerous microorganisms requiring unique environmental conditions (Bajpai, 2017; Mao et al., 2015). Regardless, AD has also been predicted to serve a pivotal role in the future of renewable energy (Khalid et al., 2011; Papargyropoulou et al., 2014; Hagos et al*.,* 2017).

2.1.1 Process Microbiology

With regards to the process microbiology of AD, it was initially thought to be a 2-stage process of acidogenesis and methanogenesis (Anderson and Yang, 1992). Hydrolysis of complex organic polymers was later discovered to occur before acidogenesis and methanogenesis (Haandel and Lubbe, 2007). However, further studies have shown that states that biological conversion of organic matter into methane occurs in 4 stages involving hydrolysis, acidogenesis, acetogenesis and methanogenesis (Jingura and Matengaifa, 2009; Khalid et al.,2011; Mata-Alvarez et al., 2014; Angelidaki and Bastone, 2010; Mao et al., 2015; Ren et al., 2018; Bajpai, 201; Rabii et al., 2019). Figure 2-1 shows the anaerobic pathway as summarized by Rabii et al (2019). From the Figure 2-1, the very first step is the hydrolysis stage which occurs when hydrolytic organisms produce hydrolytic enzymes for the breakdown and transformation of organic polymers such as lipids, protein, starch fat, oil and grease to soluble monomeric compounds such as amino acids, monosaccharides and long chain fatty acids. These monomeric compounds are essentially substrates for the acidogenic bacteria. In the digestion of high solid organic waste, hydrolysis of complex polymers to soluble compounds is a slow process and it has been described as the rate-limiting step (Khalid et al.,2011; Mata-Alvarez et al., 2014).

The next stage is acidogenesis or acidogenic fermentation of the monomeric compounds produced in the first stage by various facultative and obligate anaerobic bacteria. This stage leads to the production of volatile fatty acids (VFA), ammonia, CO_2, H_2, H_2S and other by-products. In this stage, the pH of the digester drops to between 4.5 and 5.5.

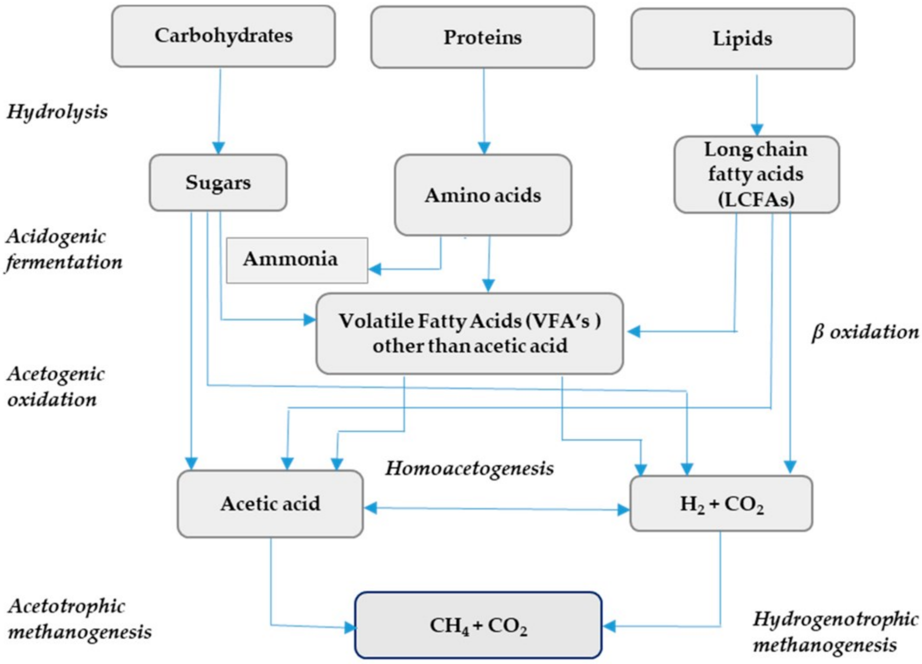

Figure 2-1: Anaerobic digestion pathway (Rabii et al., 2019)

Temperature affects the amount of VFA produced in this stage as more VFA (especially propionate) is chronically higher under thermophilic conditions than in mesophilic condition (Khalid et al., 2011).

The third stage of anaerobic digestion is acetogenesis which is basically when the products from the acidogenic stage are degraded into acetate, H_2 and CO_2. In addition, higher organic acids such as propionic and butyric acid are converted to acetic acid and hydrogen. The hydrogen in this phase is been regarded as a waste product as it is considered inhibitory to the long chain fatty acid oxidation by acetogenic bacteria. However, because of the syntrophic relationship that exists between methanogens and the acetogens, the hydrogenutilizing methanogens consume the hydrogen for methane production (Angelidaki and Bastone, 2010; Wilkinson, 2011). It is worth mentioning that there is sometimes no clear distinction between the acetogenic and acetogenic reactions taking place because both reactions produce acetate and H_2 which are both substrates for the methanogenic bacteria (Bajpai, 2017; Rabii et al., 2019).

The last stage of anaerobic digestion is methanogenesis. This is a critical phase because all the intermediates produced in the previous phases are converted into methane, CO_2 and water by the methanogenic archaea. This phase is also very slow due when compared to the other phases due to the slow growing rate of methanogens. According to Sawayama et al. (2004) CO_2 and 70% of methane is produced from acetate by the action of acetoclastic methanogens. The reduction of CO_2 with hydrogen through the action of hydrogenotrophic methanogens produces the rest of the methane. Methanogenesis is extremely sensitive to temperature and pH fluctuations and can be easily inhibited by low pH, high VFA and ammonia. As noted earlier, to prevent the inhibition of the oxidation of long chain VFAs to acetate, hydrogen scavenging or hydrogenotrophic methanogens help maintain a low partial pressure by consuming the hydrogen produced by the acetogens (Wilkinson, 2011). This will therefore minimize the accumulation of VFAs in the digester.

2.1.2 Anaerobic Co-digestion (ACo-D)

In anaerobic systems, the treatment of multiple liquid and/or solid wastes is referred to as anaerobic co-digestion (Mata-Alvarez et al., 2011; Shah, 2015). The process microbiology of ACo-D is similar to what happens in AD. While co-digestion is more common to anaerobic digesters, it is also carried out in bioreactor landfills and referred to as co-disposal (Chan et al., 2002).

ACo-D will normally be applicable to existing facilities where current capacity is underutilized or in excess (Koupaie et al., 2014). Therefore, it has the potential of promoting greater system efficiency, economic benefits and enhanced energy production when compared to mono-digestion. The core of this practice is the selection of the appropriate and complimentary substrates in order to avoid counterproductive results (Nielfa et al., 2015).

One of the main reasons for conducting ACo-D is the selection of the optimum blend ratios of the substrates in order to maximize possible outputs. Therefore, the co-digestion of complimentary co-substrates in the proper percentages during co-treatment maximizes substrate conversion of biodegradable organic matter to biogas through syntrophic interaction of the microbial population thereby producing a synergistic effect (Esposito et al., 2012; Shah, 2015; Achinas et al. 2019). Some of the other advantages of co-digestion includes the nutritional balance of total organic carbon (TOC), nitrogen and phosphorus ratio (Crolla and Kinsley, 2008), dilution of inhibitory compounds (Chen et al., 2008; Pastor et al., 2013), homogenization of particulate matter (Braun and Wellinger, 2003), increase in buffer capacity and promotion of greater reduction in greenhouses gas emissions (Mata-Alvarez et al., 2011). On the other hand, ACo-D can also lead to an increase in the total COD concentration of both the input materials and the effluent. Also, additional power maybe be required for operation. Relevant co-digestion studies are discussed in chapters 4-5 of this work.

2.2 Bioreactor Landfills

According to the United States Environmental Protection Agency (USEPA), a bioreactor landfills is a "municipal solid waste landfill that operates to rapidly transform and degrade organic waste. The increase in waste degradation and stabilization is accomplished through the addition of liquid and air to enhance microbial processes" (USEPA, 2009) According to Reinhart (2002) the four main justifications for the bioreactor landfill technology are "i) to increase potential for waste to energy conversion, ii) to store and/or treat leachate, iii) to recover air space, and iv) to ensure sustainability".

Bioreactor landfills are operated and controlled to promote the rapid degradation of the organic portion of MSW and to bring forward the inert state of a landfill in a relatively short period (Grossule et al., 2018; Reinhart et al., 2002; Yuen, 2001). In this landfill types, waste is treated and stabilized in a bioreactor rather than simply buried or entombed as the case was in a conventional landfill. Although the mechanism of waste degradation in bioreactor landfills is very much similar to the conventional landfill, the major difference lies in the fact that the conditions are optimized in the bioreactor for an increased waste degradation through the addition of liquid and or air, waste shredding, temperature management pH adjustment and nutrient addition (Ahmadifar et al*.,* 2016; Grossule et al., 2018). Opportunities also exists to harness energy from the waste, recover space through rapid waste settlement, store and treat leachate through gradual organic attenuation. Therefore, some of the benefits of operating a landfill as a bioreactor are reduced environmental impact, reduced post-closure care and maintenance risk, improved leachate quality, increased gas production over a shorter period and rapid waste settlement (Reinhart et al., 2002; Warith, 2002). Bioreactor landfills are traditionally operated as anaerobic mainly for collection of biogas (Grossule et al., 2018; Nwaokorie et al., 2018).

2.2.1 Anaerobic bioreactor landfills

In anaerobic bioreactors, biodegradation and stabilization of waste occurs in the absence of air and oxygen leading to the production of biogas (Ahmadifar et al., 2016; Warith, 2002; Grossule et al., 2018; Nwaokorie et al., 2018). In addition, leachate is recirculated to maintain optimum moisture content and improve biogas production. Figure 2-2 shows a modern anaerobic landfill bioreactor

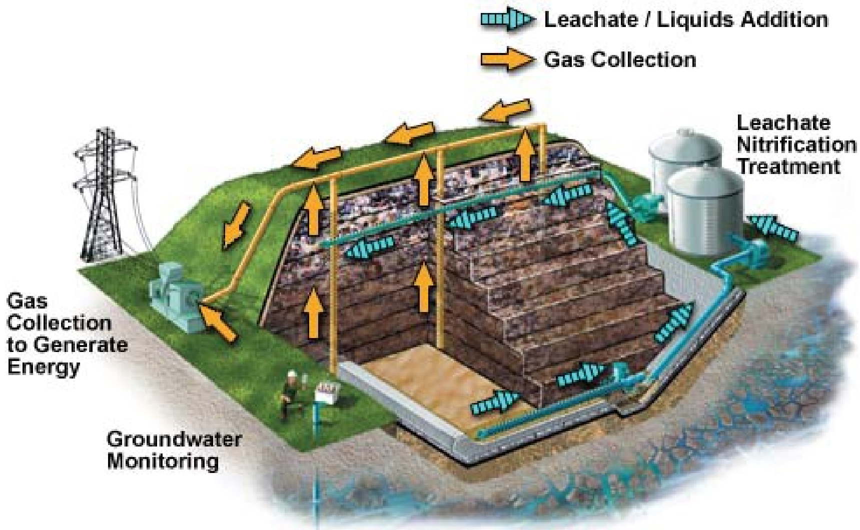

Figure 2-2: A schematic of a modern anaerobic bioreactor landfill (USEPA, 2009)

In this bioreactor, the production of biogas is the main feature and similar to other anaerobic systems, biogas production depends on the waste composition, moisture, pH, temperature, alkalinity, nutrient availability and absence of toxic and inhibitory compounds (Chan et al*.,* 2002; Valencia et al*.,* 2009). However, the rate at which biogas is produced will depend on the rate of the hydrolysis of the substrate and will decrease over time (Kjeldsen et al., 2002). Up to 90% of the carbon degraded in an anaerobic bioreactor landfill is converted into biogas, while the remaining 10% stays in the dissolved organic load of the leachate (Huber-Humer et al., 2011).

Unlike conventional landfills, biogas produced in this bioreactor is captured in gas collection and recovery systems. It is then cleaned, and the methane content is harnessed for energy generation.

In anaerobic bioreactors, many researchers agree that biodegradation of waste in an anaerobic bioreactor occurs sequentially in five major phases (Grossule et al., 2018; Nwaokorie et al., 2018; Pohland, 1996; Kjeldsen et al., 2002; Warith, 2002; Pohland and Kim, 2000). These phases are however quite similar to the processes that occur in anaerobic digesters because the microbial population appear to be similar (Pohland and Kim, 2000). Major bacterial groups such as the hydrolytic bacteria, fermentative, acidogenic, acetogenic, methanogenic and sulphate-reducing bacteria have been identified in both processes which leads to eventual CH_4 and CO_2 formation. (Warith, 2002). The difference however is that the substrate composition (carbohydrate, fat and protein) and conditions in anaerobic digesters are well controlled to ensure optimization (El-Fadel et al., 1997). In contrast, waste composition in landfills is highly heterogeneous, porous and under predominantly under-saturated conditions because moisture addition is usually insufficient to allow for optimal biodegradation of the total weight of landfilled waste. Moreover, moisture is often added intermittently and distributed unevenly (Fei et al., 2016). Consequently, the typical value for CH_4 content in biogas from an anaerobic digester is estimated at 45- 85%, while the typical landfill CH_4 gas content is estimated as 45 - 60% (Angelidaki and Bastone, 2010). Figure 2-3 shows the phases involved in a landfill stabilization process.

The first phase is the initial adjustment phase occurs when the waste is initially placed in the landfill. At this time, the there's air intrusion and nitrogen concentration is at maximum. Also, there is an initial lag time and acclimation period when moisture accumulates to support and develop the microbial population. Fresh waste usually contains all the trophic bacteria groups required to attain methanogenesis (Reinhart and Al-Yousfi, 1996). The initial adjustment stage is usually less than a month.

In the second phase known as the transition phase, the oxygen is highly depleted and so the landfill condition transforms from aerobic to anaerobic thereby causing hydrolysis and hydrocarbon breakdown in the waste. The displacement of oxygen at this point causes an acid (VOA). Also, ammonia is expected to be present in the leachate due to the hydrolysis and fermentation of protein containing compounds increase in the concentration of CO_2. At the end of this phase, it is expected that the leachate will have measurable concentration of chemical oxygen demand (COD) and volatile organic compounds.

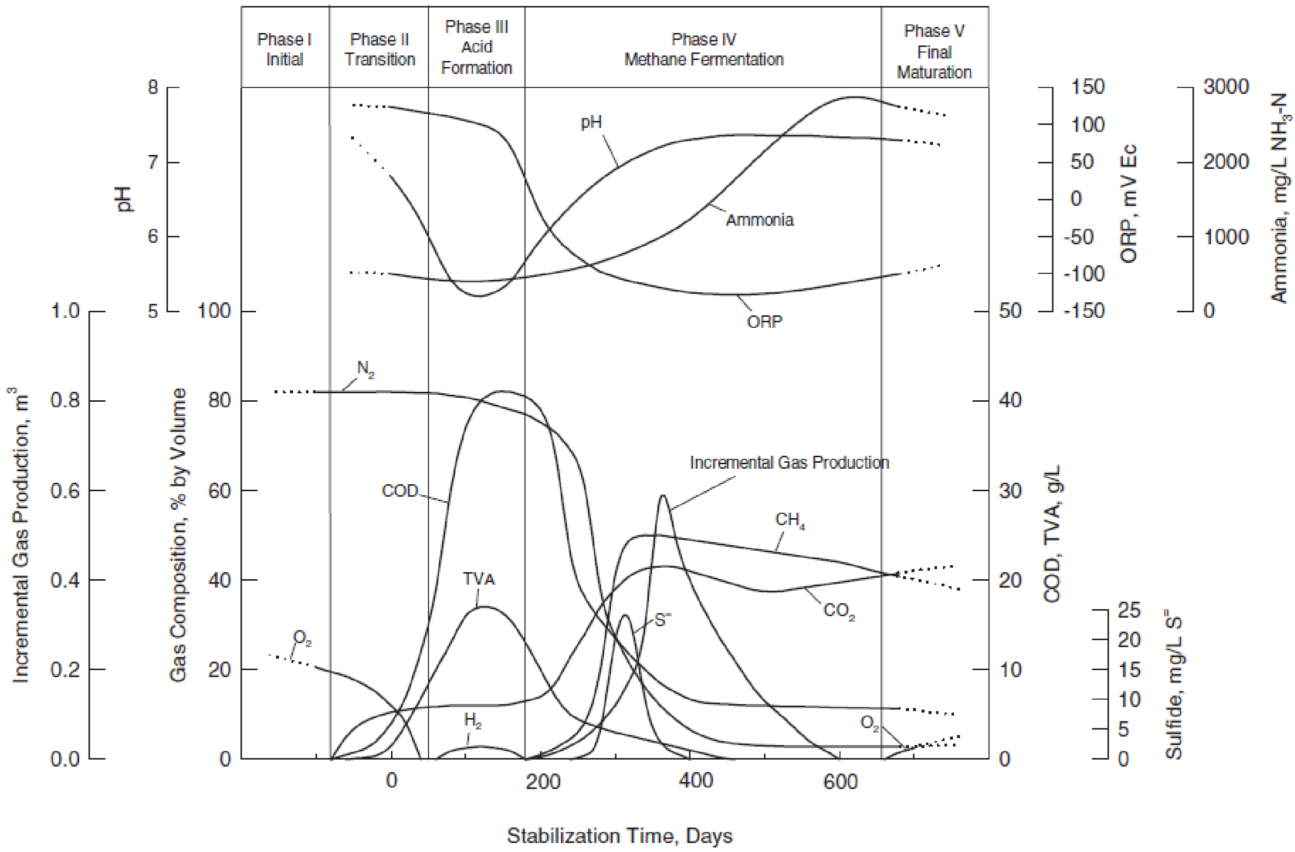

Figure 2-3: Phases involved in a landfill stabilization process (Kim and Pohland, 2003).

The third phase is the acid formation phase. Here, intermediate VOAs (mainly acetic and butyric acid) are produced at high concentrations due to the continuous hydrolysis and conversion of biodegradable organics present in the waste. CO2 is the main gas generated here and lesser amount of H_2 is also formed. The COD, BOD and conductivity of the leachate at this stage increases significantly due to the dissolution of organic acid into the leachate. The production of VOAs and CO_2 causes a low pH value. At low pH value, heavy metals and inorganic constituents are solubilized. In the methane fermentation phase, methanogenic organisms convert the acetic acid and hydrogen gas formed the in the previous stage to CH_4 and CO_2. Sulphate and nitrate in the system are reduced to sulphide and ammonia respectively. The pH value at this stage also rises to a more neutral value of 6.8 to 8 which supports methanogenic bacteria growth.

The methane fermentation phase is the most important phase because the maximum biogas production occurs at this phase. This phase also allows the removal of heavy metals present in the leachate through complexation and precipitation. The optimum temperature for methane formation has been reported to occur between 35^{o}C and 40^{o}C for mesophilic bacteria, and between 50^{o}C to 60^{o}C for thermophilic bacteria (Grillo, 2014).

The last stage is the maturation phase. In this phase, microbial activity is highly limited due to decreased substrate and nutrient availability. The BOD:COD is usually less than 0.1 and as a result, biogas production is negligible and the leachate strength remains constant with lower concentration values than the earlier phases. However, humic-like substances are produced due to the decomposition of resistant organics which may continue over a period. The undigested substrates are also likely to be rich in lignin (Jayasinghe et al., 2013). It is important to note that the duration of these phases is not definite but depends on factors such as the organic substrate, nutrient availability, moisture content and compaction level.

Operating an anaerobic bioreactor landfill may be a cost-effective and sustainable method to manage MSW due to its low energy requirements and ease of operation. It may also be beneficial because the waste degradation is accelerated, leachate is treated during recirculation and more importantly, methane potential of the organic waste is harnessed for electricity generation.

2.2.2 Factors affecting biogas production and waste degradation in anaerobic bioreactor landfills

Biogas production and waste biodegradation in bioreactor landfills may be impacted by waste composition and age as well as operating conditions such as moisture content, pH, alkalinity, temperature, ammonia concentration and nutrient availability etc (Akindele and Sartaj, 2018; Jokela et al., 2002; Jokela and Rintala, 2003; Sponza and Agdad, 2004; Nair et al., 2014 Bilgili et al., 2009; Muller et al., 2015; Pearse et al., 2018).

Of all the above factors, moisture content is the most critical parameter affecting performance of bioreactor (Warith, 2002; Chan et al., 2002; Sponza and Agdad, 2004). Studies have shown that moisture presence in a landfill can greatly improve the microbial degradation of waste by providing an aqueous environment which facilitates better synergy among insoluble substrates, soluble nutrients, and microorganisms in the landfill cell. Chan et al (2002) observed that moisture presence in a bioreactor ensures an improved mass transfer to prevent the development of stagnant zones in landfill cells. According to USEPA, moisture presence and control will enhance rapid MSW degradation and make the waste less hazardous due to degradation of organics and sequestration of inorganics (USEPA, 2009). Valencia et al., 2009 also stated that moisture helps dilute high concentrations of inhibitory substances.

The movement of moisture through the waste body during waste biodegradation leads to the production of a highly contaminated liquid called landfill leachate (El-Fadel et al., 2002; Valencia et al., 2009).

Leachate recirculation or recycle is the most practical method to control the moisture content of waste in a bioreactor landfill (Warith, 2002; Grossule et al., 2018; Ahmadifar et al., 2016; Reinhart et al., 2002). This technique is the most investigated technique in anaerobic bioreactor landfills (Yuen, 2001; San and Onay, 2001; Warith, 2002, Sartaj et al., 2010; Pearse et al., 2018). Recirculation of leachate in a bioreactor facilitates pH buffering, distribution of nutrients and enzymes, dilution of inhibitory compounds, recycling, and distribution of methanogens (Reinhart and Al-Yousfi, 1996; Chan et al., 2002). This practice also improves biogas production with the additional benefit of providing treatment of the leachate as it moves through the waste mass. (Reinhart et al., 2002; Yuen et al., 2001; Bilgili et al., 2009). Therefore, it has also been discovered to reduce cost of leachate management (Reinhart et al., 2002) and suggested to improve leachate quality and ultimately reduce the landfill stabilization time from several decades to a few years (Reinhart and Al-Yousfi, 1996).

Low pH results from VFA production accumulation (acidogenesis) in a landfill while ammonification results in the production of ammonia from organic nitrogen (protein and amino) breakdown in MSW. Since ammonia is stable under anaerobic landfill conditions, moisture presence or recirculating leachate will increase ammonification rates and consequently result in high ammonia accumulation and increased leachate toxicity (Jokela et al., 2002; Jokela and Rintala, 2003; Sun et al., 2011). This makes nitrogen removal an important aspect in management of bioreactor landfills (Jokela et al., 2002; Jokela and Rintala, 2003).

Temperature affects biogas production and waste degradation since the rate of waste biodegradation tends to increase with increase in temperature. Temperatures in landfills and the amount of heat generated from biochemical reactions occurring in the waste can be influenced by the climatic conditions of the area, the type of waste, thermal properties of waste as well as the age of the landfill (Yeşiller et al., 2015). Temperatures above 55^{o}C in MSW landfills are considered elevated temperatures (ETs) in the literature (Reinhart et al., 2020). Not only do ETs pose significant challenges to landfill operators, but these occurrences violate regulatory standards, impair gas extraction, leachate collection systems and could impact the structural reliability of the landfill, leading to escape of toxicants. Moreover, microbes rarely thrive above 70 -75 ^{o}C thus impacting waste degradation (Berquist and Van Geel, 2020). A wide range of temperatures in landfills have been reported in the literature. Townsend et al. (1996) reported temperatures of up to 60^{o}C in the middle layer of a bioreactor landfill in Florida. Temperatures below freezing temperature in MSW landfills were also observed in a Quebec landfill (Berquist and Van Geel, 2020). For bioreactor landfills in cold climates, raising the temperature of the leachate/waste interface in the presence of moisture is economical and can also help improve landfill performance rather than increasing the temperature of the whole in-place waste (Abdallah et al., 2014).

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Chapter 3- Enhancing Biogas Production from municipal solid waste through recirculation of blended leachate in simulated bioreactor landfills[1]

3.1 Abstract

This study is an attempt to assess biogas production improvement from organic fraction of municipal solid waste in simulated bioreactor landfills through recirculation of blended landfill leachate. The blends were prepared from young landfill leachate (<5years) and old landfill leachate (>5years). In this study, various old and new leachate blends (66.6%New:33.3%Old, 33.3%New:66.6%Old) as well as 100%New and 100%Old were recirculated through 6 laboratory scale bioreactors using open-loop and closed-loops modes under mesophilic conditions over a period of 161days. Compared to the control bioreactor where 100% New leachate was recirculated and operated as a closed-loop, cumulative biogas production was improved by as much as 77% to 193% when a leachate blend of 33%New:67%Old was recirculated. Furthermore, comparison of the results from open-loop and closed-loop operated bioreactors indicated that there was approximately 28% to 65% more biogas in open loop bioreactors. The Gompertz model produced a better fit ($R^2 > 0.99$) than first-order and Logistic Function models. Leachate blending reduced the lag phase by almost half, thus help alleviating the ensiling during the start-up phase.

[1] A version of this chapter has been published as "Aromolaran, A. and Sartaj, M., 2021. Enhancing biogas production from municipal solid waste through recirculation of blended leachate in simulated bioreactor landfills. Biomass Conversion and Biorefinery, pp.1-16". It is reproduced here with the permission of the copyright holder.

3.2 Introduction

Bioreactor landfills (BLFs) are a development of conventional landfills in which specific operational procedures are employed to stimulate the microbial degradation and stabilization of organic fraction of municipal solid waste (OFMSW) and to enhance biogas production and recovery. Design and operation of landfills as BLF helps promote sustainable development and circular economy, could cause a reduction of the contaminant life span of the landfill and the cost of long-term monitoring, and reduces greenhouse gas emissions (Warith 2002; Behera et al., 2010; Sandip et al., 2012; Grossule et al., 2018; Nwaokorie et al., 2018; Nguyen et al., 2019; Agdag et al., 2020). The biodegradation of waste in a landfill environment is affected by several factors such as waste composition and age, operational conditions, pH, moisture content, temperature, nutrients availability, etc. (Bilgili et al., 2009; Khalid et al., 2011; Muller et al., 2015; Pearse et al., 2018). However, moisture content has been determined as the most critical parameter (Warith, 2002; Chan et al., 2002; Sponza and Agdad, 2004). Although there are no clear-cut rules in the literature for the optimum moisture content in BLFs, moisture content less than 20% w/w could affect the transport of nutrients and mass transfer of organic substrate and potentially retard anaerobic waste degradation and gas production (; Cho et al., 2012; Townsend et al., 2015; Cossu et al., 2016). On the other hand, moisture content greater than 40% w/w is suggested to improve degradation and enhance biogas generation (Mehta et al., 2002; Knox et al., 2018). Pearse et al. (2018) suggested that a moisture content between 25-60% would result in increased gas production rate and methane percentage in the produced biogas. The main process used for the control of the moisture content of waste in BLFs is leachate recirculation.

The benefits of leachate recirculation are numerous and have been well documented by several scholars (Warith, 2002; Grossule et al., 2018; Bilgili et al., 2009; Sponza and Agdad, 2004; Reinhart and Al-Yousfi, 1996; Reinhart et al., 2002; Yuen, 2001; Benson et al., 2007; Sanphoti et al., 2006; Bilgili et al., 2007; Sartaj et al., 2010). However, leachate recirculation, if not properly managed, could cause methanogenic inhibition due to the high concentration of volatile fatty acids (low pH) which are known to be toxic to methanogens. Accumulation and presence of high concentrations of ammonia, also known to have inhibitory effects, during the recirculation of leachate might also occur under anaerobic conditions, which still remains as one of the main challenges in operation of BLFs (Grossule et al., 2018; Pearse et al., 2018; San and Onay, 2001; Akindele and Sartaj, 2018; Jokela and Rintala, 2003; Montecchio et al., 2019; Ledakowicz and Kaczorek, 2004). The state of inhibited microbial activity and stalled waste stabilization and biogas production in landfills has been referred to as ensiling (O'Keefe and Chynoweth, 2000). Imbalance between acidogenesis and methanogenesis has been reported as the main cause for ensiling. Low alkalinity in landfill leachate to provide pH buffer capacity plays a role as well (O'Keefe and Chynoweth, 2000; Chynoweth et al., 1992; Cho et al., 2012; Town and Dumonceaux, 2016). When a landfill becomes ensiled, anaerobic degradation of organic waste is severely hampered during the start-up phase and methane production remains retarded for up to a year, even in recirculating bioreactor landfills (Chynoweth et al., 1992). In fact, recirculating fresh leachate within the same landfill portion will not correct the ensiling condition (O'Keefe and Chynoweth, 2000), but will instead accelerate early hydrolysis and acidogenesis which ultimately leads to VFA accumulation (Yuen, 2001; Sun et al., 2011).

Some remedial methods have been proposed to address the challenges of ensiling and inhibition of biogas production during anaerobic digestion (AD) process. O'Keefe and Chynoweth, 2000 investigated phase separation in simulated laboratory landfill cells where collected leachate from the cells was treated in an up-flow anaerobic sludge blanket reactor before recirculation. Phase separation resulted in increased rates of biodegradation and greater stability. The second AD reactor served to convert VFAs generated in the cells and to increase the buffering capacity of leachate. Town and Dumonceaux (2016) introduced a stable consortium capable of catabolizing acetate and producing methane into laboratory batch digesters as a potential bio-augmentation tool to alleviate acidic conditions due to accumulation of VFAs. This resulted in reduction of acetate accumulation and increase of biogas production. The characteristics of different types (age) of leachate or waste have been exploited by the sequential linking of different aged cells (O'Keefe and Chynoweth, 2000; Sun et al 2011; Poggi-Varaldo et al., 2005) and recirculating old (mature) leachate or a mixture of both old and new leachate to the newer portions of a landfill (Erses and Onay, 2003; Nair et al., 2014). Compared to new leachate, old leachate has a more balanced (adapted) mix of anaerobic microbial consortia with a significantly higher presence of methanogens lower VFAs content, higher pH, and higher alkalinity (Castrillón et al., 2010). Therefore, if old leachate is recirculated through new waste bodies, it could balance the unfavorable characteristics of the new leachate; mainly the low pH, the high concentrations of ammonia, and the excess VFAs. Moreover, the addition of old leachate will facilitate the rapid establishment of a balanced acidogenic and methanogenic microbial population and enhances pH buffer capacity (O'Keefe and Chynoweth, 2000; Jun et al., 2009). On other hand, young landfill leachate contains substances that are biologically easier to degrade. Recirculating a mix of fresh and old leachate would have the advantages of both types; the old leachate portion supplies microorganisms that are methanogenically acclimated and starved of substrate, and the new leachate portion or leachate within the fresh waste supplies in the substrate required for the AD process, thereby improving biogas yield (Muller et al., 2015 O'Keefe and Chynoweth, 2000; Erses and Onay, 2003; Nair et al., 2014; He et al., 2005).

To accelerate waste stabilization and gas production in a new landfill, Erses and Onay (2003) recirculated anaerobically digested old leachate. This study was conducted using two 96L PVC reactors (simulating old and young landfills) loaded with approximately 13kg of compacted and mixed solid waste. The young landfill reactor was maintained under acidogenic conditions and operated in 4 different stages to quicken the transition from acidogenic to methanogenic phase. COD values in the young landfill reactor increased from 10,000 mg/L to 20,855 mg/L during the first stage due to the prevailing acidogenic conditions, and decreased to 11,109 mg/L at the end of second stage while biogas production rates increased significantly due to the recirculation of old leachate. The authors concluded that the old landfill leachate with low organic content, high buffering capacity, and acclimated anaerobic microorganism could be utilized in young landfills for a faster waste stabilization. O'Keefe and Chynoweth, 2000 observed an increase in methane production and a reversal of ensiling in a leach-bed reactor when a strong buffering methanogenic leachate from an up-flow anaerobic sludge blanket reactor was circulated. Moreover, in a set of bio-methane potential (BMP) experiments conducted on samples of OFMSW, Nair et al. (2014) compared different leachate blends of old and new leachate (66.7%New;33.3%Old, 33.3%New;66.7%Old) as well as 100%New and 100%Old in order to evaluate the proof of concept and the effect of the leachate blends on biogas production. Biogas production increased up to 41% when 100% old leachate was used compared to the sum of independent biogas productions from the organic fraction, leachate blend and inoculum. However, it has been argued in the literature that BMP assay experiments, though fast, simple, and inexpensive to estimate bio-methane potential (Bilgili et al 2009) do not fully represent waste degradation processes in landfills due to some experimental factors such as low solids to liquid ratio, small sample size, moisture content and moisture flow, etc. (Pearse et al., 2018;

Cho et al., 2012; Krause et al., 2016). For instance, the moisture content in BMPs is often higher than the saturation levels with a high ratio of liquids (inoculum, deionized water, liquid buffer, and nutrient medium) to waste sample. This is quite different in real BLFs where the maximum amount of moisture available is equivalent to the field capacity of the landfilled waste, which depends on factors such as composition and the degree of compaction of the waste. Secondly, BMP reactors contain small sample sizes usually in the range of a few to tens of grams; these limited sample sizes may potentially misrepresent the entire waste fraction of the landfill due to heterogeneous nature of the waste encountered. For a detailed review on history, methods and protocols as well as limitations of BMP assay, readers are referred to Pearse et al. (2018). To address these issues, it was recommended to conduct experiments in larger reactors (≥ 2L), under high solid concentrations and under continuous mode (Landfill BMP (LBMP)) as opposed to batch mode (Pearse et al., 2018). This not only helps to simulate a real landfill scenario but also it gives a more realistic prediction of the biogas generation. Moreover, larger reactor sizes contain a diverse microbial population which could minimize the effect of chemical inhibition or microbial competition compared to the small-sized serum bottles used for BMPs that contain a small microbial population which may reduce VFA buildup and restrain the impact on biogas production (Pearse et al., 2018; Krause et al., 2016). Furthermore, the application of mathematical models are regarded as common and helpful tools to estimate the quantity and rate of biogas production as well as to help improve, understand and predict the performance of AD process and BLFs (Pearse et al., 2018; Townsend et al., 2015; Bilgili et al., 2007; Krause et al., 2016; Themelis et al., 2007; Kaza et al., 2018; Kafle et al., 2012).

Therefore, this study aims to investigate the effects of the recirculation of blends of new and old leachates in enhancing anaerobic degradation, process stability and biogas production using simulated lab-scale bioreactor landfill columns. This is because despite the conclusions drawn by Nair et al., 2014 on how leachate blending can improve biogas production, the effect of recirculating blended leachate on biogas production during the treatment of MSW in bioreactor landfills has not been investigated under continuous column studies by researchers. In fact, nothing has been discussed so far in the open literature about how leachate blending affects ensiling in bioreactor landfills. The specific objectives of the current study are (i) to evaluate the effect of recirculating different leachate blend ratios of new and old leachate on the biogas production in large simulated bioreactor landfill reactors treating OFMSW, (ii) to compare the effect of open–loop (replacing leachate) and closed–loop (same leachate) leachate recirculation on the biogas production, and (iii) to evaluate and compare different models for simulation of the anaerobic digestion process and biogas production in BLFs.

3.3 Materials

3.3.1 Organic fraction of Municipal Solid Waste (OFMSW)

MSW samples were collected from a local landfill site (Moose Creek, ON, Canada). The landfill is a bioreactor landfill site that has been accepting residential waste for the past 18 years. Approximately 200kg of gravity sorted OFMSW was collected from the feed to compost section of the landfill. Waste composition includes wood chips (23%), yard waste (19.2%), paper (7.7%), cardboard (34.6%) and food waste (15.3%). The collected waste samples were hermetically sealed in 20 L plastic buckets and transported to the University of Ottawa (Ottawa, ON, Canada) where they were stored at a temperature of 2°C. As needed for the experiments, the waste samples were removed from cold storage and allowed to stand for 24 hours at laboratory room temperature before use. When preparing for the lab experiments, waste samples were hand sorted to remove non-biodegradable materials such as stones, metals, plastic, and glass if any. Then the waste samples were mixed thoroughly using the quartering technique to ensure homogeneity before they were loaded into the simulated column reactors. The moisture content of the waste as received was 65.1%±2.2 and the volatile solids content was 71.6±9.5%.

3.3.2 New and Old Leachate

The new leachate was collected from an enclosed leachate reservoir within the landfill site (Moose Creek, ON). The leachate was collected from recent cells and was less than two years old. On the other hand, the old landfill leachate was obtained from a local engineered landfill (Carp, ON, Canada). The old landfill leachate was between 15 to 25 years old. In both cases, the leachate was collected in 20L plastic buckets, transported to the University of Ottawa and then stored at a temperature of 2° C until they were used. The leachates were allowed to stand for 24 hours under laboratory condition to reach the room temperature before usage (23±1 °C).

3.4 Methods

3.4.1 Experimental Setup

The experiments were conducted in six identical plexiglass simulated BLF columns, each measuring 180mm x 180mm x 900mm (approximately 29liters). The setup schematic for the column reactor is shown in Figure 3-1. All six bioreactors were operated in a temperature-controlled room at 30±2°C (mesophilic temperature) to enhance the growth of anaerobic bacteria. To ensure anaerobic conditions, rubber gaskets were placed between the columns and lids and reinforced with quick release toggle clamps. Each reactor was loaded with 20kg (wet weight) of OFMSW. Through compaction, a density of approximately 900-950 kg/m^3 was achieved in all reactors. Ceramic Raschig rings with 0.2m thickness in addition to a non-woven geo-textile material were installed at the bottom of each reactor as a drainage layer. This drainage layer will help to retain the waste in the column and prevents the release of small particles into the piping system. A port at about 3cm from the bottom of each column was used to collect leachate sample from the column reactor. For physicochemical analysis of the leachate, samples of the leachate exiting the columns were collected weekly. The excess leachate was then placed into the leachate blend reservoir for recirculation. Six peristaltic pumps (Masterflex, Cole-Parmer, Chicago, Illinois) were used for recirculating approximately 1.2 L of leachate every week for each reactor. The relatively low recirculation rate was selected to eliminate leachate flooding in the column due to the low filtration rate of the compacted waste bed. However, the recirculated leachate volume represents 6% of the waste volume in the column, and this is within the optimal recommended recirculation volume of 2.7-30% of waste bed volume as suggested in the literature (Sponza and Agdad, 2004). Biogas was collected and measured using wet-tip gas meters (Wet tip Gas Meter Co., Nashville, TN). The reactors were operated as either open- or closed-loop. Reactors were a total of 3 open-loop and 3 closed-loop columns, as shown in Table 3-1. In the open-loop, a portion of the leachate in the leachate reservoir was withdrawn and replaced with an equal volume of old leachate. However, in the closed-loop, no old leachate substitution/supplementation/replacement was conducted (leachate replaced per week). Instead, the original blend prepared was recirculated throughout the experiment. As shown in Table 3-1, the investigated blend ratios were selected based on Nair et al. (2014). pH in the control reactors were adjusted gradually through the addition of $NaHCO_3$ and stopped when the pH of the collected leachate stabilized around 7. The reactors were operated for a total of 161 days.

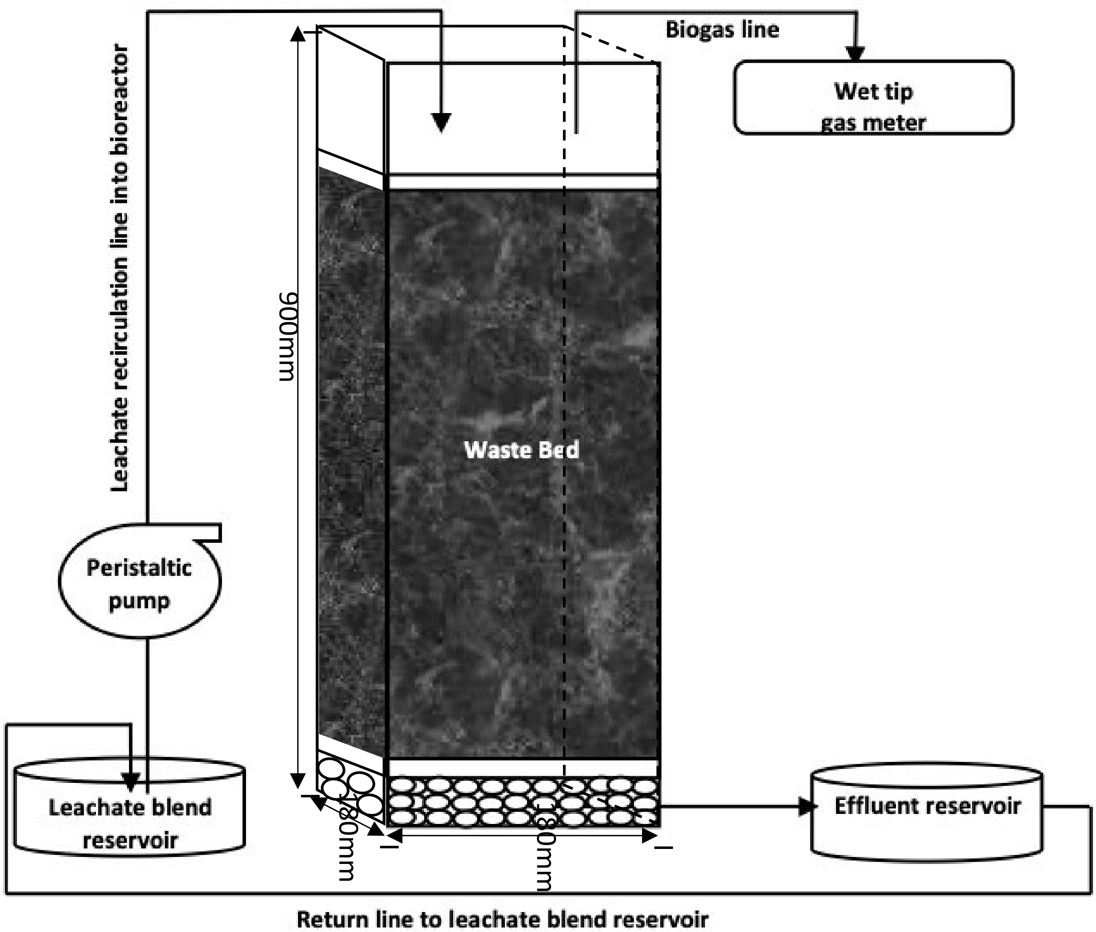

Figure 3-1: Schematic of the simulated bioreactor landfill.

Table 3-1: Experimental Setup

Reactor code	Leachate blend code	Blend composition	Recirculation loop	Reactor leachate replaced per week(L)
2N1O-OP	2N1O	66.6%New; 33.3%Old	Open	0.5
2N1O-CL	2N1O	66.6%New; 33.3%Old	Closed	0
1N2O-OP	1N2O	33.3%New; 66.6%Old	Open	1
1N2O-CL	1N2O	33.3%New; 66.6%Old	Closed	0
3N0O-CL	3N0O	100%New	Closed	0
0N3O-OP	0N3O	100%Old	Open	1.5

N=New leachate, O=Old leachate, OP=Open loop, CL=Closed loop

3.4.2 Physico-chemical analysis

The analysis conducted for this study followed standard methods (APHA, 2012). All samples collected from the six columns were analyzed weekly for pH, total alkalinity, chemical oxygen demand (COD), volatile fatty acid (VFA), and total ammonia-nitrogen (TAN). The quantities of leachate produced and recirculated were recorded weekly. Total solids (TS) and volatile solids (VS) of both leachate and MSW were determined according to standard method 2540G. Alkalinity analysis was done based on TNTplus™870 reagent vials (Method 10239, HACH USA). COD was determined based on HACH TNT 822 (250-15,000 mg/L) including spectrophotometer, heating block, and supplies. VFA and TAN were determined based on HACH TNT plus™ 872 reagent vials (Method 10240) and TNT plus™ 832 reagent vials (Method 10205), respectively.

3.4.3 Biogas volume and composition

Volume of gas were measured in all six bioreactors with the aid of wet-tip gas meters (Wet tip Gas Meter Co., Nashville, TN). The measured biogas volumes were adjusted to STP (0°C and 1atm) using the Equation 3-1 below (Nguyen et al., 2019; Kafle and Kim, 2012).

$$V_{STP} = \frac{V\ .\ 273\ .\ (760-Pw)}{(273+t)\ .760} \qquad \text{Equation 3-1}$$

Where: V_{STP} is the volume of gas at standard temperature (0°C) and pressure(1atm) (L); V is the volume of gas measured at temperature t (L); t is the temperature of gas or the ambient space (^{0}C); Pw is the vapor pressure of water as a function of temperature (mmHg).

Biogas samples were collected weekly from all the bioreactors, and the biogas composition was analyzed using a GOW-MAC gas chromatograph (Series 400, Gow-Mac Instrument Co., USA) fitted with a HayeSep® N 80/100 mesh, (5’ x 125’) and Molesieve equipped with a thermal conductivity detector (TCD). The HayeSep column N80/100 was used for N_2, CH_4, and CO_2 percentage analysis using Helium as the carrier gas. The temperatures of the column, detector, and injector were 120°C, 130°C, and 130°C respectively.

3.4.4 Data Analysis and Model Comparison

In this study, the cumulative methane production was calculated for each of the bioreactors. Then, two sigmoidal models; the modified Gompertz and modified Logistic model, and a first-order kinetic model were applied and compared to simulate the process performance in the six bioreactors. Given the complexity of the AD process in anaerobic bioreactors, applying only one model to simulate the process might be insufficient. Whereas, carefully comparing different models gives reliable and true kinetic parameters. Hence the need for a model comparison. During anaerobic biodegradation studies, Zhen et al. (2016) compared the predictions of 3 models (Gompertz, cone and first-order kinetic models) while El-Mashad et al. (2013) and Zhao et al. (2016) compared 4 models (Gompertz, Fitzhugh, Cone and first-order kinetic models). The authors observed different parameter precision for the same experimental data. The modified Gompertz model (GM) has been suggested as a good fit and is often used to describe the methane accumulation during AD experiments (Cossu et al., 2016; Lo et al., 2010; Altas, 2009), including landfill bioreactor studies (Mahar et al., 2016; Sandip et al., 2012). The modified Gompertz model is shown below as Equation 3-2.

$$\beta(t) = \beta o.\ \exp\left(-\exp\left(\frac{Rm.e}{\beta o}(\lambda - t) + 1\right)\right) \qquad \text{Equation 3-2}$$

Where: $\beta(t)$ is the methane accumulation (L/kg) at specific time, *t* is the time (day) over the digestion period. βo is the methane production potential (L/kg). *Rm* is *the* maximum methane production rate (L/kg.d), λ is the lag phase (day), and *e* = 2.7183.

The modified Logistic model (LM) is also usually used during anaerobic fermentation and methane production (Altas, 2009; Donoso-Bravo *et al*., 2010). It has also been applied to estimate methane production from landfill leachate (Pommier et al., 2007). The modified logistic model is shown in Equation 3-3.

$$\beta(t) = \frac{\beta o}{\{1+exp[\frac{4Rm.}{\beta o}(\lambda - t)+2]\}} \quad \text{Equation 3-3}$$

Where all parameters are the same as explained in Gompertz equation.

Finally, a first-order model (FO) in Equation 3-4 was applied to estimate the hydrolysis rate constant. This equation has been modified to include a lag phase (λ) (Zhang et al., 2018).

$$\beta(t) = \beta o[1- exp(-k(\lambda - t)] \quad \text{Equation 3-4}$$

Where k is the hydrolysis rate constant (first-order methane production rate) (k, day^{-1}) (Alqaralleh et al., 2016). While the logistic model assumes the rate of gas production to be proportional to the microbial activity (represented by the amount of gas already produced and to the substrate concentration), the Gompertz model assumes that the rate of gas production is proportional to the microbial activity with the proportionality parameter decreasing with time by first-order kinetics (Donoso-Bravo et al., 2010). The lag phase here implies the minimum time taken to produce biogas or taken for bacteria to acclimatize to the environment while the maximum methane production rate (*Rm*) describes the specific growth rate of methanogenic bacteria (Kafle and Chen, 2016). All models were completed by Microsoft Excel (2016) using the solver method.

3.5 Results and Discussion

The results of this study will be discussed in this section as follows: Leachate characteristics, Process parameters (pH , VFA , COD; Biogas production; And biomethane production kinetics modeling results.

3.5.1 Leachate Characteristics

The characteristics of both leachates are shown in Table 3-2. The values in the table represent the mean ± standard deviation for triplicates.

Table 3-2: Characteristics of the new and old leachate used in this study.

Parameter	Unit	New leachate	Old leachate
Alkalinity as $CaCO_3$	mg/L	9,360±331	3000±105
Chemical oxygen demand (COD)	mg/L	53,400±225	2640±215
Total ammonia nitrogen (TAN)	mg/L	2260±53	889±32
VFA (as acetic acid)	mg/L	20,730±344	299±34
Total solids (TS)	g/kg	68.1±2.2	5.31±1.2
Volatile solids (VS)	g/kg	39.6±3.2	1.18±2.1
pH		6.59±0.01	7.71±0.02

It can be observed from Table 3-2 that the concentration of COD, VFA, and TAN are observed to be higher in the new leachate compared to the old leachate. While the COD value of old leachate is 2640 ±215mg/L, the young leachate has a higher value of 53,400 ±225mg/L. The TAN concentration of old leachate was 889 ±32mg/L compared to the concentration of young leachate which had 2260 ±53mg/L. In terms of VFA, old leachate had a value of 299 ±34mg/L while the young leachate had 20,730±344 mg/L. This is not unusual as new leachate is typically from fresh waste, with active acidogenic reactions and therefore it is highly contaminated. Old leachate, on the other hand, is from more stabilized waste and within methanogenic stages. The COD value of leachate is indicative of the organic strength of the leachate, and it generally decreases as the landfill gets older. COD values for new leachate are typically greater than 10,000 mg/L and may extend to hundreds of thousands (mg/L) depending on the waste composition in the landfill (Christensen et al., 2001). Exceptional cases of lower COD for the new leachate also exist in the literature, for example, Aziz et al. (2007) reported a new leachate from a 3 years old landfill with a COD value of 3600mg/L, and Kulikowska and Klimiuk (2008) reported an initial COD at the beginning of a landfill as low as 1800mg/L. However, for the current study, the new leachate used for the experiments had a COD value of 53,400 mg/L, this high COD value is consistent with Nair et al. (2014) and Ozturk et al. (2003). On the other hand, the old leachate is often characterized by lower COD values due to high refractory organic content. Chiemchaisri et al. (2009) reported a COD range of 1,613 – 4,506 mg/L for old leachate in Thailand. This range is consistent with the 2640 mg/L COD value measured for the old leachate used in this study.

The average pH was 6.59 for the new leachate in this study which is comparable to the 4.3-7.0 range reported by Chiemchaisri et al. (2009) and Ozturk et al. (2003), for new leachate. Also, a pH of 7.7 for the old leachate in this study is within the pH range values reported by Valencia et al. (2009). The high VFA and COD, and low pH in the new leachates and new landfills are ascribed to the active acidogenic stage. In contrast, old leachate is characterized by low VFA and high pH values due to VFA conversion to CH_4 and CO_2. Consequently, the leachate characteristics are ideal in achieving the objective of this study.

3.5.2 pH

The variations in average pH values for the six experimental columns are illustrated in Figure 3-2. In anaerobic digesters and bioreactor landfills, the initial anaerobic degradation process involves the fermentation of the complex polymers (protein, fats, and carbohydrate) to monomeric organic compounds (amino acids, long chain fatty acids, and sugars). Subsequently, the monomeric compounds are fermented by the acidogenic bacteria, and this leads to the production of volatile fatty acids, H_2, NH_3, and H_2S. At this acidogenic stage, the pH of the system becomes highly acidic and typically within the range of 4.5 -5.5 (Pearse et al., 2018; Zia et al., 2020). The action of the acetogens converts the VFAs and other compounds into acetate and CO_2. Afterwards, a decrease in the concentrations of VFA, CO_2, and H_2 appears due to their consumption by methanogens leading to the production of methane. The conversion of VFAs to methane and CO_2 causes an increase in the pH of the system to be in the range of 6.8 – 7.2 (Zia et al., 2020). During the first 5 weeks of leachate recirculation in this study, the pH in all the columns was averagely between 4.9 and 5.8. The initial pH values were on the acidic scale and could be evidence that the acidogenic bacteria governed the system at that early stage of the experiments leading to the production of VFAs, which caused the low pH in the system. At the 4th week, despite the low pH of 5.62, 5.88 and 5.83 in 1N2O-OP, 1N2O-CL and 0N3O-OP respectively, the methane percentage in the biogas was observed to be 7.5% in 1N2O-OP, 7% in 1N2O-CL and 4% in 0N3O-OP.

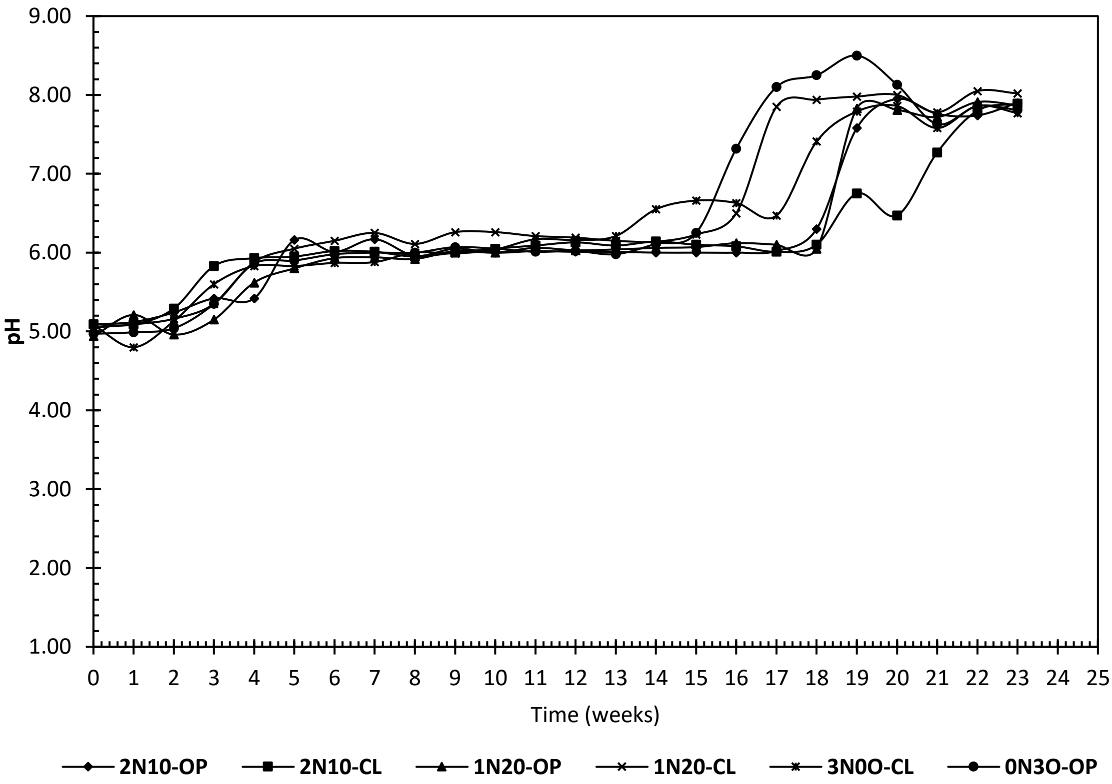

Figure 3-2: The average pH values of leachate samples from bioreactors.

This occurrence of methane in the biogas despite the very low pH in the system has been associated with the likely presence of hydrogenotrophic methanogens within the waste bed (Agdad and Sponza, 2005). This observation agrees with the experience of Agdad and Sponza (2005), who observed methane production at a pH of 5. Acid habituation or adaptive tolerance response is believed to be the major reason for the resistance of anaerobes at low pH (Hall et al., 1995). With the presence of ammonium bicarbonate alkalinity which helps maintain a near neutral pH inside the cells, the methane production becomes possible at low pH (Agdad and Sponza, 2005; Speece, 1983). At the end of the 1st week, the addition of 1N sodium bicarbonate into leachate before recirculation led to a slow but gradual increase in the pH in all the reactors.

The slow increase in pH despite the addition of buffer could be a result of the high organic concentration which characterized the acidogenic phase (Erses et al., 2003). A major phase shift into stable methanogenesis was observed after almost 15 weeks of recirculation when the pH approached 6.5 and above. Moreover, no inoculum was added at the start of the experiment, thus explaining reasons for the delay. On the other hand, the VFAs in the columns witnessed over 60% reduction by the 15th week. By week 21, the average pH values in all the 6 reactors were above 7, in addition to the observed gradual increase in the methane percentage in the biogas, confirmed the fact that the reactors were all in a methanogenic stage.

3.5.3 VFA

The production of VFA in anaerobic systems occurs mainly during the acid formation stage which involves the fermentation hydrolytic products such as amino acids, monosaccharides and long chain fatty acids produced during the initial AD phase (hydrolysis) (Zia et al., 2020). Figure 3-3 shows the VFA concentration variation during the study period. During leachate recirculation in the columns, the VFA concentrations peaked within the first 14 days and between 38600mg/L – 42,700mg/L. VFA production during the anaerobic biodegradation of easily digestible substrates such as food is rapid and high (Cho et al., 2012). Also, high substrate concentration could lead to rapid acidification of anaerobic systems. The high VFA concentrations in all the reactors are quite comparable to the high COD values observed at the same time; this can be explained not only due to the concentration of the leachate blends addition but also due to active hydrolyzation of the organics to VFA (Agdag et al., 2020; Sponza and Agdag, 2004). For instance, despite the initial low VFA concentration in the old leachate, 0N3O-OP with 100% old leachate recirculation had a VFA value of 40,100mg/L by the 2nd week. The fluctuations in the VFA concentrations as shown in Figure 3-3 are assumed to be related to the re-introduction of VFA into the columns during recirculation.

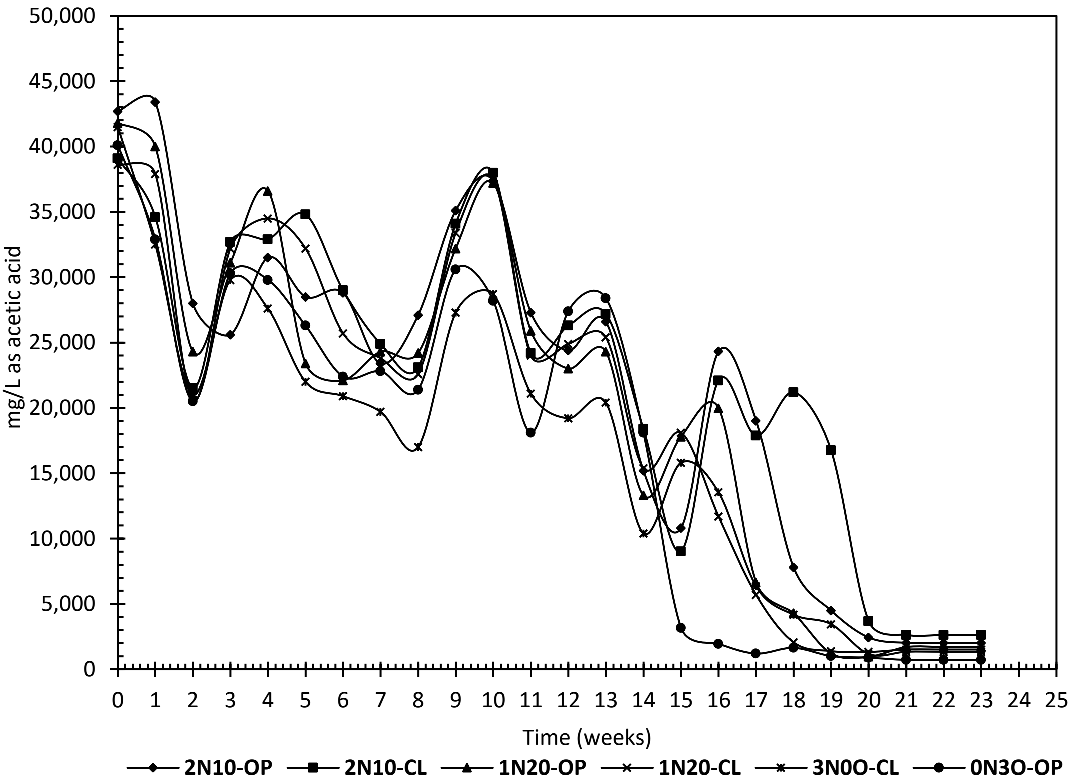

Figure 3-3: The average VFA variation of leachate samples from the bioreactors.

The TVFA:Alkalinity ratio for a stable anaerobic digestion process has been suggested to be less than 0.8 depending on the system and other operating conditions (Behling et al., 1997). This means it is possible that the columns experienced extreme instability during the process (also known as ensiling) since this ratio exceeded 1 in all the columns. This could have been due to the extremely high COD and VFA concentration in the columns. However, methane concentrations were generally above 50% were measured in the biogas produced from all the 6 reactors. Methane production at high VFA concentration can be attributed to the presence of hydrogen-consuming bacteria produced from the complex organics and amino acids when VFA is accumulated in the anaerobic reactor (Sponza and Agdad, 2004).

Figure 3-3 shows a gradual trend of reduction in the VFA concentration as leachate recirculation progressed through the study; a possible evidence that the VFA was getting converted into biogas by the methanogens causing the simultaneous and gradual rise in pH values. Final VFA concentration in the reactors (when compared to the highest value) shows a range of 93.3% - 98.2% conversion in the bioreactors. The reduction in the VFA concentration in all the 6 reactors is a proof that leachate recirculation promotes VFA conversion to methane which agrees with the conclusions drawn by Sponza and Agdad (2004) and Ledakowicz and Kaczorek, (2004).

3.5.4 COD

Figure 3-4 shows the variation in COD of leachate samples collected from the 6 bioreactors. Prior to recirculation, the COD values of the leachate blends were 24,000mg/L in 1N2O-OP and 1N2O-CL, 52,300mg/L in 2N10-OP and 2N1O-CL, 73,000mg/L in 3N0O-CL and 2,500mg/L in 0N3O-OP. However, upon the first round of recirculation, the COD values of the effluent from the reactors 2N10-OP, 2N1O-CL, 1N2O-OP, 1N2O-CL, 3N0O-CL and 0N3O-OP were between 111,300mg/L and 121,890mg/L. This significant increase in the COD values is expected due to the high organic content of the waste (Ahmadifar et al., 2016). For instance, in 0N3O-OP which had only old leachate recirculated (3O) with an initial COD value of 2500mg/L, the COD value was raised to 119,800mg/L after the first recirculation, which falls within the same range for the leachate collected from the other 5 reactors. The similar COD values recorded from all the 6 bioreactors might also emphasize the fact that the waste composition used was uniform in all the bioreactors. The further increase in COD observed in all the bioreactors after 2 weeks signifies the prevalence of anaerobic conditions, dissolution of organic matter and hydrolysis (Ahmadifar et al., 2016; San and Onay, 2001). Unfortunately, values reported from 3N0O-CL were affected by flooding from the wet-tip gas meter.

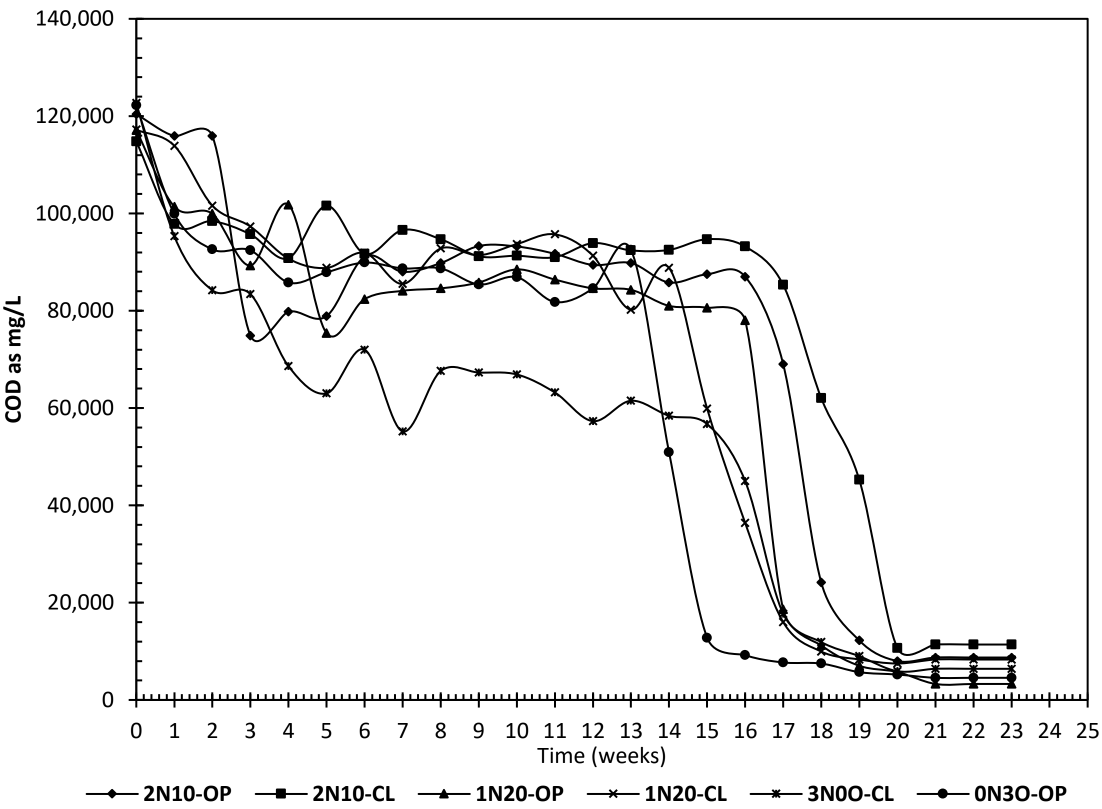

Figure 3-4: Average COD variation of leachate samples from the bioreactors.

After about 5 weeks of operation, a drop in the COD values was observed in all the reactors, possibly due to the increased microbial activity in the reactors as the recirculation process continued. This drop in COD was also coincidental with the general increase in the pH in all the reactors signifying a likely phase shift into the beginning of acetogenesis.

The next stage was a rather stable period which might have been related to the usual longer duration associated with waste stabilization under anaerobic conditions. The stable period also indicates accumulation of organics in the reactors which means hydrolysis was occurring at the same rate as methanogenesis (Ahmadifar et al., 2016). A steep decline in the COD values was evident in all reactors towards the end of the study signifying the establishment of full methanogenic conditions and final stabilization phase in the bioreactor. The steep decline was first observed in 0N3O-OP when the COD value dropped from 84600mg/L and 92,500 between the 14th and 15th week respectively. It declined further from 50,900mg/L to 12,800mg/L between the 16th and 17th week. Similarly, 1N2O-CL COD values dropped from 88,000mg/L on week 16 to 16,000mg/L on week 19. The situation was the same in 1N2O-OP when the COD dropped from 78000mg/L on week 18 to 18,600mg/L on week 19. In 2N10-OP, the COD dropped from 87,000 on week 18 to 24,150mg/L on week 20 while 2N1O-CL COD values dropped from 85,300mg/L on week 19 to 10,670mg/L on week 22. It is, however, unsurprising to observe that 0N3O-OP supplemented with 3 parts of old leachate was the first to experience the drop in the COD values followed by 1N2O-OP and 1N2O-CL which both had 2 parts of old leachate, and later 2N10-OP and 2N1O-CL which contained only 1 part of old leachate. The trend observed in this study seems to indicate that depending on the amount of old leachate present in the leachate blend; old leachate could hasten organic concentration attenuation and waste stabilization in young anaerobic landfills due to its dilution effect as well as a balanced consortium of micro-organisms which is able to easily break down the organics. This attests to the fact that leachate blending can enhance biogas production in landfill bioreactors.

Although the experiments were terminated after 161 days, it is reasonable to predict an eventual full stabilization of the waste given the trend of lower COD values in all the reactors at the end of the study. Percentages of COD reductions in the reactors (between maximum and minimum values) were calculated as between 91.2% and 97.3%. The values are comparable to results obtained by Saphonti et al. (2006) where 91.02% and 91.22% COD removal in 2N10-OP (recirculating leachate only) and 2N1O-CL (recirculating reactor with supplemental water addition), respectively, when 5kgCOD/m^3/d was applied to BLFs treating MSW. Similarly, Ahmadifar et al. (2016) reported 92% COD removal in recirculating anaerobic bioreactors where there was a maximum 64,900mg/L of COD. Overall, the results of this study has shown that leachate recirculation in anaerobic bioreactor landfills undoubtedly increases the extent of organic waste stabilization. It also positively affects leachate quality by providing some treatment for the recirculated leachate (Warith, 2002; Saphonti et al., 2016).

3.5.5 Biogas Production

The average cumulative biogas productions (CBP) from the bioreactors are represented in Figure 3-5. The values were obtained by summing the average daily biogas production for each of the bioreactors during the experimental period. As shown in Figure 3-5, the average total biogas produced in 2N10-OP, 2N1O-CL, 1N2O-OP, 1N2O-CL, 3N0O-CL (Control) and 0N3O-OP were 977.4L, 761.2L, 1982.2L, 1198.1L, 676.1L, and 1084.1L, respectively. The highest biogas production was observed in 1N2O-OP while 0N30-CL had the lowest. Although leachate recirculation improves biogas production in landfills, a general observation from Figure 3-5 is that reactors recirculating leachate blends that contained old leachate had more biogas production compared to reactors with no old leachate content. While 2N10-OP, 2N1O-CL and 3N0O-CL showed a similar trend and experienced a lag even until the 11th week, those three bioreactors had recirculation using leachate blends with just one-third old leachate for 2N10-OP and 2N1O-CL or no old leachate as in 3N0O-CL. On the other hand, bioreactors with two third old leachate content in the leachate blend as in 1N2O-OP and 1N2O-CL, or all old leachate as for 0N3O-OP had a similar trend and experienced lag for about 3-6 weeks. The effect of old leachate addition can easily be ascribed for the improved and faster cumulative biogas production in 1N2O-OP (1982.2L) and 1N2O-CL (1198.1L) where the recirculated leachate blends contained 67% old leachate, and 0N3O-OP (1084.1L) where 100% of the recirculated leachate was old leachate. Furthermore, 100% supplementation with old leachate could be suggested to quicken biogas production as observed in 0N3O-OP where up to 83.8% (compared to the initial) increase in biogas production occurred within the first 6weeks.

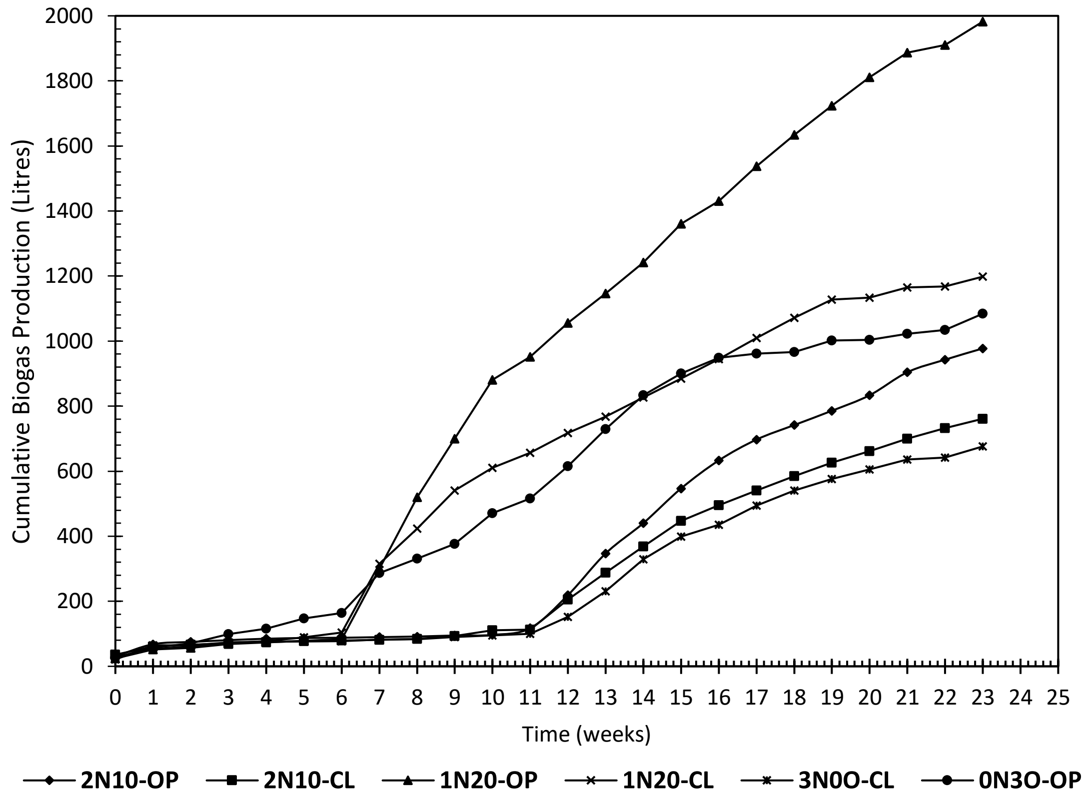

Figure 3-5: Average cumulative biogas production (CBP) from the bioreactors.

Similarly, 71%% and 73% increase in biogas volume was observed in 1N2O-OP and 1N2O-CL respectively within the same timeframe. In contrast, percentage biogas volume increase of 73.5%, 68.1% and 79% observed in 2N10-OP, 2N1O-CL and 3N0O-CL respectively did not occur until the 11th week. Consequently, the behavior of 1N2O-OP, 1N2O-CL and 0N3O-OP can be best explained as due to the presence of a balanced consortium of microorganisms and high buffering capacity of the old recirculated leachate which is suggested to help reduce the time required to achieve the methanogenic phase in the bioreactor landfill. On the other hand, the use of just 33% old leachate in the recirculating leachate blend used for 2N10-OP and 2N1O-CL proved to be insufficient to quickly activate methanogenic activity in the bioreactors, hence there was a significant delay in starting the biogas production. Similarly, in 3N0O-CL where only new leachate was recirculated, the bioreactor 3N0O-CL had the lowest cumulative biogas production of 676.1L. Although the organic load in all the 6 bioreactors were quite comparable at the beginning of the experiments, in the case of 3N0O-CL (control), the population of the fast-growing acidogenic microorganisms could have exceeded the slow-growing methanogenic and acidogenic microorganisms thereby delaying the VFA conversion and ultimately inhibiting and delaying the biogas production in this reactor (Sponza and Agdad, 2004). These results are evidently corroborated in the trends assumed by the COD and VFA graphs.

The highest methane yield of 144.62L/kg DW in 1N2O-OP is similar to 143.95 and 141.28L/kgDW reported by Sandip et al., 2012 during anaerobic bio-stabilization of MSW and sludge in simulated bioreactor landfills after 280days. The calculated yield from the other bioreactors in this study are 71.6 L/kgDW, 57.3 L/kgDW, 87.1 L/kgDW, 50.7 L/kgDW and 82.6 L/kgDW in 2N10-OP, 2N1O-CL, 1N2O-CL, 3N0O-CL (Control) and 0N3O-OP respectively. Evidently, leachate blending can be thus be suggested to also improve methane yield and

2N1O provides the optimal blend ratio. These values are consistent and within the range of 34.4 – 84.7L/kgDW reported during operation of simulated bioreactor landfills albeit under varying operation conditions and duration in San and Onay (2001), Agdag and Sponza (2005), Sanphoti et al. (2006), Alkaabi et al. (2009) and Ahmadifar et al. (2016).

One of the objectives of this study was to evaluate the effect of operating the reactors as an open loop (occasionally supplementing portions of old leachate) versus a closed loop where no old leachate was supplemented. In comparison to the control, the highest biogas improvement was observed in 1N2O-OP (open loop) with 193.2% and the lowest improvement was in 2N1O-CL (closed loop) with only 12.6% improvement. The other reactors, 2N10-OP (open loop), 1N2O-CL (closed loop) and 0N3O-OP (open loop) had 44.7%, 77.2% and 60.3% biogas production improvement, respectively. Ara et al. (2015) observed a 140% improvement in biogas production during co-digestion of 75% OFMSW and 25% TWAS (Thickened waste activated sludge).

Figure 3-6 compares the biogas production from the bioreactors operated as open loop against the closed loop operated bioreactors. To understand the effect of blending, biogas improvement comparison conducted on a case-by-case basis (open loop against closed loop) i.e. 2N10-OP (open loop) against 2N10-OP (closed loop), 1N2O-OP (open loop) against 1N2O-OP (closed loop) suggests that the operation of the reactors as open loop performed better than a closed loop where there was 28.4% - 65.4% increase in biogas production in the open loop over closed loop.

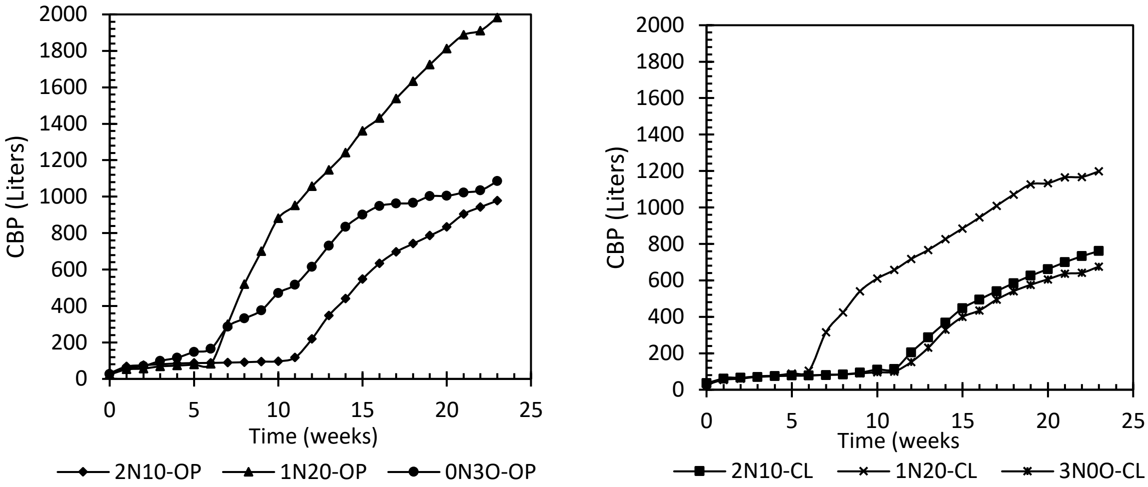

Figure 3-6: Comparison of average cumulative biogas production (CBP) in open loop (OP) and closed loop (CL) operated bioreactors.

Although 0N3O-OP produced more biogas than both 2N1O-CL and 2N10-OP bioreactors, it is practical to state that the 2N1O-CL is suitable since 0N3O-OP was only operated with old leachate and cannot therefore be regarded as a blend. However, the supplementation of landfills with old leachate will enhance biogas production over non-supplementation. Supplementing a landfill with 100% old leachate (open loop) might only hasten methanogenesis but will not fully optimize biogas production as in 0N3O-OP. The above results have therefore shown that blending old and young leachate has the potential of improving biogas production when combined in the right ratio. In this study, 2N10 can be suggested to be the optimal blend ratio.

3.5.6 Models result

The application of kinetics models to AD processes helps to evaluate the process efficiency and the parameters involved in the process. (Martin et al., 2018; Nguyen et al., 2019). For this study, the modified Gompertz model (GM) and Logistic model (LM) (Equation 3-2 and 3-3) were used for the non-linear modeling of the methane production data obtained from the bioreactors during anaerobic biodegradation. In addition, a linear regression using the First-order (FO) model was applied to evaluate the hydrolysis rate constant k(day^{-1}). The results of the 3 models are shown in Table 3-3 as well as Figure 3-7. Table 3-3 summarizes the results obtained from the non-linear modelling for both GM and LM as well as the FO model.

The degradation rate constant is a measure of the biodegradability of substrates. A higher k value is more desirable since this indicates a higher degradation rate. The k values obtained from the FO model for this study were between 0.010 – 0.022 day^{-1}. The values however offer little information on how degradation varies in the 6 bioreactors with different leachate blends. Low k value could be ascribed to the high percentage of yard waste and woody waste in the OFMSW used in this study. Yard and wood waste contain substantial lignin which makes them difficult to degrade (Krause et al., 2016). Bilgili et al. (2007) reported k value of 0.0157 day^{-1} in a leachate recirculating bioreactor treating OFMSW. Similarly, Gunaseelan (2004) also reported k values between 0.016-0.122 for fruits and 0.053-0.125 day^{-1} for vegetables. The above shows k value will vary and will be affected by the waste composition since each of the successive hydrolysis products from OFMSW components is degraded by different bacterial population (Nielfa et al., 2015). Miron et al. (2000) suggested k values are bound to vary and cannot serve as universal constants (even when a good correlation is obtained) because it is not more than a specific calculation for a given substrate under certain conditions.

The R^2 values in both GM and LM were over 0.99 indicating the ability of both models to predict the cumulative methane production (CMP) during an anaerobic process. While the R^2 values from the FO model in 3 cases (1N20-OP,1N2O-CL and 0N3O-OP) were higher than 0.92, however the value was less than 0.80 correlation in 2N1O-OP, 2N10-CL and 3N0O-CL thus indicating a comparatively poor fit for the methane production. The pattern assumed by the models in estimating the lag phase λ values was quite similar. In general, longer lag phases were estimated by the GM compared to the others for all the 6 bioreactors. However, the lag phase values in the models appear to have some correlation with the presence of old leachate in the reactors. While the control reactor (3N0O-CL) had the longest lag phase estimated, the pattern assumed by the other reactors is 1N2O-CL< 1N2O-OP < 0N3O-OP < 2N1O-CL< 2N10-OP. The delay in starting the methane production is not unusual in the AD process.

Table 3-3: Parameters estimated from Modified First Order, Modified Gompertz and Modified Logistic model

Reactor	Measured CH_4 (L)	Modified First Order Model					Modified Gompertz Model					Modified Logistic Model				
		β_o (L/kg)	k ($week^{-1}$)	λ (week)	R^2	Δ%	β_o (L/kg)	Rm (L/kg.week)	λ (week)	R^2	Δ%	β_o (L/kg)	Rm (L/kg.week)	λ (week)	R^2	Δ%
2N1O-OP	501.5	635.3	0.12	10.8	0.756	21.1	508.5	58.9	10.7	0.998	1.4	474.5	61.9	11.0	0.995	5.4
2N1O-CL	401.8	494.0	0.13	10.8	0.752	18.7	408.0	46.4	10.5	0.998	1.5	381.3	48.4	10.9	0.996	5.1
1N2O-OP	1012.4	1390.5	0.07	5.6	0.951	27.2	1063.6	75.8	5.3	0.995	4.8	979.1	79.6	5.8	0.991	3.3
1N2O-CL	610.2	749.7	0.09	5.0	0.947	18.6	626.5	49.9	4.7	0.993	2.6	591.4	51.2	5.1	0.989	3.1
3N0O-CL	355.1	429.8	0.14	11.2	0.715	17.4	358.8	45.9	11.2	0.999	1.0	339.1	47.5	11.5	0.997	4.5
0N3O-OP	577.9	709.0	0.1	6.2	0.923	18.5	594.1	51.8	5.9	0.997	2.7	555.8	56.2	6.6	0.998	3.8

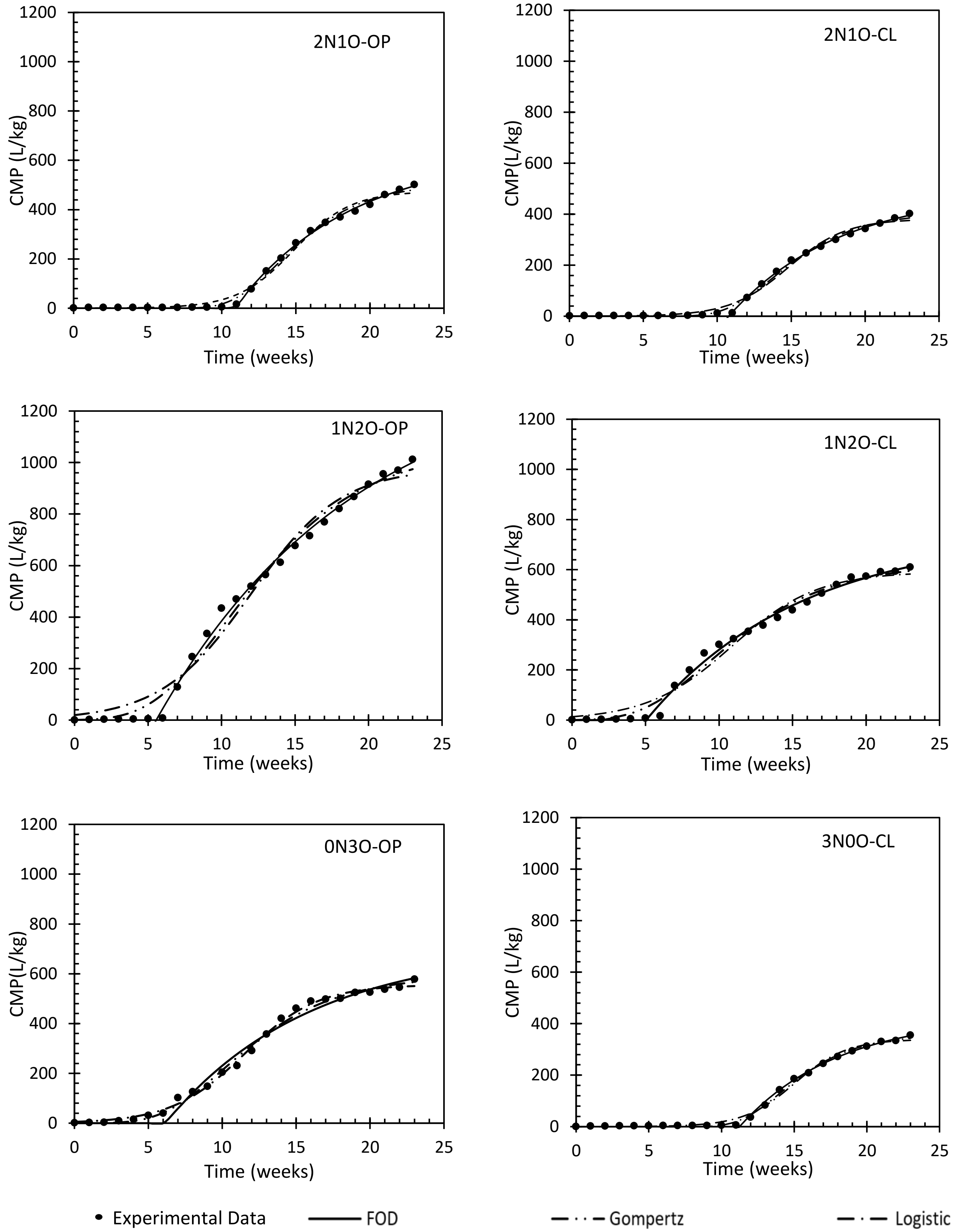

Figure 3-7: Cumulative methane production (CMP) graphs as predicted by First-Order, Gompertz and Logistic models in the bioreactors.

Although this study was operated without the input of a digester inoculum, the delay could have resulted from the required extended microbial acclimation time, methanogenic inhibition due to high VFA concentration, and/or inadequate available anaerobic inoculum which is crucially needed to quickly establish methanogenesis phase in the reactors.

This phenomenon was similar to the experience of Cho et al. (2012) who reported a 50-day lag period before methane production occurred during MSW biodegradation in lysimeters. Cossu et al. (2016) also reported lag periods of 168 and 192 days in 2 anaerobic bioreactors treating MSW. These conditions are often encountered because waste composition in landfills is highly heterogeneous, porous and under predominantly under-saturated conditions insufficient to allow for optimal biodegradation of the total weight of landfilled waste. Therefore, they are not operated as anaerobic digesters where the conditions are fully optimized for biogas production. In addition, moisture is often added intermittently and distributed unevenly. In contrast, the substrate composition (carbohydrate, fat and protein) and conditions in anaerobic digesters are well controlled to ensure biogas optimization and degradation (El-Fadel et al., 1997).

As regards the methane yield βo (L/kg), the trend is similar to the actual experimental results where 1N2O-OP, 1N2O-CL and 0N3O-OP produced the highest amount of methane (with Gompertz methane yield values of 1063.6, 626.5, and 594.1 L/kg respectively) while the lowest were in 2N10-OP, 2N10-CL and 3N0O-CL (with Gompertz methane yield values of 508.5, 408.0, and 358.8 L/kg respectively). Compared to control (3N0O-CL), the estimated biomethane yield increased by 13.7-196.4% as a result of leachate blending. This again emphasizes the potential of old leachate in improving biogas in landfills. Using GM, Figure 3-8 easily explains this point and the effect of leachate blending by comparing 2N1O-OP against 2N1O-CL (right) and 1N2O-OP against 1N2O-CL (left) in the graphs. It is, therefore, possible that the methane production was enhanced in the open loop reactors due to old leachate supplementation in the reactors.

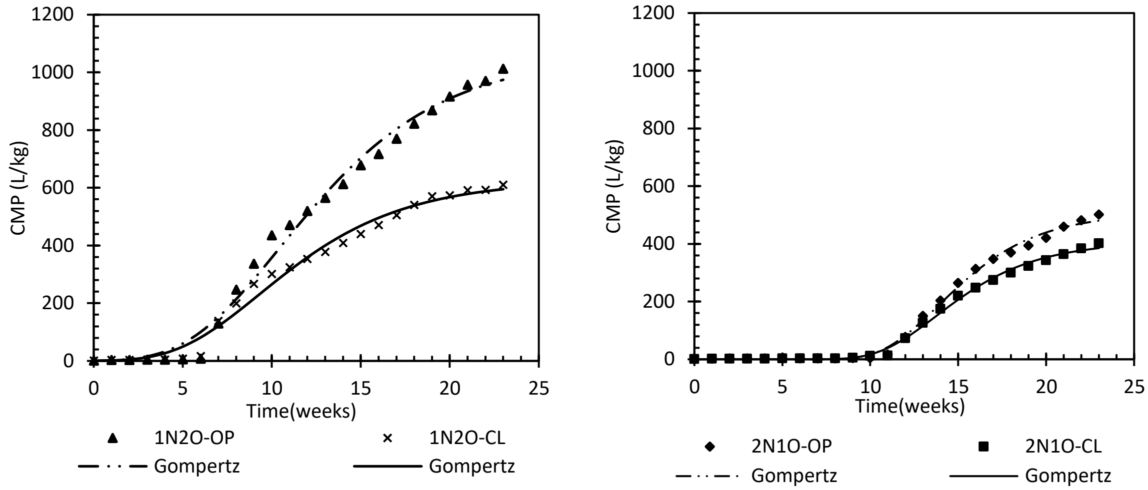

Figure 3-8: Cumulative methane production (CMP) graphs as predicted by Gompertz models in the bioreactors showing the effects of leachate blending.

While FO over-estimated the methane yield, the LM underestimated the values. The difference between the experimental and the predicted methane production (Δ%) computed for each case showed that the highest deviation was in FO models which was 17.4 ≤Δ%≤27.2. However, the deviation in GM was 1.4 ≤Δ%≤4.8 while the LM was within 3.1≤Δ%≤5.4. The GM provided the least deviation in 5 of the 6 cases and thus indicating a greater reliability. While El-Mashad (2013) concluded the FO model least validated the experimental data from co-digestion of switch grass and Spirulina platensis algae, Bilgili et al. (2007) reported a good fit for methane production using the FO model during OFMSW treatment in leachate recirculating bioreactors and Sandip et al. (2012) reported a good fit when they applied the GM during MSW treatment in bioreactor landfills. According to Pitt et al. (1999), interpreting biogas production model parameters may be challenging sometimes, and models with several parameters may not allow comparison of different feedstocks. The situation with the maximum methane production rate Rm(L/kg/wk) seems to indicate the methane production rate in the open loop bioreactors than the closed loop. From the results of the experiment and models, it is therefore safe to assume that 2N1O represents an optimal blend ratio for an optimal biogas production regardless of either the bioreactor is operated as closed or open loop.

3.5.6 New leachate contribution to cumulative methane production

To account for the contribution of the new leachate to the CMP, the COD value of new leachate (5.3g/L) was used by assuming a theoretical COD conversion to CH_4 of 1gCOD = 350mL CH_4 for calculations. Results show that % contribution was between 0% in 0N3O-OP to 5.4% in 3N0O-CL.

3.6 Conclusions

Different leachate blending and recirculation scenarios as methods to improve biogas production in simulated bioreactor landfills were investigated. The results showed that instead of recirculating only young leachate or only old leachate, biogas production can indeed be improved through the recirculation of leachate blended with old leachate. When compared to the control reactor recirculating only young leachate, biogas production improved between 77.2% to 193.2% when a blend of 1N2O (1 new leachate part and 2 old leachate part) is used. Furthermore, operating a bioreactor as an open-loop (with old leachate supplementation) has great benefits compared to the closed-loop (with no old leachate supplementation). Results showed that reactors operated as open-loop produced between 28.1% to 65.4% more compared to reactors operated as closed-loop. Consequently, real-life bioreactors can improve overall biogas production if leachate blending is implemented as an integral part of the recirculation operation scheme. Two empirical non-regression models (Gompertz and Logistic) and a first order model were applied to the experimental data. Although both Gompertz and Logistic models were useful and produced a good fit for the experimental data with deviations less than 5%, the Gompertz model produced the better fit while the modified first order produced the least fit with double digit deviations. Leachate blending also resulted in significant reduction of the estimated lag phase (almost by half) indicating that it could help alleviating the ensiling issue at the start-up phase of landfills and faster start of biogas production.

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Chapter 4-Biogas production from sewage scum through anaerobic co-digestion: The effect of organic fraction of municipal solid waste and landfill leachate blend addition[2]

4.1 Abstract

The objective of this biochemical methane potential (BMP) assay is to investigate the synergistic effect of percentage sewage scum (SS) addition; 10%, 20% and 40% (volatile solids basis) on biogas production during mesophilic co-digestion with various organic substrates viz; organic fraction of municipal solid waste, old leachate, new leachate and a leachate blend prepared from 67%old leachate and 33%new leachate under sub-optimal condition. Results show that despite a low inoculum to substrate ratio (ISR), the net cumulative bio-methane yield was improved with increased sewage scum percentage during co-digestion. Meanwhile, the addition of 40% sewage scum to the individual co-substrates improved net cumulative bio-methane yield by 28.2% - 67% when compared to their respective mono-substrate digestion bio-methane yield. Furthermore, reactors containing leachate blends consistently produced more biogas over other sets due to the effect of blending. Consequently, existing facilities can incorporate either SS addition or leachate blending as environmentally friendly strategies to improve biogas production during waste treatment. Kinetic modelling applied to the bio-methane production data shows modified Gompertz equation achieved a better fit with up to an R^2 value of 0.999. Finally, co-digestion substantially reduced the lag time encountered during mono-digestion.

[2] A version of this chapter is to be published as "Aromolaran, A. and Sartaj, M., 2021. Biogas production from sewage scum through anaerobic co-digestion: The effect of organic fraction of municipal solid waste and landfill leachate blend addition. Waste Management & Research". A revised version of the manuscript has been submitted and reproduced here.

4.2 Introduction

The demand for renewable and sustainable energy production has now become a global concern, resulting in a fast-growing rate of 16.4% per year over the period of 2007-2017 (Rezaeitavabe et al., 2020; Baghbanzadeh et al., 2021). As a mature, energy-efficient and eco-friendly technology, anaerobic digestion (AD) of organic wastes (agriculture waste, manure, organic fraction of municipal solid waste (OFMSW), sewage sludge, etc.) has been proposed as a pathway for renewable bio-energy production in the form of biogas (Ara et al., 2015).

While some of organic waste source streams, especially OFMSW, has been investigated more often than others, there is interest to widen the range of alternative substrates and co-substrates used for bio-energy production, sewage scum (SS) being one example. SS (also known as clarifier skimming) is the sewage solid which is often buoyed up by entrained fat, oil and grease (FOG), gas, plastic material, soaps, waxes or other impurities floating on the surface of primary settling tanks, secondary treatment, and secondary settling tanks in wastewater treatment plants (WWTPs) (Young, 2012). In WWTPs, FOG is suggested to represent between 25–40% of total chemical oxygen demand (COD) of wastewater (Young, 2012).

Strict regulations prohibiting landfilling of organics in Europe and North American territories makes composting or AD a viable option (Long et al., 2012). When it comes to AD, lipids and FOG-rich wastes such as SS are attractive sources of biogas production due to the high number of C and H atoms in their molecule, which connotes a high methane potential (0.7–1.1m^3 CH_4 kg^{-1} VS).

The treatment and digestion of other solid or lipids rich wastes and wastewater have also been widely conducted in high-rate anaerobic reactors, e.g., upflow anaerobic sludge blanket

(UASB) reactor, expanded granular sludge bed (EGSB) reactor, hybrid UASB reactor etc (Jeganathan et al., 2006; Gomes et al., 2011; Long et al., 2012) as well as batch reactors (Cavaleiro et al., 2008). Although biogas can be collected, instability and operational issues such as foaming, clogging, scum build-up, sludge-bed washout and even failures have been reported in high-rate reactors (Gömeç, 2006; Jeganathan et al., 2006; Long et al., 2012). For instance, Jeganathan et al., 2006 treated a complex oily wastewater from the food industry in three different UASB configurations. Although a COD removal efficiency of over 80% was achieved at organic loading rate (OLR) of 3kgCODm^{-3}d^{-1} while process failure occurred at higher OLRs due to sludge floatation and biomass washout caused by high concentration of FOG.

In addition, low rate of hydrolysis of lipids can lead to long chain fatty acid (LCFA) accumulation, along with that of other anaerobic intermediates such as ammonia (Akindele and Sartaj, 2018), H_2S (Grosser et al., 2020) and VFA (Kashi et al., 2017) which could potentially cause methanogenic inhibition and ultimately process failure. Cirne et al. (2007) concluded that even though the digestion of lipid-rich substrates increases methane yield, it could also result in a pH reduction especially if the slower growing methanogens cannot utilize the VFAs present in the digester at the same rate of the acetogenic bacteria. So far, virtually nothing has been discussed in the open literature concerning the treatment of SS as a sole substrate using high-rate reactors.

Some studies have however suggested that methanogenic inhibition by LCFA can be reversed through microbial community acclimatisation and calcium addition (Pereira et al., 2004; Martín-González et al., 2010). Two-phased systems consisting of a continuous stirred tank reactor (CSTR) and anaerobic reactor has also been successfully tested to address the challenges of treating FOG rich wastes (Kim et al., 2004). Regardless, mono-digestion or sole degradation of

FOG-laden wastes is generally not of wider interests as some FOG wastes not only show poor biodegradability when treated as sole substrates, (Salama et al., 2019) but the carbon to nitrogen (C:N) ratio is often beyond the widely recommended optimum value of 20-30, leading to lack of nutrients when excess substrate amount is used (Silvestre et al., 2011).

To enhance biogas production and overcome some of the issues of inhibition and process failures, anaerobic co-digestion (ACo-D), which is the simultaneous digestion of complimentary solid or liquid organic wastes combined in the proper percentages has also been widely recommended (Ara et al., 2015; Grosser et al., 2020). Asides the improvement of kinetic performance of the resulting substrate mixture, synergistic outcomes are also possible (Li et al., 2015; Kashi et al., 2017; Achinas and Euverink, 2019). This is usually facilitated by nutrient balance (Crolla and Kinsley, 2008), dilution of inhibitory intermediates and increase in buffering capacity (Ara et al., 2015). The high specific methane generation potential of FOG wastes makes them an ideal substrate for co-digestion with a variety of complimentary organics to boost biogas yield (Long et al., 2012; Awe et al., 2018; Salama et al., 2019).

It is therefore not surprising that ACo-D experiments involving FOG-rich wastes collected from various sources are abundant in the literature. Table 4-1 presents a summary of some studies that suggests improved methane or biogas yield achieved through synergism during ACo-D with FOG wastes. Meanwhile, Grosser et al. (2020) noted ACo-D of grease trap sludge with sewage sludge improved biogas production but did not affect biogas composition. However, excessive substrate concentration or high loading rate of FOG waste in the influent-co-digestion mixture could still cause a process failure (Silvestre et al., 2011). Therefore, successful ACo-D involving FOG rich wastes will depend on the source and type of FOG waste, temperature, and reactor configuration in order to avoid failure (Shakourifar et al., 2020).

Similar to ACo-D, the concept of leachate blending exploits the combination of markedly different properties of landfill leachate types to improve biogas yield. In a BMP study, Nair et al. (2014) showed that blending of new and old landfill leachate could improve biogas yield by 19-41%. Leachate blending was suggested to act as a form of treatment and stabilization for the high organic load in new leachate by addition of acclimatized microorganisms (methanogens) and alleviating inhibitory effects of ammonia and VFAs. This concept was recently tested and proved in bioreactor landfills recirculating leachate blends (Aromolaran and Sartaj, 2021).

ACo-D experiments involving SS are still few and limited studies have examined the effect of adding SS to OFMSW or leachate blend (blend of fresh and old leachate). Based on previous studies, it is reasonable to hypothesize that the addition of SS can bring about a positive effect on biogas production during co-digestion with substrates such as OFMSW or landfill leachate. However, further research on mesophilic ACo-D of SS and other organic substrates is urgently required, especially to determine if SS addition in ACo-D mixture can bring about improved biogas production even under sub-optimal condition, for example, low ISR.

Table 4-1: Selected literature on ACo-D involving FOG wastes.

Analyzed Mixture	Mixing ratio	Process Temp. (^{0}C)	Digester configuration	Observed effect on methane yield	Observed synergistic effect (%)	Reference
TWAS: FOG	40:60(VS)	70	Batch	$0.67 m^3 CH_4\ kgVS^{-1}$	112.7% increase in CH_4 yield	Alqaralleh et al., 2016
Sewage Sludge: FOG	36.6:63.4 (COD)	35	CSTR	$0.31 m^3 CH_4\ kgCOD^{-1}$	410% increase in biogas	Alanya et al., 2013
TWAS: FOG	64:36 (VS)	37	CSTR	$0.6 m^3 CH_4\ kgVS^{-1}$	137% increase in CH_4 yield	Wan et al., 2011
(PS+TWAS):FOG	(42:58):5(VS)	35	Batch	$0.692 m^3 CH_4\ kgVS^{-1}$	61% increase in biogas	Young, 2012
OFMSW: SS	6;1(VS)	55	CSTR	$0.49 m^3 CH_4\ kgVS^{-1}$	36%increase in CH_4 yield	Martín-González et al., 2011
Sewage Sludge: FOG	77:23(VS)	35	CSTR	$0.37 m^3 CH_4\ kgVS^{-1}$	138% increase in CH_4 yield	Silvestre et al., 2011
(PS+TWAS): GTW	60:40(VS)	35	CSTR	-	68% increase in CH_4 production	Shakourifar et al., 2020

*PS – Primary Sludge, TWAS – Thickened waste activated sludge; GTW-Grease trap waste.

Through the application of different kinetic models to the AD process, variables such as lag phase, hydrolysis constant, maximum methane production and methane production rate can be estimated in order to evaluate the efficiency of the process (Martín et al., 2018). However, existing literature on modelling in AD has been suggested to be complex and inconsistent, thus, drawing reliable conclusions on these variables has remained a challenge due to the complexity of the AD process and differences in operating conditions such as pH, temperature, various substrate concentrations and inoculum sources (Martín et al., 2018). Even with a high correlation coefficient, some of the widely applied models were reported to inadequately explain mechanisms the entire course of the AD process especially under critical conditions (Martín et al., 2018).

It is in this regard that the application of linear and non-linear regression kinetics modelling has recently been suggested and applied to co-digestion studies such as Martín et al., 2018, Pan et al., 2019 and Ponsá et al., 2011. A comparison of kinetic models applied to ACo-D processes can assist researchers to effectively evaluate, optimize process efficiency and monitor variables involved in the process (Martín et al., 2018; Nielfa et al., 2015; Nguyen et al., 2019). Consequently, the three central objectives of this study were to (i) investigate and assess the effect of SS loading (VS basis) on biogas production during the mesophilic ACo-D with OFMSW under low ISR, (ii) investigate the effect of leachate addition during mesophilic ACo-D with SS under low ISR, and (iii) investigate the co-digestion biodegradation kinetics by comparing three relevant kinetic models.

4.3 Materials and Methods

4.3.1 Materials

The SS used in this study was collected from the surface of a primary sedimentation tank of the wastewater treatment plant in Gatineau, QC, Canada. The inoculum used was also obtained from the mesophilic digester of the plant. OFMSW, New and old leachate source, collection and storage were documented in Aromolaran and Sartaj, 2021. The characteristics of the samples and inoculum are shown in Table 4-2. The values in the table represent the mean ± standard deviation for triplicates.

Table 4-2: Characteristics of the substrates and inoculum used in this study.

Parameter	New leachate (NL)	Old leachate (OL)	Leachate Blend (LB)	OFMSW	Sewage Scum (SS)	Inoculum
Alkalinity mg L^{-1} as $CaCO_3$	9,360±331	3,000±105	6,940±90	6,986±20	1,810±23	4,980±10
COD mg L^{-1}	53,400±225	2,640±215	27,070±10	114,490±10	21,800±105	16,280±18
TAN mg L^{-1}	2,260±53	889±32	1,700±89	248±32	323±39	98.1±5
VFA mg L^{-1}	20,730±344	299±34	6,770±93	18,300±201	96±10	330±109
TS g kg^{-1}	68.1±2.2	5.31±1.2	25.05±9	126.2±9.1	459.7±34	5.42±0.1
VS g kg^{-1}	39.6±3.2	1.18±2.1	12.09±2.8	78.3±5.2	451.3±11	3.14±0.01
pH	6.6±0.1	7.7±0.2	7.3±0.1	4.9±0.3	7.8±0.2	7.4±0.1

4.3.2 Experimental Setup

Table 4-3 shows the experimental design. The experiments were conducted in two phases. In phase 1, single substrate AD tests were conducted to determine the BMP of all substrates; SS, OFMSW, NL, OL and LB (33.3% NL and 66.7% OL). This blend was selected based on results from Aromolaran and Sartaj, 2021. In the second phase, co-digestion experiments were conducted to investigate the effect of % SS addition on biogas production from ACo-D of OFMSW and SS as well as the effect of addition of leachate blend during ACo-D of SS and leachate. This was done by varying the % SS (VS) in the bottles containing the co-substrates digested in the first phase. The bottle composition and mixing ratio considered were 10%VS SS: 90%VS substrate, 20% VS SS: 80%VS substrate and 40%VS SS: 60%VS substrate, where substrate was OFWSW, NL, OL, or LB. With the exception of the OL reactor which was conducted in a 1L reactor with 750mL working volume, all other batch anaerobic experiments were conducted in 250mL glass serum bottled with a working volume of 150mL. All BMP bottles were prepared in duplicates and each contained a total of 1g VS load (Prabhu and Mutnuri, 2016). The ISR has been recognized as a key parameter which affects both the efficiency and accuracy of the anaerobic biodegradability of an organic substrate (Dechrugsa et al., 2013).

Table 4-3: BMP Experimental Setup.

Sample ID	Sewage Scum (SS) (%)*	Sewage Scum (SS) (g)	New Leachate (NL) (g)	Old Leachate (OL) (g)	Leachate Blend (LB) (g)	OFMSW (g)	Inoculum (mL)
Single Substrate Digestion							
SS		1.7					70
NL			19.7				70
OL				661.2			70
LB					65		70
OFMSW						9.9	70
BLANK							70
Co-digestion with OFMSW							
10SS+OFMSW	10	0.17				8.97	70
20SS+OFMSW	20	0.35				7.97	70
40SS+OFMSW	40	0.69				5.98	70
Co-digestion with Leachate							
10SS+NL	10	0.17	17.73				70
20SS+NL	20	0.35	15.76				70
40SS+NL	40	0.69	11.82				70
10SS+OL	10	0.17		595.07			70
20SS+OL	20	0.35		528.95			70
40SS+OL	40	0.69		396.71			70
10SS+LB	10	0.17			58.52		70
20SS+LB	20	0.35			52.01		70
40SS+LB	40	0.69			39.01		70

*Based on VS. Inoculum to substrate ratio of $0.3 gVS.gVS^{-1}$ was maintained in all reactors.

While BMP assays should not yield a significant positive or negative effect on biogas production, reducing the amount of inoculum in the assay has been suggested to lead to less optimal digestion (Brulé et al., 2013). In contrast, Fernández et al. (2001) had observed that a ISR of around 0.03 was actually sufficient in achieving a maximum biodegradation of brewery spent grains at a concentration of 70 g L^{-1} (56 g VS L^{-1}). Although methane production was quick, hydrolysis was slow. Regardless, low ISR ratios in ACo-D studies are few in the open literature. Therefore, ISR of 0.3gVS gVS^{-1} was maintained in all reactors. Inoculum without the addition of any substrate was used as the control. In addition to the substrates, 70mL of anaerobic inoculum and alkalinity was added to all the BMP bottles by adding equal amounts of $NaHCO_3$ and $KHCO_3$ in order to achieve an estimated 4000±1000 mg L^{-1} as $CaCO_3$. The pH of the bottles were maintained within the range of 6.5 and 8.2 as prescribed by Speece (1983). The bottles were purged with nitrogen gas for about one minute in order to maintain anaerobic conditions. No supplemental nutrients were added to the bottles since the inoculum is a viable source of micronutrients, trace elements and vitamins, as well as pH-buffering capacity for the biodegradation of substrates. C:N ratio of young leachate is usually around 10 while C:N ratio of old leachate could be anywhere below 2 (Trabelsi et al., 2010). For OFMSW, the C:N ratio can be between 11.4-27 depending on the source (Prabhu and Mutnuri, 2016). FOG rich wastes such as sewage scum however have very high carbon and hydrogen atoms are therefore recommended as co-substrates with other substrates with improper C:N ratio (Long et al., 2012). The bottles were sealed using self-healing caps and silicon. The BMP bottles were then agitated on a New Brunswick Scientific Controlled Environment Incubator Shaker Model G-25 rotating at 100rpm at 30±1°C.

4.3.3 Analytical Procedure

To prevent pressure build-up in headspace, biogas production from the BMP bottles were vented and measured daily using a U-tube manometer. The measured biogas volumes were converted to STP (0°C and 1atm) using the Equation 4-1 below (Kafle and Kim, 2012).

$$V_{STP} = \frac{V\ .\ 273\ .\ (760-Pw)}{(273+T)\ .760} \qquad \text{Equation 4-1}$$

Where: V_{STP} is the volume of gas at standard temperature (0°C) and pressure (1atm) (L); V is the volume of gas (L) measured at temperature T; T is the temperature of gas (^{0}C) or the ambient space; Pw is the vapor pressure (mmHg). of water as a function of temperature.

Biogas measurement was terminated when the measurable biogas production was less than 1% change in the volume of biogas recorded in the previous 3 days. The net biogas volume for the samples were computed by deducting the biogas contribution of the inoculum (blank). Biogas composition was analysed weekly using a GOW-MAC gas chromatograph (Series 400, Gow-Mac Instrument Co., USA) equipped with a thermal conductivity detector (TCD). The analysis conducted on the samples followed standard methods (APHA, 2012). All samples collected from all BMP bottles were analysed for pH, total alkalinity, COD, VFA, and total ammonia-nitrogen (TAN) in triplicates. Total solids (TS) and volatile solids (VS) were determined according to standard method 2540G. Alkalinity test was based on TNTplus™870 reagent vials (Method 10239, HACH USA). COD was determined based on TNTplus™ 823 (Method 10212, HACH, USA) including spectrophotometer, heating block, and supplies. TAN was determined based on TNT plus™ 832 reagent vials (Method 10205, HACH, USA) while VFA was determined based on TNT plus™ 872 reagent vials (Method 10240, HACH, USA).

4.3.4 Data Analysis

Many models have been applied in order to simulate the anaerobic digestion process and predict methane production. Due to the complexity of the AD process, kinetic model comparison has been suggested as a strategy to obtain reliable and true parameter estimation (Pan et al., 2019). Consequently, three common kinetic AD models were applied and assessed in this study;

first-order equation (FO), modified Gompertz model (GM), and Logistic function (LF) shown in equations 4-2, 4-3 and 4-4, respectively (Alqaralleh et al., 2016; Aromolaran and Sartaj, 2021).

$\beta(t) = \beta o[1- exp(-k(-t)]$ - Equation 4-2

$\beta(t) = \beta o.\ \exp(-\exp(\frac{Rm.e}{\beta o}(\lambda - t) + 1))$ - Equation 4-3

$\beta(t) = \frac{\beta o}{\{1+exp[\frac{4Rm.}{\beta o}(\lambda - t)+2]\}}$ - Equation 4-4

Where: $\beta(t)$ is the biogas accumulation (mL gVS^{-1}) at specific time, *t* is the time (hour). βo is the ultimate production potential (mL gVS^{-1}). *Rm* is *the* methane production rate (mL gVS^{-1} hr^{-1}), λ is the lag phase (hour), and *e* = 2.7183. *k* is the hydrolysis rate constant (hr^{-1}) (Alqaralleh et al., 2016). λ, βo, R_m, and *k* were fitted using the generalized reduced gradient non-linear regression algorithm of solver on Microsoft Excel with minimum residual sum of squared errors between experimental data and the model curve (Brown et al., 2001). Maximum number of iterations was set at 100 in all cases.

4.3.5 Synergistic effects

Synergistic effects are produced due to the inner reactions of the various components in a co-digestion study. However, since no other method for examining synergistic effects under sub-optimal process conditions has been reported, the existing methods were adapted in this study. The $CY_{calculated}$ in each co-digestion ratio was estimated based on the net experimental CBY of mono-digestion of each substrate using equation 4-5 (Pan et al., 2019; Ara et al., 2015; Abudi et al., 2016).

$CY_{calculated}$ (t) = Net $CBY_{substrate1}$ (t) x P_1 + Net $CBY_{substrate2}$ (t) x P_2 Equation 4-5 where t is the digestion time in hours; $CY_{calculated}$ (t) is the estimated biogas yield at the t (mL gVS^{-1}); Net $CBY_{substrate1}$(t) is the measured biogas yield of substrate1 only at the t (mL gVS^{-1}); P_1 is the percentage of substrate1 in the mixture (%); Net $CBY_{substate2}$ (t) is the measured biogas yield of substrate2 alone at the t (mL gVS^{-1}); and P_2 is the percentage of substrate2 (%) in the co-digestion mixture. Synergistic effect exists if the $CY_{calculated}$ is more than the net CBY from the BMP co-digestion experiment. Furthermore, the ratio of the net experimental CBY is compared with the $CY_{calculated}$ according to equation 4-6 (Nielfa et al., 2015).

$$\alpha = \frac{\text{Net Experimental CBY}}{\text{CYcalculated}} \qquad \text{Equation 6}$$

if α > 1; the co-digestion mixture has a synergistic effect in the net experimental CBY

if α = 1; the substrates work independently from the co-digestion mixture

if α < 1; the co-digestion mixture has a competitive or antagonistic effect in the final mixture.

4.4 Results and discussion

4.4.1 Single substrate digestion

The net average CBY evolved from the substrates after 27days (648 hours) of operation are presented in Figure 4-1. A 5% standard error was applied to all plots. When the net CBY (per mass of VS) is considered, the results show the LB sample had the highest biogas of 351.6±3.1mL gVS^{-1} followed by OFMSW (322±7.9mL gVS^{-1}), NL (301.8±3.1mL gVS^{-1}), OL (66.8±2mL gVS^{-1}) and the least measured in the SS with 31.6±0.3mL gVS^{-1}. The observed methane yields and percentages were 14.2±0.5mL gVS^{-1} (44.9%CH_4), 205.2±1.3mL gVS^{-1} (67% CH_4), 34.7±0.4 (51.9% CH_4), 242.6±0.3mL gVS^{-1} (69% CH_4) and 219.0±9.3 mL gVS^{-1} (68% CH_4) for SS, NL, OL, LB and OFMSW respectively. Higher biogas production in the LB sample can be ascribed to the synergistic effect of leachate blending where the OL with a greater buffering capacity could supply a more acclimated methanogenic consortia which leads to a rapid methanogenesis of the organic load from the NL (Nair et al., 2014; Aromolaran and Sartaj, 2021). The reported biogas yield value of 351.6±3.1mL gVS^{-1} from LB in this study is in line with the 321mL reported by Nair et al. (2014) digesting a similar blend of leachate. In addition, biogas yield from the OFMSW sample in this study (322±7.9mL gVS^{-1}) agrees with the past research works.

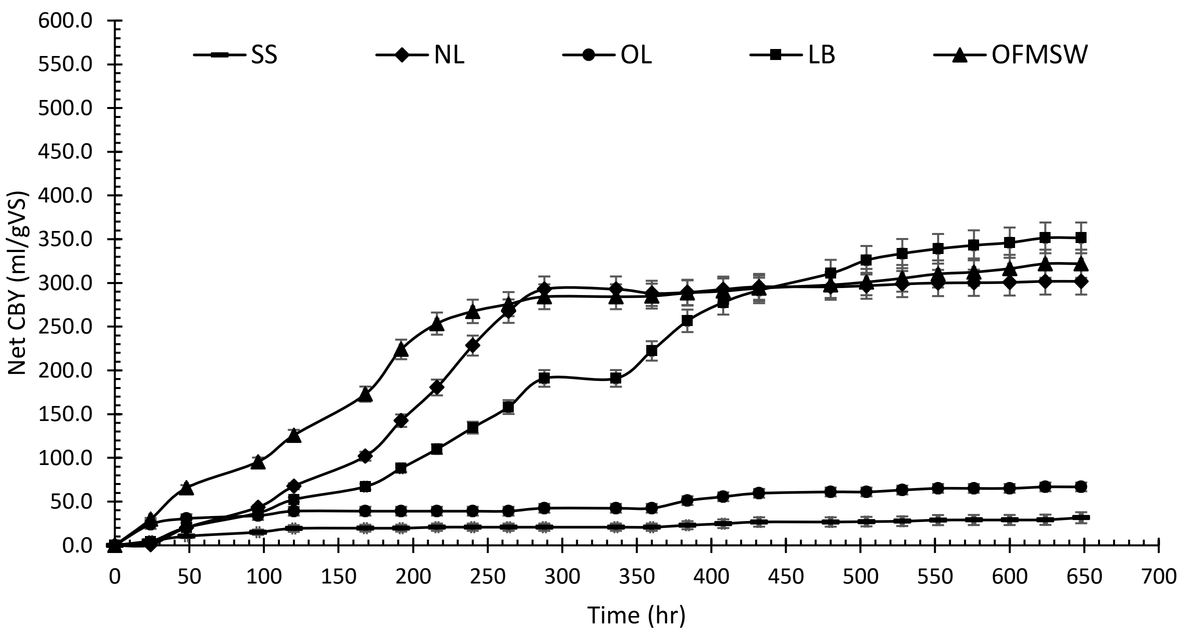

Figure 4-1: Net Cumulative Biogas Yield from single substrate digestion experiment. (SS: Sewage scum, NL:New leachate, OL: Old leachate, LB: Leachate blend, OFMSW: Organic fraction of municipal solid waste)

Ara et al. (2015), Bala et al. (2019), Pavi et al. (2017) and Abudi et al (2016) reported biogas yields of 225mL gVS^{-1}, 228mL gVS^{-1}, 215mL gVS^{-1} and 214.5mL gVS^{-1}, respectively during OFMSW digestion. There is an obvious process imbalance in SS, and this could probably be related to the low ISR in this study as well as the LCFA accumulation and imbalance in certain FOG wastes as single substrates (Salama et al., 2019; Awe et al., 2018). It is important to note that although lipid wastes are known to be highly biodegradable, the biodegradability is often limited by LCFA accumulation and inhibition. Therefore, poor degradability expressed here is not in the context of substrate recalcitrance but as a result of the inhibition caused by LCFA accumulation. Asides these factors, the initial concentration of VFA present for conversion into biogas by the methanogenic bacteria could have been another factor why low biogas yield was obtained from the SS reactor. VFA has been regarded as the main metabolic intermediate during AD (Ara et al., 2015). As a matter of fact, rapid acidification or VFA accumulation are major issues affecting mono-substrate digestion as they result in imbalance in acidogenesis and methanogenesis rates.

The VFA concentration during the first week shows that the LB was 4237.4mg L^{-1}, the NL was 3527.4mg L^{-1} while the OFMSW, OL and SS were 2237.4mg L^{-1}, 174.4mg L^{-1} and 74.1mg L^{-1}, respectively. However, percentage VFA reduction at the end of the study were 78% (811 mg L^{-1}), 36.3% (111 mg L^{-1}), 81% (818 mg L^{-1}) and 58.9% (918 mg L^{-1}) in NL, OL, LB and OFMSW respectively except for SS where the VFA concentration had increased to 1550mg L^{-1}. These results indicate VFA conversion might have been affected by the low ISR ratio in the reactors, thereby inhibiting optimal biogas production. It has also been reported that the presence of high propionic acid in the VFA is detrimental to methanogenesis, as it is thermodynamically difficult to degrade. Therefore, maximum biogas potential of SS was not only achieved due to possible inhibition (Pastor et al., 2013).

When it comes to SS treatment, high-rate anaerobic reactor at a carefully selected OLR can be applied for the treatment of SS preferably after a pre-treatment (Gomes et al., 2011). This option will have the benefit of improving the biodegradability as well as the biogas yield. However, there may be additional cost implications.

4.4.2 Co-digestion of SS and OFMSW

One of the objectives of this study was to investigate the co-digestion of SS and OFMSW with a low ISR. Figure 4-2 shows the average net CBY evolved from OFMSW with 10%, 20%, and 40%SS (VS basis) addition as well as CY in each case. It can be deduced from Figure 4-2 that 10%SS+OFMSW,20%SS+OFMSW and 40%SS+OFMSW produced a net CBY of 292.1±0.6mL gVS^{-1} (54.9%CH_4), 324.8±3.1mL gVS^{-1} (65%CH_4), and 450.1±1.6mL gVS^{-1} (68%CH_4) respectively. This indicates a positive synergism in net CBY with increasing %SS. The digestion of OFMSW has been suggested to be potentially cumbersome and subject to potential biogas inhibition partly due to rapid acidification, scarce bio-available nutrients (especially nitrogen) and presence of improper materials (Panigrahi and Dubey, 2019). Hence the need for co-digestion with complimentary substrates. Despite low ISR, the improvement in net CBY can be ascribed to synergism as well as a balanced acidogenic and methanogenic consortia produced due to ACo-D (Ara et al., 2015; Salama et al., 2019). The highest increase when comparing net CBY and CY in the 3 co-digestion scenarios involving OFMSW was 118.7% observed in the case of 40%SS+OFMSW with a net CBY of 450.1±1.6 mL gVS^{-1} and a CY of 205.8 mL gVS^{-1}. With a net CBY of 292.1±0.6mL gVS^{-1} from 10%SS+OFMSW, there was no significant effect with regards to the CBY from OFMSW alone (a -0.3% increase).

In the case of the 20%SS+OFMSW which produced a net CBY of 324.8±3.1mL gVS^{-1}, this co-digestion mixture did not significantly improve net CBY either when compared to the net CBY of OFMSW alone. However, with a CY of 263.9mL gVS^{-1}, there was a 23.1% increase when comparing the net CBY and CY, thus indicating that the co-digestion mixture indeed produced more biogas than expected. This increase translates to an α of 1.2 and indicates evidence of synergistic effect in the final biogas production. The 40%SS+OFMSW produced 39.8% more net biogas than OFMSW alone. 40%SS+OFMSW produced the highest net CBY involving OFMSW and SS.

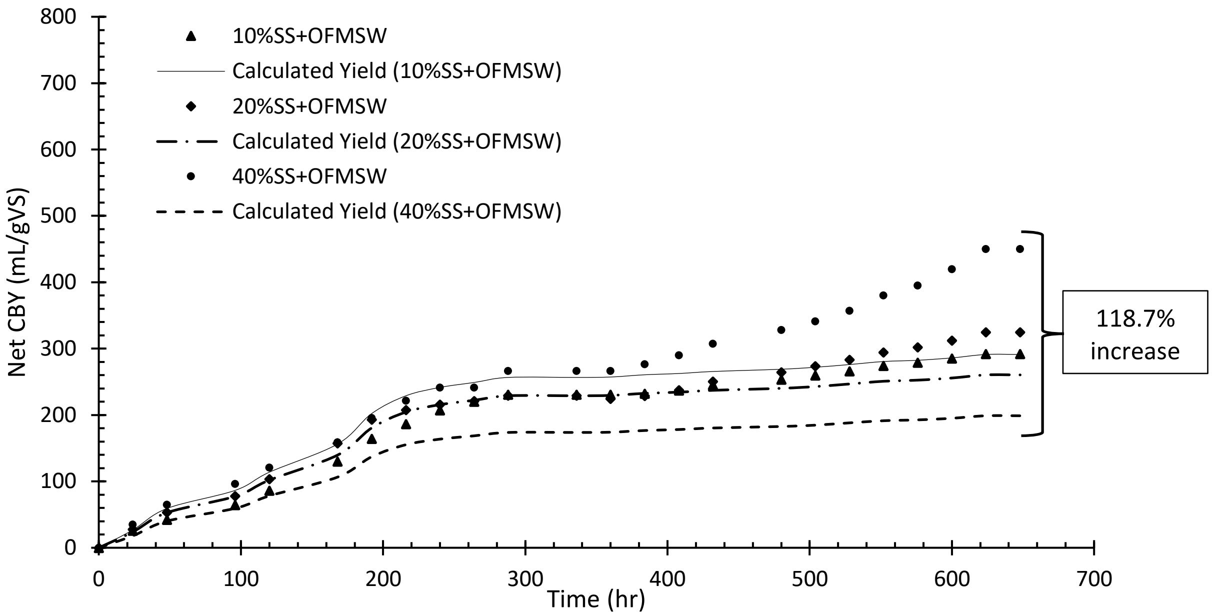

Figure 4-2: Net Cumulative Biogas Yield from OFMSW and various %SS addition (VS basis).

The net CBY from this mixture also produced 54.1% and 38.6% more net biogas than 10%SS+OFMSW and 20%SS+OFMSW respectively. This indicates an increase in net CBY with increase in %SS. Instead of digesting SS alone, overall results show the net CBYs were improved by 9.2-, 10.2- and 14.2-fold increases when 10%SS, 20%SS and 40%SS were respectively added to SS due to synergism during co-digestion. As shown in Figure 4-2, a 118.1% increase was observed in 40%SS+OFMSW considering the fact that the CY value was 205.8 mL gVS^{-1}. This translated to an α of 2.2 which indicates there is some evidence of synergism in the final biogas production. It is noteworthy that the high % improvement in biogas production reported in this study during addition of SS to OFMSW could also be related to the low ISR used in this experiment. Also, the shape of the graphs in Figure 4-2 indicates diauxic characteristics where multiphasic biogas production is quite obvious. This pattern of biogas production has been previously reported during microalga mono-digestion (Markou et al., 2020), ACo-D digestion of low carbohydrate with high-fat agricultural wastes (Kim and Kim, 2017) as well as cow manure with food waste or leaves or straw (Ashekuzzaman and Poulsen, 2011), industrial paper wastes (Walter et al., 2016) and treatment of fat-rich diary wastewater (Cavaleiro et al., 2008). Diauxic pattern has been suggested to occur when microorganisms consume two or more substrates at differing rates, thus causing a two-phased reaction outline (Markou et al., 2020). It could also be signs of methanogenic inhibition. Diauxic pattern in this study can also be attributed to metabolic adjustments during the biodegradation of the various components of the ACo-D mixture including the presence of FOG-rich content (Kim and Kim, 2017). This is because measured methane production yield in all reactors are well within the range of βo (mL gVS^{-1}) estimated by the applied kinetic models.

4.4.3 Co-digestion of SS and Leachate

This study also aims to evaluate the effect of SS co-digestion with leachate samples (OL, NL and LB). As shown in Table 4-4, the 10%SS+NL reactor produced almost the same net CBY (303.2±3.1mL gVS^{-1}) as the NL alone (301.8±3.1mL gVS^{-1}). However, 14.6% and 63.6% improvement were observed in the case of 20%SS+NL (345.9±0.6mL gVS^{-1}) and 40%SS+NL (493.6±2.8mL gVS^{-1}) in relation to digestion of NL alone. These results indicate there is some synergistic benefit when NL is co-digested with SS. The α values greater than 1 show that the mixture (co-digesting NL with SS) had some synergetic effect in the final biogas production. In Table 4-4, the α value of 1.1, 1.4, and 2.3 obtained from 10%SS+NL, 20%SS+NL and 40%SS+NL corresponds to 10.3%, 39.6% and 122.4% improvement in biogas production respectively. This can be further observed in Figure 4-3 where the net CBY and the CY from the 20% SS and 40%SS additions is compared. The net CBY was observed to improve by 9.6-, 10.9- and 15.6-folds in 10%SS+NL, 20%SS+NL and 40%SS+NL respectively when considered along with the net CBY from SS alone. Methane yield and percentages were observed to be 206.2±10.7 mL gVS^{-1} (65.1%CH_4), 235.2±5.2 mL gVS^{-1} (68%CH_4) and 296.1±28.3 mL gVS^{-1}(59.8%CH_4) in 10%SS+NL, 20%SS+NL and 40%SS+NL respectively. The results proves the benefit of ACo-D over mono-digestion.

Table 4-4: Net CBY and CY for different co-digestion mixtures.

SAMPLE ID	%SS*	% NL*	%OL*	%LB*	%OFMSW*	Net CBY ($mLgVS^{-1}$)	CY ($mLgVS^{-1}$)	% increase (Net CBY-CY/CY) x 100	Synergistic effect α
Single substrate digestion									
SS	100					31.6±0.3			
NL		100				301.8±3.1			
OL			100			66.8±2.0			
LB				100		351.6±3.1			
OFMSW					100	322.0±7.9			
Co-digestion with OFMSW									
10%SS+OFMSW	10				90	292.1±0.6	293.0	-0.3	0.9
20%SS+OFMSW	20				80	324.8±3.1	263.9	23.1	1.2
40%SS+OFMSW	40				60	450.1±1.6	205.8	118.7	2.2
Co-digestion with leachate									
10%SS+NL	10	90				303.2±3.1	274.8	10.3	1.1
20%SS+NL	20	80				345.9±0.6	247.8	39.6	1.4
40%SS+NL	40	60				493.6±2.8	193.7	154.8	2.5
10%SS+OL	10		90			87.3±1.4	63.3	38.0	1.4
20%SS+OL	20		80			131.6±0.6	59.8	120.2	2.2
40%SS+OL	40		60			154.7±1.4	52.7	193.3	2.9
10%SS+LB	10			90		380.1±3.1	319.6	19.0	1.2
20%SS+LB	20			80		439.1±3.2	287.6	52.7	1.5
40%SS+LB	40			60		497.2±3.1	223.6	122.4	2.2

*Based on VS.

Among the substrates used in this study, the OL had the most depleted biodegradability. As mentioned earlier, the OL had a net CBY of 66.8±2.0mL gVS^{-1}. Compared to OL alone, the 10%SS+OL (87.3±1.4mL gVS^{-1}), 20%SS+OL (131.6±0.6mL gVS^{-1}) and 40%SS+OL (154.7±1.4mL gVS^{-1}) improved net CBY by 30.7%, 97% and 131.6% respectively. Observed methane yield and percentages were 55.6%CH_4, 64.5%CH_4 and 67.3%CH_4 in 10%SS+OL, 20%SS+OL and 40%SS+OL respectively. In addition, net CBY from SS alone indicates biogas was improved by 2.8, 4.2 and 4.9-folds with the addition of 90%OL, 80%OL and 60%OL to SS respectively. The results show that the co-digestion of OL and SS enhanced net CBY mainly due the synergistic effect of co-digestion. When comparing the net CBY and CY, 40%SS+OL translated to the highest value of 193.3% increase (shown in Table 4-4 and Figure 4-4) further proving the positive effect of ACo-D due to the required microbial population presence. In addition, α values from all the 3 different %VS additions to OL are greater than 1 emphasizes the presence of positive synergism in the mixture. Similar to NL and OL, in the case of LB, the improvement in net CBY was proportionate with increasing %SS and reducing LB content. While the net CBY from LB alone was 351.6±3.1mL gVS^{-1}, the study shows a biogas improvement of 8.1%, 24.9% and 41.4% was obtained with 10%, 20%, 40%SS additions respectively. The increase in biogas with increase in %SS can as well be ascribed to the effect of co-digestion and leachate blending (Nair et al., 2014). Observed CH_4 yield and percentages from 10%SS+LB, 20%SS+LB and 40%SS+LB reactors are 64.2%, 65.7% and 68% respectively. As opposed to SS digestion alone, the net CBY improved by 12.0, 13.9 and 15.7-fold in 10%SS+LB, 20%SS+LB and 40%SS+LB respectively. Table 4-4 also shows the differences in net CBY and CY in all these cases discussed above.

A more interesting observation in the case of the LB is the improved performance of the sample over other leachate samples used as co-substrates on a case-by-case basis (i.e 10%, 20% and 40%SS addition). From the results, the samples containing LB produced the highest net CBY of 380.1±3.1mL gVS^{-1}, 439.1±3.2mL gVS^{-1} and 497±3.1mL gVS^{-1} in 10%, 20% and 40%SS addition respectively. Although the net CBY from 40%SS+NL and 40%SS+LB were 493.6±2.8mL gVS^{-1} and 497.2±3.1mL gVS^{-1} respectively. Nonetheless, the net cumulative CH_4 production was higher in 40%SS+LB with 338.1±30.6mL gVS^{-1} (68% CH_4) and 296.1±28.3mL gVS^{-1} (59.8%CH_4) in 40%SS+NL which reinforces the benefit leachate blend in a co-digestion mixture. The greater number of methanogens in old leachate in the presence of young leachate has been suggested to help improve overall biogas production (Nair et al., 2014). Figure 4-3 compares the net CBY and CY from the 20%SS addition to each leachate substrate. The net CBY from 20%SS+LB represents a

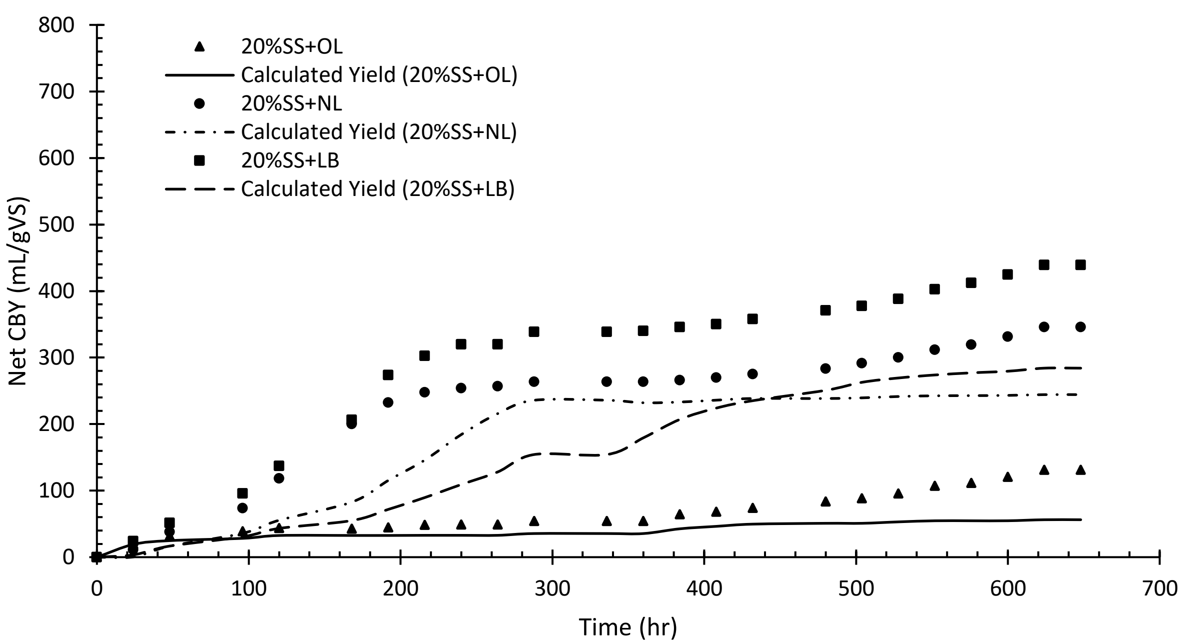

Figure 4-3: Net Cumulative Biogas Yield (CBY) from 20% SS and 40% addition to Old, New Leachate and Leachate Blend compared to the various Calculated Yield (CY).

233.6% improvement over the 20%SS+OL sample and 26.9% improvements over 20%SS+NL sample.

Figure 4-4 also shows the same trend for the case of 40%SS addition to different leachate types. The benefit of leachate blending over other co-digestion leachate mixtures in this study is therefore obvious. As stated earlier, high % improvement and synergism observed in this study could also be related to the low ISR used during ACo-D with the leachate samples. The shape of the two graphs of Figure 4-3 and Figure 4-4 also suggests diauxic characteristics as observed in ACo-D of SS and OFMSW. The experimental CH_4 yield in all reactors are well within the range of βo (mL gVS^{-1}) distribution estimated by the applied kinetic models with the exception of 20SS+OL where a significant difference was observed in estimations by FO and MG models.

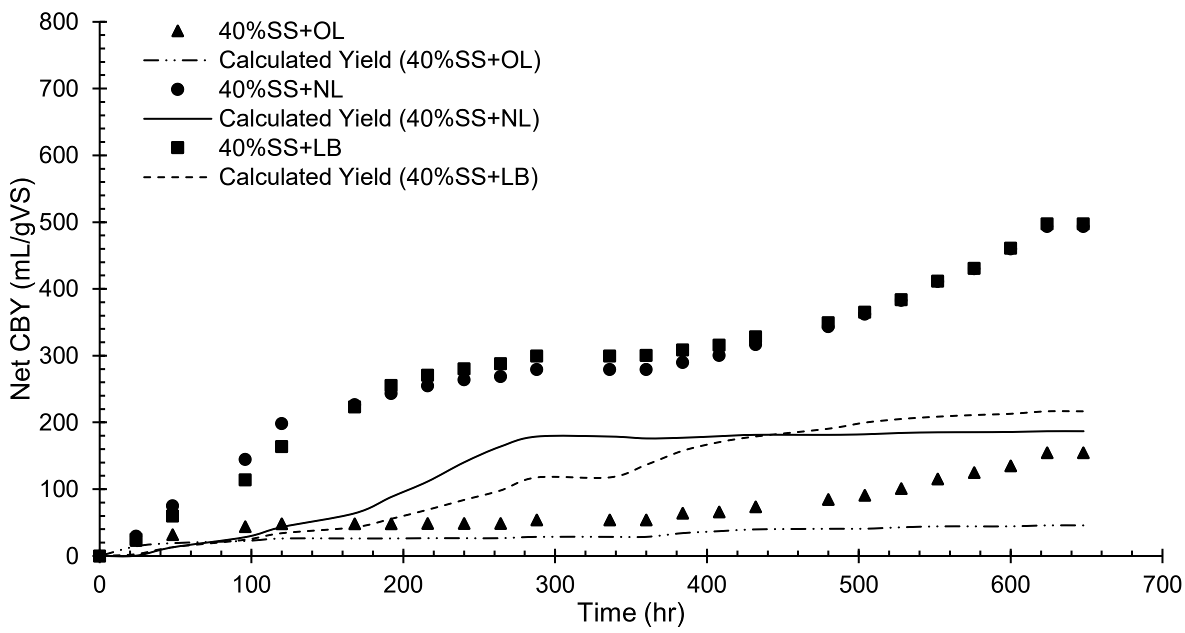

Figure 4-4: Net Cumulative Biogas Yield (CBY) from 40% SS addition to OL, NL and LB compared to the various Calculated Yield (CY).

While some studies have considered 10-30%VS FOG content (Davidsson et al., 2008) and reported 9-27% increase in methane production, other researchers such as Wan et al., 2011 observed up to 137% increase in methane yield during co-digestion of TWAS and 64% VS of FOG. Recently, Shakourifar et al. (2020) reported 68% increase in specific CH_4 production when mixed grease trap waste(40%VS) and mixed primary sludge and TWAS were co-digested. Failure occurred beyond 40%VS content of mixed grease trap waste (Shakourifar et al., 2020). However, the practicality of the optimal ratio also needs consideration and hence the reason a higher SS addition percentage higher than 40%VS content was not considered in this study. Consequently, the results of this study show that the 40% SS addition has best improved biogas production in all co-digestion mixtures with the various co-substrates due to positive synergism in the reactors.

4.4.4 Anaerobic biodegradability

Table 4-5 shows the comparison of the degradability of mono-substrates and when co-digested with SS. Calculations were based on theoretical or absolute conversion of net COD ($COD_{destroyed}$) to CH_4 (350mL.gCOD^{-1}) (Xie et al., 2017). Therefore, it can be observed from Table 4-5 that biodegradability was in the order of LB>OFMSW>NL>OL>SS and consistent with the mLCH$_4$.gVS^{-1} values observed during the BMP. While OL is low in organic content and expected to exhibit poor biodegradation tendencies, poor biodegradability in SS is as a result of the methanogenic inhibition by LCFA and VFA as reported earlier in this study. Of interest however is that the biodegradability was subsequently improved in the co-digestion modes with increasing % addition of SS. Highest improvement was observed in the 40%SS cases and the least improvement was in the 10%SS cases. The results therefore suggest co-digestion with SS can improve ultimate biodegradability of the mixture (Xie et al., 2017).

Table 4-5: Biodegradability of different substrates in mono-digestion and co-digestion modes.

Sample	Net COD	VS	BMP		Degradability
	$g.L^{-1}$	$g.L^{-1}$	$mLCH_4.gVS^{-1}$	$mL.CH_4.gCOD^{-1}$	%[1]
Single substrate digestion					
SS	8.8	5.3	14.2	8.5	2.4
NL	8.1	5.3	205	134.5	38.4
OL	0.3	0.94	35	106.7	30.5
LB	9.4	5.3	243	136.4	39.0
OFMSW	8.6	5.3	219	135.1	38.6
Co-digestion with OFMSW					
10%SS+OFMSW	6.7	5.3	160.6	127.5	36.4
20%SS+OFMSW	5	5.3	211.1	222.9	63.7
40SS+OFMSW	6.8	5.3	306.1	237.0	67.7
Co-digestion with Leachate					
10%SS+NL	6.5	5.3	206.2	169.0	48.3
20%SS+NL	4.8	5.3	235.2	257.6	73.6
40%SS+NL	5.6	5.3	296.1	282.1	80.6
10%SS+OL	0.4	1.4	48	176.8	50.5
20%SS+OL	0.8	1.8	89.5	201.8	57.7
40%SS+OL	1	2.7	105.2	277.5	79.3
10%SS+LB	8.4	5.3	258.5	163.8	46.8
20%SS+LB	6.3	5.3	298.6	249.3	71.2
40%SS+LB	6.3	5.3	338.1	286.5	81.9

[1]Assuming complete COD conversion (1gCOD = 350mL CH_4).

4.4.5 Kinetic Models Comparison and Results

Figure 4-5 shows the graphical plot of the estimated cumulative methane yield (CMY) using the three kinetic models against time (hours) from the 40%SS addition only, as an example, to all the substrates. Table 4-6 shows the comparison of the parameters estimated from FO, MG and LF models when the experimental results of this study were applied. The coefficient of correlation (R^2) value from the three models shows that the FO ranged between 0.935-0.992, while the MG and LF ranged between 0.937 – 0.999 and 0.925– 0.998 respectively. When ultimate methane production, β_o (mL gVS^{-1}) is considered in the 3 models in the co-digestion experiment, it is obvious that it aligns well with the net CBY as it increases with the increase in %SS addition, further proving the fact that the addition or co-digestion with SS will enhance net CBY over mono-substrate digestion. The 40%SS produced the highest B_o (mL gVS^{-1}) over the 10% and 20%SS additions to OFMSW and leachate samples. However, similar to the experimental results, B_o estimated from FO models was observed to reduce to 185mL gVS^{-1} at 10%SS+OFMSW from 264mL gVS^{-1} estimated from OFMSW alone. B_o (mL gVS^{-1}) estimated from the MG and LF were also reduced under the same condition as well and remained consistent with the experimental results. In the above scenario, B_o (mL gVS^{-1}) estimated also reduced when the values from the NL alone is compared to the 10%SS+NL. It is however possible there was insufficient bioavailable nutrients within the co-digestion mixture to handle the added organic load in both scenarios. When the methane production R_m (mL gVS^{-1} hr^{-1}) estimated by the MG and LF is considered within the single substrate digestion experiment, higher values of 1.27 and 1.28 mL gVS^{-1}.hr were estimated by the MG and LF models respectively for NL. Considering the fact that the LB samples were 0.64 and 0.68 mL gVS^{-1} hr^{-1} from the respective MG and LF models, it is possible that the rate of methane production was delayed due to microbial acclimation and VFA conversion time in the leachate mixture. This is despite the fact that the LB had produced the highest methane quantity amongst the substrates digested individually. OFMSW had estimated R_m (mL gVS^{-1} hr^{-1}) values of 0.77 mL gVS^{-1} hr^{-1} and 0.81 mL gVS^{-1} hr^{-1} from MG and LF respectively. This may suggest the presence of high soluble organics within the reactor for improved methane production rate. In general, the LF estimated higher values than the MG in this case.

When it comes to the co-digestion involving leachate samples, the LB containing reactors could be observed to have higher rates estimated by LF and MG in the 3 instances of SS addition. However, the model estimated R_m (mL gVS^{-1} hr^{-1}) values in the NL and LB appears to increase with 20%SS and reduce when 40%SS were added. The decreased rate could mean the methane production rate was slightly inhibited by the high lipid content as it approached 40%SS as observed in 40%SS+LB and 40%SS+NL. This suggests a higher organic load was a factor. In contrast, the R_m (mL gVS^{-1} hr^{-1}) in the OL co-digestion mixtures increased with increasing %VS of SS at a very low rate. This could be connected to the fact that introduction of SS increased the organic VS load in the presence of adapted methanogens in the OL facilitated a positive synergism for improved methane production.

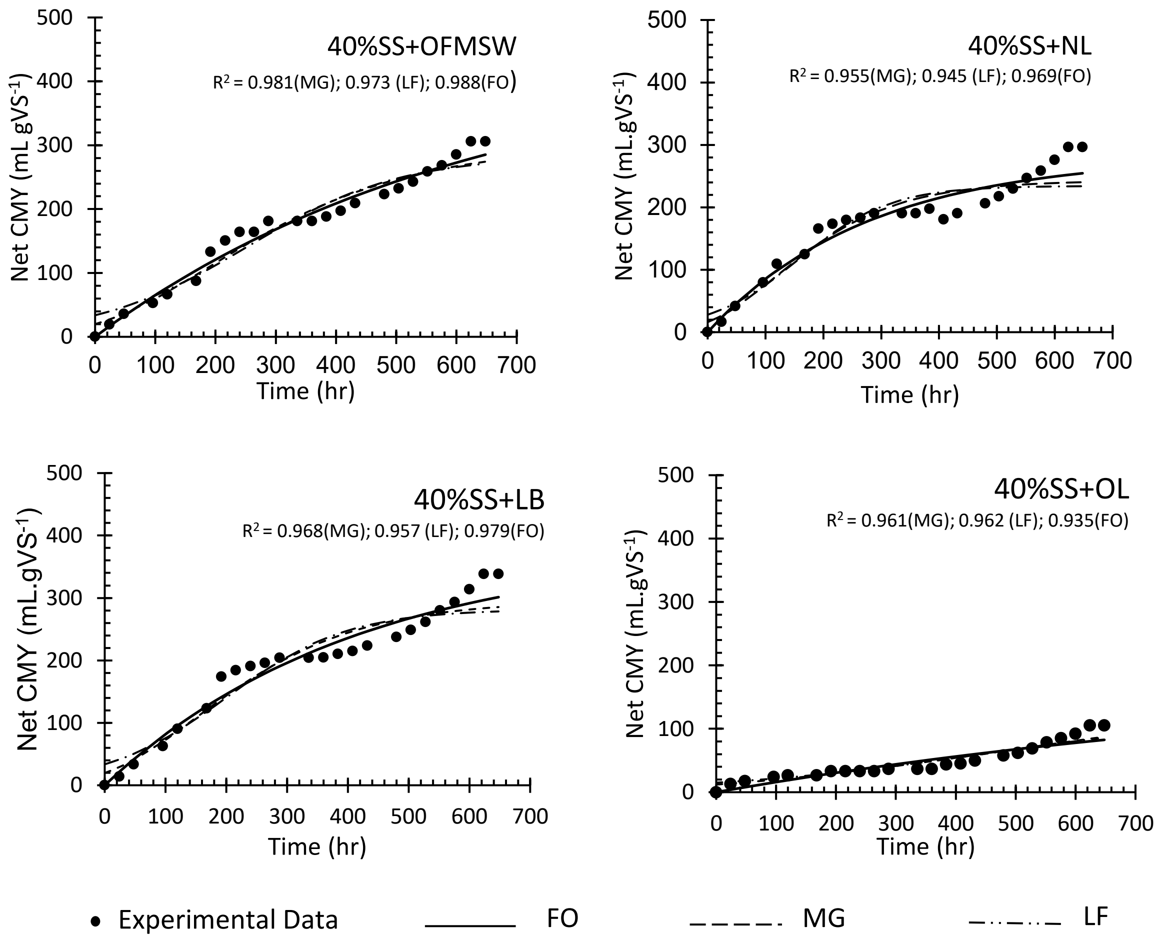

Figure 4-5: Model plot of Cumulative Methane Yield from 40%SS addition to the various substrates used in this study.

Kinetic phases of a bacteria are lag phase, exponential growth phase and stationary phase (Morales et al., 2017). The lag phase λ (hr) refers to an adjustment period where the bacteria cells are expected to modify and take advantage of the new environment (Swinnen et al., 2004). λ (hr) is often influenced by environmental conditions as well as preincubation conditions. λ (hr) values estimated by MG and LF are closely related and follow a similar pattern in both single substrates and ACo-D experiments. The LF appears to overestimate the lag time in contrast to the MG value. The estimated λ (hr) values from the MG and LF models from the single substrate digestion appears to emphasize the fact that a longer λ (hr) was required for an improved methane production. High TAN concentration could have been a factor as it affects methane production (Akindele and Sartaj, 2018). While the OFMSW had estimated values of 43.7hr (MG) and 57.9hr (LF), the TAN was only 248±32 mg L^{-1}. On the other hand, NL experienced a higher lag time with estimated values of 122.4hr (MG) and 128.1 hr (LF), suggested to be as a result of a higher TAN value of 2,260±53mg L^{-1} in the reactor.

In the co-digestion experiment, the λ (hr) appears to reduce consistently with increase in %SS. Compared to the single substrate experiment, all λ (hr) values estimated from the co-digestion experiment were shorter. In this study for instance, while OFMSW alone had an estimated value of 43.7hr and 57.9hr from MG and LF respectively, these durations reduced to 25.1hr (MG) and 41.2hr (LF) upon adding 10%SS despite the reduction in βo (mL gVS^{-1}). The λ (hr) values in the co-digestion of SS and OFMSW in this work is lesser to values reported by Ponsá et al (2011) where 8.9days (213.6hr) was reported for OFMSW+vegetable oil and 9.1days (218hr) was reported for OFMSW+animal fat. Difference in FOG type as well as inoculum source might have been a reason for the difference (Salama et al., 2019). Similar reduction in λ (hr) was observed in 10%SS+NL where the lag phase was reduced by almost 50%. β_o (mL gVS^{-1}) however improved when 10%SS+LB sample but there was a reduction in the lag phase value from 94.1hr(MG) and 112.1hr(LF) to 88hr(MG) and 100.8 (LF) and thus signifying the positive effect of SS addition through lag time reduction and improvement of methanogenic activities.

Table 4-6: Parameters estimated from the FO, MG and LF models.

Sample	Measured CH_4 (mL gVS^{-1})	First Order (FO)			Modified Gompertz (MG)				Logistic Function (LF)			
		β_o (mL gVS^{-1})	k (hr^{-1})	R^2	β_o (mL gVS^{-1})	R_m (mL $gVS^{-1}.hr^{-1}$)	λ (hr)	R^2	β_o (mL gVS^{-1})	R_m (mL $gVS^{-1}.hr^{-1}$)	λ (hr)	R^2
Single substrate digestion												
SS	14.2±0.5	14.8	3.0E-03	0.960	12.6	0.03	0.0	0.937	12.6	0.03	0.0	0.925
NL	205.2±1.3	283.1	2.5E-03	0.953	205.8	1.27	122.4	0.991	203.8	1.28	128.1	0.995
OL	34.7±0.4	55.0	1.7E-03	0.971	39.8	0.07	0.0	0.968	37.4	0.07	0.0	0.966
LB	242.6±0.3	345.5	1.8E-03	0.983	266.8	0.64	94.1	0.999	245.6	0.68	112.2	0.998
OFMSW	219.0±9.3	264.1	3.1E-03	0.985	215.8	0.77	43.7	0.996	209.8	0.81	57.9	0.997
Co-digestion with OFMSW												
10%SS+OFMSW	160.6±8.3	185.0	3.1E-03	0.989	152.7	0.49	25.3	0.991	146.8	0.53	41.2	0.991
20%SS+OFMSW	211.1±11.3	248.0	2.7E-03	0.992	200.2	0.51	1.2	0.988	189.6	0.52	10.5	0.981
40%SS+OFMSW	306.1±32.1	443.0	1.6E-03	0.988	300.7	0.58	0.0	0.981	283.1	0.56	0.0	0.973
Co-digestion with Leachate												
10%SS+NL	206.2±10.7	219.7	3.8E-03	0.973	186.9	0.85	51.8	0.985	183.2	0.93	68.0	0.986
20%SS+NL	235.2±5.2	239.5	4.1E-03	0.974	205.2	1.02	49.5	0.984	201.0	1.11	62.2	0.982
40%SS+NL	296.1±28.3	281.9	3.3E-03	0.969	242.9	0.76	0.0	0.955	234.2	0.74	0.0	0.945
10%SS+OL	48.0±0.9	48.5	3.5E-03	0.950	44.8	0.11	0.0	0.937	45.4	0.10	0.0	0.941
20%SS+OL	89.5±29.5	176.0	9.0E-04	0.965	171.4	0.13	0.0	0.980	115.2	0.13	0.0	0.980
40%SS+OL	105.2±33.1	192.0	8.7E-04	0.935	183.4	0.14	0.0	0.961	126.5	0.13	0.0	0.962
10%SS+LB	258.5±28.6	347.8	2.4E-03	0.972	250.5	1.12	88.0	0.994	244.8	1.20	100.8	0.996
20%SS+LB	298.6±19.2	322.1	3.6E-03	0.978	269.0	1.15	45.5	0.986	261.9	1.26	61.0	0.984
40%SS+LB	338.1±30.6	381.7	2.4E-03	0.979	296.3	0.72	0.0	0.968	281.6	0.70	0.0	0.957

4.6 Conclusions and Recommendations

This work investigated the effect of SS loading (VS basis) on biogas production during the mesophilic ACo-D with OFMSW and leachate addition under low ISR. Biodegradation kinetics was also investigated by comparing 3 kinetic models.

- In spite of low ISR, experimental results from this study indicated that increasing percentages of sewage scum during co-digestion with 4 different substrates (OFMSW, NL, OL and LB) enhanced biodegradability and methane production due the effect of positive synergism during co-digestion. Net CBY exceeded the CY in all instances in further acknowledgement of the benefit of co-digestion.
- The addition of 40%SS(VS) was observed to have promoted the highest biogas production during ACo-D with OFMSW or leachate. In the co-digestion involving addition of leachate, leachate blending was observed to have played a major role in improving the net CBY due to increased synergism and high methanogenic population present in old leachate.
- Kinetic model application to the methane data showed that the LF and MG provided a better estimation of the parameters than the FO. Methane production was achieved quickly through lag phase reduction due to synergistic effect of co-digestion.
- Low biogas production was observed in SS possibly due to insufficient microbial load causing inhibition and poor biodegradability. It is therefore worth investigating the pre-treatment of SS prior to treatment, for instance, in high-rate anaerobic digesters.
- Further studies are needed to develop methods for calculating and reporting observed synergism under sub-optimal process conditions. These methods must be different from

methods for observation of synergism under optimal conditions in standardized BMP experiments.

- Finally, it is recommended that the effect of inoculum macronutrient, micro-nutrients and activity on a standard substrate should be investigated. In addition, the effect of inoculum adaptation during primary and secondary substrate addition as a function of time should be investigated.

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Chapter 5 - Enhancing biomethane production through trinary co-digestion of sewage scum and municipal solid waste with thickened waste activated sludge and leachate blend addition

5.1 Abstract

Anaerobic co-digestion (ACo-D) has been adjudged as a sustainable pathway to improve renewable biomethane production over mono-substrate anaerobic digestion (AD). Despite the huge biogas potential of sewage scum (SS), there is limited information on its use and effect in trinary mixtures. For the first time, the biomethane potential (BMP) involved in the ACo-D of SS, organic fraction of municipal solid waste (OFMSW) was investigated in this study using either thickened waste activated sludge (TWAS) or leachate blend (LB) as a tertiary component. This was done to compare two co-digestion alternatives i.e in a wastewater treatment plant (WWTP) and a bioreactor landfill (BRL). Compared to the mono-digestion of TWAS, results show that biomethane yield was enhanced in by as much as 32.4 - 121.6% in trinary mixtures with SS and OFMSW mainly due to the effect of positive synergism. Furthermore, LB addition improved biomethane production in trinary mixtures of SS:LB: OFMSW by 38% than in corresponding trinary mixtures of TWAS. Whereas an optimal combination of 40%SS:10%TWAS:50%OFMSW and 20%SS:70%LB:10%OFMSW produced the highest biogas yield of 407mL.gVS-1 and 487mL.gVS-1 respectively. The application of the first order model showed that lower hydrolysis rates promoted methanogenesis with k = 0.04day^{-1} in both 20%SS:70%LB:10%OFMSW and 20%SS:50%LB:30%OFMSW. Estimations by the modified Gompertz and logistic function were conclusive methane production rate improved by as much a 60% in a trinary mixture over the production rate during mono-digestion of TWAS alone. Finally, biodegradability within the co-digestion mixtures improved over mono-digestion of TWAS or LB alone.

5.2 Introduction

The global demand for renewable energy has been reported to have increased within the last decade by at least a factor of two to three due to depleting fossil fuel reserves and increasing greenhouse gas emission (Baghbanzadeh et al., 2021). To meet this demand, biomethane production through anaerobic digestion (AD) has attracted wide interests and therefore considered to be one of the most highly investigated pathways to produce renewable energy (Ara et al., 2015).

Lipid wastes which are also regarded as fat, oil and grease (FOG) have been suggested to be an attractive feedstock for energy generation through AD mainly because of their high theoretical biomethane potential (up to 1m^3 CH_4 $kgVS^{-1}$), especially when compared to protein (0.5m^3CH_4 $kgVS^{-1}$) and carbohydrate 0.4m^3CH_4 $kgVS^{-1}$ (Angelidaki and Sandars, 2004; Grosser, 2018; Salama et al., 2019). One of such waste is sewage scum (SS), also known as clarifier skimmings. However, SS has not received much attention despite its huge potential (Aromolaran and Sartaj, 2021b). SS is a sewage solid entrained with FOG, gas, plastic materials, soaps, waxes, or other impurities floating on the surface of primary settling tanks, secondary treatment, and secondary settling tanks in wastewater treatment plants (WWTPs) (Young, 2012). It can account for up to 4% of the total solids generated from WWTPs. The sole digestion of high strength FOG wastes is not of interest and can be hampered by operational issues such as digester foaming, scum floatation, clogging and mass transfer issues for soluble substrates. Other factors such as process instability and accumulation of long chain fatty acids (LCFA) could potentially inhibit methanogenesis during anaerobic biocenosis (Long et al., 2012; Salama et al., 2019). On the other hand, anaerobic co-digestion (ACo-D) of FOG wastes with other complimentary organic substrates has been considered as an alternative strategy to overcome the challenges of digesting FOG wastes alone thereby, diluting toxicants, balancing nutrients as well as improving the kinetics and biomethane recovery among other benefits (Salama et al., 2019). Beyond the improvement in biomethane recovery during ACo-D, substrate diversification during co-digestion confers a potential advantage of a robust and enhanced microbial community for stable methanogenesis and biodegradation of the substates present, even under unstable conditions (Ziels et al., 2016; Kim et al., 2019; Wang et al., 2021).

ACo-D can utilize existing infrastructures without a major capital investment (Koupaie et al., 2014; Xie et al., 2017). Due to the huge amount of sewage sludge, municipal solid waste and leachate generated annually, treatment has become a huge concern to WWTP and landfill operators (Alqaralleh et al., 2016; Nair et al., 2014). To address concomitantly these issues and challenges with mono-digestion of FOG wastes, the subject of the co-digestion of FOG wastes with sewage sludge or organic fraction of municipal solid waste (OFMSW) has been investigated by scholars with interesting results indicating improved biomethane recovery through positive synergism and process stability. Martín-González et al. (2011) co-digested source-collected OFMSW with WWTP FOG waste at a ratio of 6:1 (VS basis) and reported a 36% increase in biomethane yield relative to the yield from OFMSW alone. At a ratio of 36.3;63.4 (COD basis), Alanya et al. (2013) reported a 410% improvement in biogas production when sewage sludge was co-digested with sewage scum collected from primary clarifiers and scum concentration tanks. Also, Alqaralleh et al. (2016) investigated a mixture of thickened waste activated sludge (TWAS) and WWTP FOG waste at a ratio of 60:40 (VS) and reported a 112.7% increase in biomethane yield over digesting TWAS alone. Recently, Shakourifar et al. (2020) reported up to 68%

improvement in biomethane yield when a comixed primary sludge and TWAS were co-digested with grease trap waste (GTW) at a ratio of 60:40 (VS). Finally, Aromolaran and Sartaj (2021b) reported a 39.7% improvement in biomethane production over mono-digestion of OFMSW alone during co-digestion of SS and OFMSW at a ratio of 40:60 (VS). The same study indicated that biomethane production was enhanced by 39.3% when a leachate blend (2parts of old leachate blend and 1 part of new leachate) was co-digested with SS (VS basis).

Despite the successes reported by some of the previous research, most of these studies focused on co-digesting only one substrate with FOG waste except for a few such as Amha et al. (2017), Grosser (2018) and Ferreira et al. (2018). Amha et al. (2017) investigated a number of possible ratios but determined that a quaternary co-digestion of 40% primary sludge (PS):40%TWAS:10%FOG:10%FW (VS basis) enhanced biomethane production by about 26% over a trinary mixture of 45%PS:45%TWAS:10%FOG (VS basis). During the AD of sewage sludge under mesophilic conditions, Grosser (2018) tested the simultaneous addition of grease trap sludge (GTS) and OFMSW to sewage sludge. According to the results, a co-digestion ratio of 4:3:3 (sewage sludge: GTS: OFMSW) improved biomethane production by as much as 130% when compared to that of sewage sludge alone (Grosser, 2018). Ferreira et al. (2018) observed the co-digestion of sewage sludge, food waste (FW) and residual glycerol combined in the ratio 89.6:10.0:0.4 (v/v%) in a pilot semi-continuous digester led to a 1.8-fold increase in methane yield when compared to the digestion of sewage sludge alone. Additionally, most of the above cited literature did not consider SS as a source of FOG. FOG wastes are known to vary differently in composition and chemical characteristics depending on the source, mechanism of collection, abatement device configuration, the device pumping frequency etc. (Long et al., 2012; Salama et al., 2019). In fact, the frequency of pump-out influences the biochemical oxygen demand (BOD), and total solids (TS) variations (Awe et al., 2018). The limited studies on this subject therefore requires further investigation in order to allow WWTPs, existing digesters and biogas plants make educated decisions on the subject of co-digestion and co-substrate selection. It would be of interest since WWTPs and digesters have been reported to be operating below capacity for a significant part of their operating life (Koupaie et al., 2014; Ara et al., 2015; Alqaralleh et al.,2016). Existing bioreactor landfills treating OFMSW and leachate with the primary objective of generating biogas would also benefit from the idea of co-disposal of OFMSW, leachate and SS (Chan et al., 2002).

Based on the reported findings in Aromolaran and Sartaj (2021b) and Grosser (2018), further investigations focusing on the optimization of mixing ratio of SS in a trinary mixture is needed and would be significant in promoting co-digestion of these waste streams for enhanced biomethane recovery under two separate scenarios i.e WWTP and landfill bioreactor. Consequently, the objectives of this study are to (i) investigate the feasibility of trinary co-digestion of TWAS, OFMSW and sewage scum in a WWTP scenario. This is permissible because it has been documented that most digesters operate at a lower organic loading rate than their design capacity (Koupaie et al., 2014). This implies at least 30% of the capacity is unutilized. ii) investigate the effect of trinary co-digestion of OFMSW, landfill leachate and sewage scum in a landfill bioreactor scenario. In both scenarios, batch biomethane potential (BMP) assay will be done to understand the synergistic effects, assess the process performance and relevant kinetic models will be applied to interpret the experimental results.

5.3 Materials and Methods

5.3.1 Materials

The sewage scum (SS) used in this study was collected from the surface of a primary sedimentation tank of the WWTP in Gatineau, QC, Canada. The thickened waste activated sludge (TWAS) was collected from the same plant. The inoculum used was collected from a mesophilic digester of Robert O. Pickard Environmental Center, Ottawa, ON, Canada. The inoculum was degassed at 40°C for one week before BMP preparation in order to remove endogenous biomethane (Holliger et al., 2016). OFMSW was collected from the compost facility of a landfill site in Moose Creek, ON, Canada. The OFMSW was mixed with tap water and homogenized using an electric blender. No other treatment was done on any of the samples. New leachate was collected from an enclosed leachate reservoir within the same landfill site while old landfill leachate was sourced from an engineered landfill site at Carp Road, Carp, ON, Canada. At the time of collection, the old landfill was estimated to be between 15 to 25 years old while the new leachate was estimated to be less than two years. All collected wastes were transported safely into the laboratory and stored at a temperature of 4°C until they were used.

5.3.2 Experimental Setup

Table 5-1 shows the experimental setup in this study. A total of 36 BMP bottles were used in this investigation. In the first phase, single substrate AD tests were conducted to determine the BMP of all substrates; SS, OFMSW, TWAS and LB (33% New leachate and 67% Old leachate). This leachate blend ratio was selected based on a previous study by Aromolaran and Sartaj (2021a). In the second phase, binary mixtures of SS and TWAS based on VS were investigated in two ratios (20SS:80TWAS and 40SS:60TWAS). Whereas, trinary co-digestion experiments based on VS were conducted with 20% SS additions to co-digestion of TWAS and OFMSW in four ratios

(10:70,30:50,50:30,70:30) in the third phase. Similarly, 20% SS (VS basis) additions to co-digestion of LB and OFMSW were performed in four ratios (10:70,30:50,50:30,70:30) in the fourth phase. 40%SS (VS basis) additions were only investigated for co-digestion of TWAS and OFMSW in three ratios of (10:50, 30:30, 50:10) due to feasibility considerations regarding the low production of SS.

Table 5-1: Experimental setup used in this study.

Sample[1]	Inoculum (mL)	SS (g)	TWAS (mL)	OFMSW (g)	LB (mL)	ISR[2]	Initial VS (g)
Single Substrates							
SS	205	3.5	0.0	0.0	0.0	2	4.83
TWAS	205	0.0	62.6	0.0	0.0	2	4.83
OFMSW	205	0.0	0.0	38.1	0.0	2	4.83
LB	205	0.0	0.0	0.0	138.7	2	4.83
Control	205	0.0	0.0	0.0	0.0	-	3.22
Binary Mixtures							
20%SS:80%TWAS	205	0.7	50.1	0.0	0.0	2	4.83
40%SS:60%TWAS	205	1.4	37.6	0.0	0.0	2	4.83
Trinary Mixtures							
20%SS: 10%TWAS: 70%OFMSW	205	0.7	6.3	26.7	0.0	2	4.83
20%SS: 30%TWAS: 50%OFMSW	205	0.7	18.8	19.1	0.0	2	4.83
20%SS: 50%TWAS: 30%OFMSW	205	0.7	31.3	11.4	0.0	2	4.83
20%SS: 70%TWAS: 10%OFMSW	205	0.7	43.8	3.8	0.0	2	4.83
20%SS: 10%LB: 70%OFMSW	205	0.7	0.0	26.7	13.9	2	4.83
20%SS: 30%LB: 50%OFMSW	205	0.7	0.0	19.1	41.6	2	4.83
20%SS: 50%LB: 30%OFMSW	205	0.7	0.0	11.4	69.4	2	4.83
20%SS: 70%LB: 10%OFMSW	205	0.7	0.0	3.8	97.1	2	4.83
40%SS: 10%TWAS: 50%OFMSW	205	1.4	6.3	19.1	0.0	2	4.83
40%SS: 30%TWAS: 30%OFMSW	205	1.4	18.8	11.4	0.0	2	4.83
40%SS: 50%TWAS: 10%OFMSW	205	1.4	31.3	3.8	0.0	2	4.83

[1] % is based on TVS; [2]Based on TVS.

All batch anaerobic experiments were conducted in 500mL glass serum bottle with a working volume of 350mL. A headspace of 30% was maintained in all bottles to prevent CO_2 absorption. All BMP bottles were prepared in duplicates to ensure reproducibility and each bottle contained a total of 4.83g VS load with an inoculum to substrate ratio (ISR) of 2. Inoculum without the addition of any substrate was used as the control. No supplemental nutrients or alkalinity was added to the bottles since the inoculum is a viable source of micronutrients, trace elements, vitamins, as well as a pH-buffer for the biodegradation of substrates. The bottles were purged with nitrogen gas for about two minutes to maintain anaerobic conditions and expel oxygen from the headspace. The bottles were then sealed using self-healing caps and silicon. The bottles were agitated on a New Brunswick Scientific Controlled Environment Incubator Shaker Model G-25 rotating at 110rpm at 40 ±2°C. The test was terminated after 43 days when the daily biogas production for three consecutive days was observed to be less than 1% of the cumulative biogas production.

5.3.3 Analytical Procedure

All samples collected from all BMP bottles were analyzed for pH, total alkalinity (TA), total chemical oxygen demand (TCOD), volatile fatty acid (VFA), and total ammonia-nitrogen (TAN) in triplicates. Total solids (TS) and volatile solids (VS) of the substates were determined according to standard method 2540G. Weekly composition of the biogas production was conducted using a GOW-MAC gas chromatograph (Series 400, Gow-Mac Instrument Co., USA) fitted with a HayeSep® N 80/100 mesh, (5' x 125') and Molesieve equipped with a thermal conductivity detector (TCD). The HayeSep column N80/100 will be used for N_2, CH_4, and CO_2 percentage analysis. Helium was used as the carrier gas. The temperatures of the column, detector, and injector was maintained at 35°C, 185°C, and 50°C respectively during runs. The analysis was conducted following standard methods (APHA, 2012).

Total Solids (TS) was determined by drying up to 25g of sample in the oven at 105^0C for 24hours. The dried sample was cooled in a desiccator and weighed until a constant weight was obtained. For the volatile solids (VS), the dried sample from the TS was heated at 550^0C for 2hours. The VS was calculated based on weight loss after ignition according to standard method 2540G (APHA, 2012). Alkalinity analysis was based on TNTplus™870 reagent vials (Method 10239, HACH USA). COD was conducted according to TNTplus™ 823 (Method 10212, HACH, USA) respectively including spectrophotometer, heating block, and supplies. TAN was determined based on TNT plus™ 832 reagent vials (Method 10205, HACH, USA) while VFA was determined based on TNT plus™ 872 reagent vials (Method 10240, HACH, USA).

Biogas production from the BMP bottles was monitored daily throughout the duration of the experiment. The net biogas volume from all the BMP bottles was obtained by deducting the biogas contribution of the inoculum (blank). Measured volumes were converted to values at STP (0°C and 1atm) according to Kafle and Kim (2012).

5.3.4 Performance Indicators

The performance of both single substrate and co-digestion were assessed using the following indicators in various sections:

i. Volatile Solids Removal (%VSR)

The %VSR was calculated using equation 5-1

$\%VSR = (VS_{initial}-VS_{final}) * 100/VS_{initial}$ - Equation 5-1

where $VS_{initial}$ and VS_{final} are the VS measured before and after the digestion process.

ii. Synergistic effects

While BMP assays do give experimental results from a co-digestion study, synergistic effects do occur due to the inner reactions of the various components in a co-digestion study. To evaluate possible synergistic effects produced during co-digestion as well as to understand the influence of each substrate in the various mixtures, Equation 5-2 was used (Nielfa et al., 2015):

$\alpha = \text{Net Experimental CMY}/CY_{calculated}$ - Equation 5-2

Where α is the synergistic index. If $\alpha > 1$; the co-digestion mixture has a synergistic effect in the net experimental CMY; if $\alpha = 1$; the substrates work independently from the co-digestion mixture; if $\alpha < 1$; the co-digestion mixture has a competitive or antagonistic effect in the final mixture (Nielfa et al., 2015). The net experimental CMY is the cumulative methane yield from the BMP tests from each co-digestion mixture (mL gVS^{-1}) while the $CY_{calculated}$ is estimated from the BMP of the sole substrates considering the VS of each substrate contained in the final mixture (mL gVS^{-1}).

iii. COD Mass Balance (COD_{MB})

The COD mass balance in this study was calculated using Equation 5-3 (Elbeshbishy and Nakhla 2012).

$COD_{MB} = (COD_{final} + COD_{CH4})/COD_{initial} * 100\%$ - Equation 5-3

Where COD_{CH4} is the total COD of the net cumulative methane production (CBP) based on 350mL CH_4 per gCOD, while $COD_{initial}$ and COD_{final} represent the initial and final total COD respectively.

iv. Anaerobic Biodegradability (%BD)

The anaerobic biodegradability in this study was calculated using equation 5-4:

$\%BD=[(mLCH_{4}.gVS^{-1}/gCOD_{destroyed})]/(\text{Theoretical } mLCH_4 \text{ per } gCOD) *(gCOD_{destroyed})]*100\%$. – Equation 5-4

where $mLCH_{4}.gVS^{-1}$ is the methane yield, $gCOD_{destroyed}$ ($gCOD_d$) is the difference between the initial and final total COD and the theoretical $mLCH_4$ per gCOD is based on 350mL (Xie et al., 2017).

v. Kinetics model application

Three commonly used kinetic AD models were applied and assessed in this study; first-order equation (FO), modified Gompertz model (GM), and Logistic function (LF) shown in equations 5-5, 5-6 and 5-7, respectively (Aromolaran and Sartaj, 2021a).

$\beta(t) = \beta o[(1- e^{-kt})]$ - Equation 5-5

$\beta(t) = \beta o. \exp(-\exp((Rm.e)/\beta o (\lambda\text{-}t)+1))$ - Equation 5-6

$\beta(t) = \beta o/(\{1+\exp[(4Rm.)/\beta o(\lambda\text{-}t) +2]\})$ - Equation 5-7

Where: β(t) is the cumulative biogas production (mL gVS^{-1}) at specific time, t is the time (hour or day). βo is the ultimate production potential (mL gVS^{-1}). Rm is the methane production rate (mL gVS^{-1} d^{-1}) or (mL gVS^{-1} hr^{-1}), λ is the lag phase (hour or day), and e = 2.7183. k is the hydrolysis rate constant (hr^{-1}) or (d^{-1}) (Alqaralleh et al., 2016). λ, βo, Rm, and *k* were fitted using the generalized reduced gradient non-linear regression algorithm of solver in 2019 Microsoft Excel with minimum residual sum of squared errors between experimental data and the model curve (Brown et al., 2001). Maximum number of iterations was set at 100 in all cases.

vi. Energy generation

The energy generation from the methane yield was derived using equation 5-8 (Okewale and Adesina, 2019; Reungsang et al., 2012).

Energy (J) = Methane yield ($mLCH_4$ $kgVS^{-1}$) *Relative density*Heating Value - Equation 5-8

Where methane relative density is 0.72$mgCH_4$ $mLCH_4^{-1}$ and methane heating value is 55.6J $mgCH_4^{-1}$.

5.4 Results and discussion

Table 5-2 shows the various characteristics of the substrates and inoculum used in this study.

Table 5-2: Characteristics of the substrates and inoculum.

Parameter	TWAS	LB	OFMSW	Sewage Scum	Inoculum
COD (mg L^{-1})	66,950±450	32,000±252	42,400±100	28,965±935	21,600 ±100
pH	5.7±0.02	7.7±0.07	5.0±0.0	4.8±0.03	7.7±0.02
TAN (mg L^{-1})	215±3	1640±22	74±2.65	93.8±0.4	1320±3
VFA (mg L^{-1})	5670±30	6,770±93	16,100±201	11,835±45	2570±10
Alkalinity (mg $CaCO_3$ L^{-1})	4475±55	8,270±62	3,195±55	1515±95	7330±42
TS (g kg^{-1})	33.2±0.19	24.81±0.03	51.65±4.82	462.3±19.5	23.17±0.74
VS (g kg^{-1})	25.66±0.15	11.59±0.1	42.17±4.59	453.5±19.9	15.7±0.02
VS/TS	0.77±0.01	0.47±0.00	0.82±0.02	0.98±0.00	0.68±0.01

± represents standard deviation based on three samples

5.4.1 Biomethane Production

5.4.1.1 Mono-substrate digestion

Figure 5-1 shows the average net cumulative biomethane yield (CMY) from the mono-substrate digestion of the various substrates. A 5% standard error was applied to all plots.

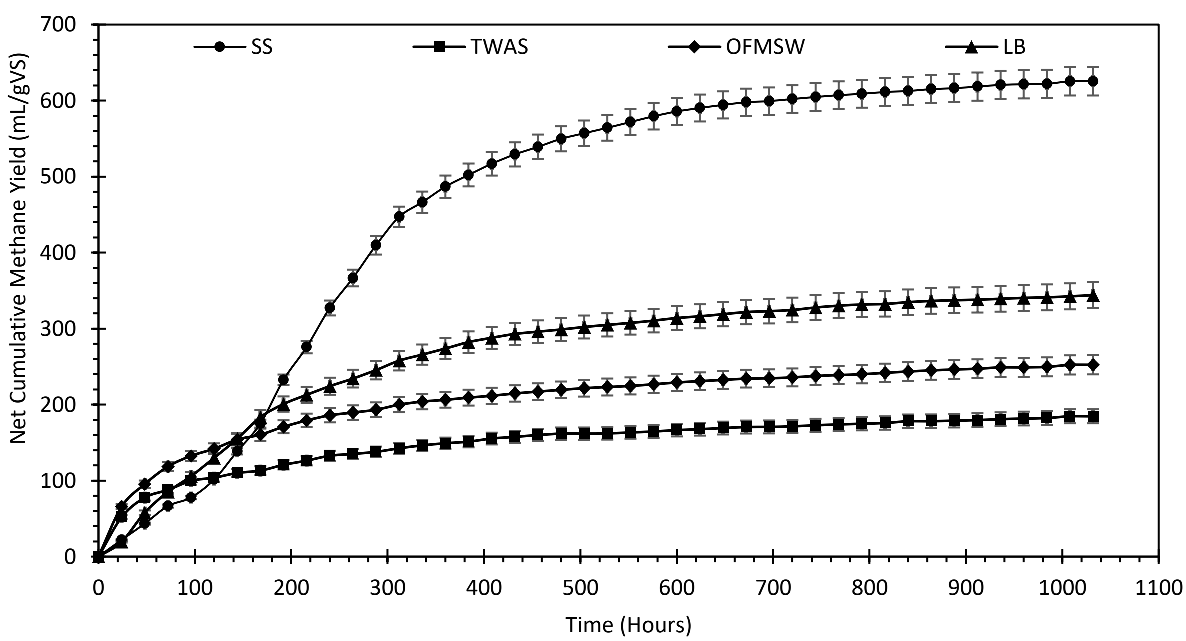

Figure 5-1: Average net cumulative methane yield (CMY) from the various single substrates used in this study.

As expected, the net CMY increased until a plateau was achieved regardless of the substrate, albeit at different rates. Net CMY and average methane concentration of 625.4mL gVS^{-1} (61.5% CH_4), 344 mL gVS^{-1} (61.4% CH_4), 252.3 mL gVS^{-1} (51.8% CH_4) and 184.6 mL gVS^{-1} (54.4% CH_4) were produced from SS, LB, OFMSW and TWAS respectively. It is important to note that SS was digested under optimal conditions in this study because the SS was not present in high concentration. However, this is not always the case when SS is digested alone. The hydrolysis of FOG wastes forms LCFA. LCFAs are known to have an inhibitory and toxicity effect on methanogens when presents in high concentration (Ziels et al., 2016; Salama et al., 2019). The results confirmed that SS had the highest and a significant biomethane yield, therefore, SS is best suited as a co-substrate during ACo-D. The high biomethane yield of FOG wastes has been associated with the high number of carbon and hydrogen atoms as well as the C:N ratio which can be as high as 22 (Wan et al., 2011; Salama et al., 2019). Moreover, limited quantities of SS are produced when compared to TWAS, OFMSW and leachate. The initial lag of 2.6days (shown later in Table 5-5) is perhaps related to LCFA production during hydrolysis. However, the reactor picked up immediately after this. The methane yield of SS in this study is within the range of 430-990mL gVS^{-1} reported in similar studies involving FOG wastes (Luostarinen et al., 2009; Kabouris et al., 2009; Girault et al., 2012; Silvestre et al., 2011; Grosser, 2018). The CH_4 yield for LB is 344 mL gVS^{-1} and is likely to relate to the effect of leachate blending. In leachate blending, the old leachate present in the mixture has been suggested to be more stabilized and abundant in methanogenic consortia, thereby quickening methanogenesis in the reactor (Nair et al., 2014). CH_4 yield of LB is higher than a previously obtained value of 242 mL gVS^{-1} in Aromolaran and Sartaj (2021b) which may relate to the fact that a low ISR was used in that study. CH_4 yield of

252.3 mL gVS^{-1} from OFMSW falls within the range of 186 – 570mL gVS^{-1} that has been reported in some literature (Owen, 1993; Davidsson et al., 2008; Ponsá et al, 2011). The methane yield of TWAS in this study (184.6 mL gVS^{-1}) falls within some previously reported values of 143-220 mL gVS^{-1} (Zhang et al., 2016). Compared to the other substrates in this study, the lower methane yield of TWAS was expected and has been suggested to relate to its low VS content, low organic load or low C:N ratio which is usually between 6-9 (Alqaralleh et al., 2016). The higher methane concentration in TWAS compared to OFMSW could be an indication methane was produced by the acetoclastic methanogens in TWAS compared to hydrogenotrophic methanogens in OFMSW (Rabii et al., 2019).

As seen in Table 5-3, the % VSR of the treated single samples in the study shows the values were within the range of 34.4% - 40.4%. Therefore, the values remained steady and showed no significant differences.

5.4.1.2 Co-digestion of TWAS in binary and tertiary mixtures

Co-digestion mixtures involving SS, TWAS and OFMSW are represented in Figure 5-2. The shape of the co-digestion mixtures shows a gradual increase in methane yield over the digestion period, until a plateau period (substrate exhaustion) is eventually reached. Exceptionally, 40%SS:50%TWAS:10%OFMSW and 40%SS:30%TWAS:30%OFMSW experienced a distinct lag time (shown later in Table 5-5) before biomethane production was substantial which might be related to the simultaneous higher SS and TWAS content as well as a metabolic adjustments and pattern of preferential consumption of a substrate with a higher surface ratio (TWAS) before a lower surface ratio substrate (SS and OFMSW), thus leading to a diauxic pattern. A similar diauxic pattern was observed during the co-digestion of low carbohydrate with high fat agricultural wastes (Kim and Kim, 2017). Biomethane production is ideally expected to improve when complimentary substrates are co-digested due to substrate diversity, dilution of inhibitory components, improved nutrient presence and higher biodegradable components (Ara et al., 2015). As seen in Figure 5-2 and Table 5-3, all co-digestion mixtures produced higher methane yields than TWAS alone.

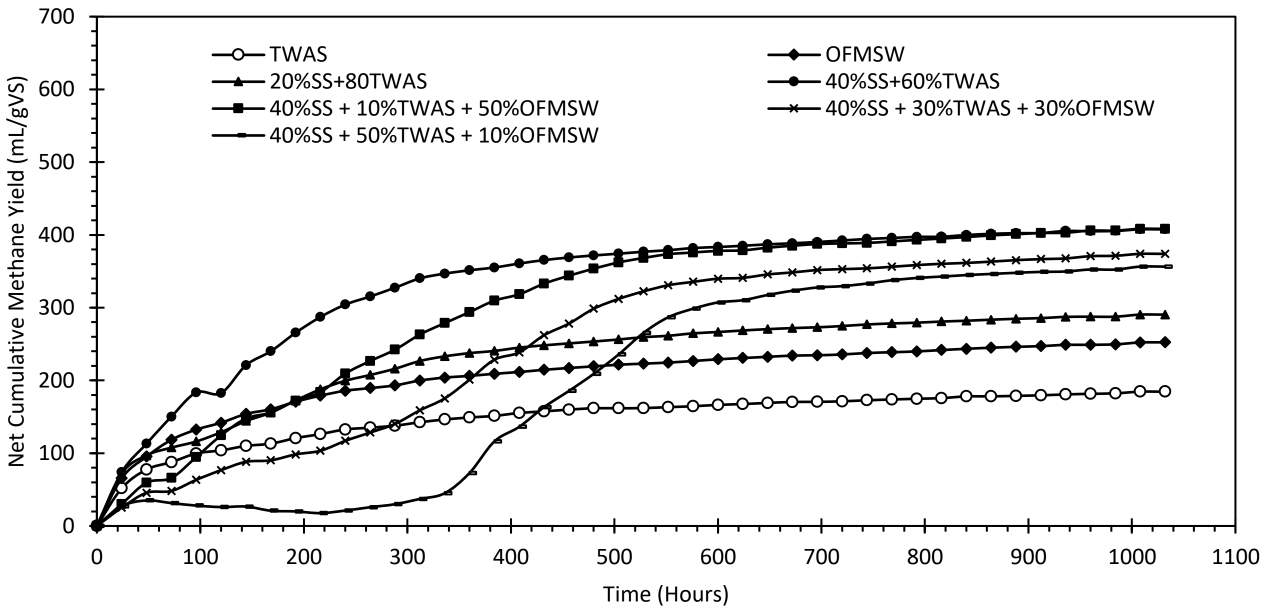

Figure 5-2: Comparison of the cumulative methane yield of mono-digestion, binary and tertiary co-digestion involving TWAS.

The improvement in methane yield shows that it is beneficial to add SS and OFMSW to TWAS during co-digestion. Based on the net CMY from TWAS alone (184.6mL gVS^{-1}), net methane yield was enhanced by 57.4%-120.8% in binary co-digestion [20%SS:80%SS (290.5mL gVS^{-1}) and 40%SS:60%TWAS (407.6 mL gVS^{-1})] and by 32.4% -121.4% in trinary co-digestion [(20%SS:70%TWAS:10%OFMSW (244.5mLgVS^{-1}) and 40%SS:10%TWAS:50%OFMSW (408.4 mLgVS^{-1})]. Improvement in methane yield could be due to the positive effect of co-digestion, higher content of SS, and increased presence of biodegradable substrates. Grosser (2018) had observed 80-128% improvement in methane production over TWAS alone when GTS was co-digested with OFMSW and TWAS.

In addition, methane concentration was also higher in both 40%SS:60%TWAS (59.4%), 40%SS: 10%TWAS: 50%OFMSW (58.8%CH_4) than in TWAS alone (51.8%CH_4). This could be related to the microbial community established in complimentary co-digestion environments which favoured the acetoclastic methanogens of methane production over the hydrogenotrophic methanogens.

Table 5-3: BMP test results in both mono-digestion and co-digestion experiments.

Substrate	Net CMP (mL)	Net CMY (mL.gVS^{-1})	$CY_{calculated}$ (mL/gVS)	% increase (Net CMY-CY)/(CY)*100	α	Average %CH_4	VSR (%)
SS	1006.3	625.0	625.0	-	-	61.5	35.3
TWAS	297.2	184.6	184.6	-	-	54.4	34.4
OFMSW	406.3	252.3	252.3	-	-	51.8	40.4
LB	553.8	344.0	344.0	-	-	61.5	36.2
20%SS + 80%TWAS	467.7	290.5	272.7	6.5	1.07	57.2	31.7
40%SS+60%TWAS	656.2	407.6	360.8	13.0	1.13	59.4	50.7
20%SS + 10%TWAS + 70%OFMSW	539.8	335.3	320.1	4.7	1.05	51.3	46.1
20%SS + 30%TWAS + 50%OFMSW	411.5	255.6	306.6	-16.6	0.83	56.9	33.5
20%SS + 50%TWAS + 30%OFMSW	566.1	351.6	293.0	20.0	1.20	56.8	36.9
20%SS + 70%TWAS + 10%OFMSW	393.6	244.5	279.5	-12.5	0.87	56.6	34.9
20%SS + 10%LB + 70%OFMSW	485.5	301.6	336.0	-10.3	0.90	56.3	30.7
20%SS + 30%LB + 50%OFMSW	642.2	398.9	354.4	12.6	1.13	58.0	32.8
20%SS + 50%LB + 30%OFMSW	716.5	445.0	372.7	19.4	1.19	61.2	34.4
20%SS + 70%LB + 10%OFMSW	783.6	486.7	391.0	24.5	1.24	61.5	34.9
40%SS + 10%TWAS + 50%OFMSW	657.5	408.4	376.2	8.6	1.09	58.8	35.6
40%SS + 30%TWAS + 30%OFMSW	602.1	374.0	381.1	-1.9	0.98	56.5	29.9
40%SS + 50%TWAS + 10%OFMSW	573.8	356.4	367.5	-3.0	0.97	55.7	29.3

From Table 5-3, the VS destruction of 50.7% was achieved in 40%SS:60%TWAS while 46.1% and 36.6% were respectively obtained in 20%SS:10%TWAS:70%OFMSW and 40%SS: 10%TWAS: 50%OFMSW respectively is greater than the 34.4% VS destruction in TWAS. From this result, it can be concluded that co-digestion can improve the destruction of VS in the mixture. Also, it is obvious that SS addition to TWAS did not have negative effect on VS destruction (Martín-González et al., 2010). It is however important to also note that although VSR indicates the extent of microbial activity and degradation during AD, improved methane yield may not necessarily accompany an enhanced VS destruction of organic substrates as observed in some trinary co-digestion cases. For instance, relative to the other co-digestion groups involving TWAS, the 46.1% VSR in 20%SS:10%TWAS:70%OFMSW did not translate to a higher methane yield. This is not uncommon as one study documented this instance during the binary co-digestion of sewage sludge and GTS from a meat processing plant (Luostarinen et al., 2009).

OFMSW addition to TWAS and SS was observed to improve methane yield across the 40%SS group. The improvement in methane yield with increasing content of OFMSW higher yields might relate to the higher fraction of OFMSW (50%VS) and SS (40%VS) which most likely also improved the C:N ratio. Sosnowski et al. (2003) reported biogas production improved with increase in the fraction of OFMSW present when co-digested with TWAS. In contrast, Xie et al. (2017) reported a decrease in biomethane potential with increasing fraction of FW in a FW: SS co-digestion mixture involving 110gFW:150g Sewage sludge and 150gFW:150g sewage sludge. Grosser (2018) did not observe any trend of improvement in methane yield with increasing content of OFMSW during co-digestion of GTS with TWAS. With a net CMY of 252.3 $mLgVS^{-1}$ (51.8%CH_4) from OFMSW only, net CMY improved the highest in 40%SS: 10%TWAS: 50%OFMSW (58.8%CH_4) by 61.9%, thus highlighting the benefit of co-digestion of OFMSW.

When considering the best performing TWAS trinary mixture (40%SS:10%TWAS:50%OFMSW) along with the best performing binary mixture

(40%SS:60%TWAS), this translates to only 0.2% improvement over the binary mixture. Contrasting results have been documented (Ara et al., 2015). Ara et al. (2015) compared ternary mixtures of OFMSW, TWAS and primary sludge (PS) against binary mixtures of OFMSW and PS and observed that the CMY of trinary mixtures digested at VS ratios of 25%OFMSW:37.5%TWAS:37.5%PS, 50%OFMSW:25%TWAS:25%PS and 75%OFMSW:12.5%TWAS:12.5%PS were respectively enhanced by 20%, 27%, and 12% when compared to their corresponding binary mixtures of OFMSW:TWAS at a ratio of 25%:75%, 50%:50%, and 75%:25%. Of note however is the fact that, since 40%SS was to be maintained, a maximum of 50% OFMSW VS content investigated in this present study while Ara et al. (2015) investigated up to 75% OFMSW VS content.

In this study, mixtures containing above 40%SS was not considered based on the low production of SS and the feasibility consideration. More importantly, the possibility of digester failure caused by LCFA accumulation exists when high FOG content is digested (Long et al., 2012). Shakourifar et al. (2020) encountered digester failure beyond 40%VS content of mixed grease trap waste co-digestion with mixed primary sludge and TWAS.

5.4.1.3 Effect of leachate blending in trinary co-digestion

Figure 5-3 compares the effect of the addition of TWAS or the use of LB in the co-digestion of 20%SS and OFMSW. In the first 20days, the trend on most of the plots shows a diauxic pattern of growth noted earlier in this study. When compared with the pattern of biomethane production in the mono-substrates shown in Figure 5-1, it is obvious the acclimation and adjustment of the anaerobic microbiota to the consumption of multiple substrates could be one of the factors responsible for this pattern.

From Figure 5-3, the plot shows the addition of LB in a trinary mixture of OFMSW and SS improved net CH_4 yield over TWAS. Considering the net CMY on a case-by-case basis i.e. comparison of corresponding mixtures, three out of the four co-digestion cases confirm this. For instance, while 20%SS:50%TWAS:30%OFMSW produced the highest net CH_4 yield of 351.6mLgVS^{-1} in the TWAS group of 20%SS, 20%SS:10%LB:70%OFMSW was the mixture with the highest net CH_4 yield of 486.7mLgVS^{-1} in both LB and TWAS group of 20%SS. This means CH4 yield was enhanced by 38.4% - 99% in the LB group over the TWAS group. Beyond the fact that the composition of the mixtures varies as well as well as the identified general benefit of co-digestion of complimentary substrates, one of the possible reasons for improved biomethane production is the effect of leachate blending. According to Nair et al. (2014), the old leachate contains a stabilized methanogenic microbial community that can quicken the conversion of organic acids contributed by the new leachate to methane, thereby quickening methanogenesis in a leachate blend. This phenomenon can improve the biomethane production in the co-digestion medium

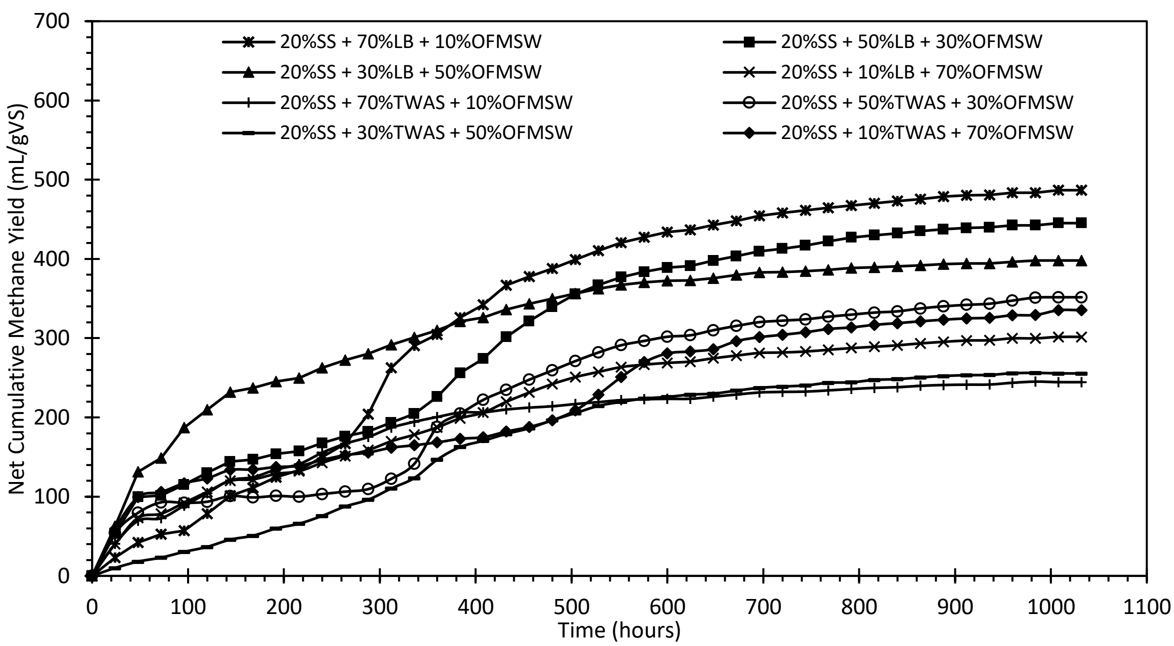

Figure 5-3: Net cumulative methane yield of 20SS digestion with OFMSW with LB or TWAS addition.

(Nair et al., 2014; Aromolaran and Sartaj, 2021b). In addition, Table 5-3 shows that the LB reactors were consistently higher in CH_4 concentration than trinary LB group of 20%SS than the trinary TWAS group of 20%SS benefit. This could also be related to the higher abundance of acetoclastic methanogens which promoted methane formation through acetate over the hydrogenotrophic methanogens in the LB group of 20%SS.

As seen in the Table 5-3 and Figure 5-3, %VSR shows there was a general tendency for incomplete VS destruction in both groups as the value remained relatively stable between 30.7% - 36.9%. However, a higher %VSR of 46.1%. in 20%SS:10%TWAS: 70%OFMSW did not translate to a higher methane yield as expected.

5.4.2 Synergistic effect during anaerobic co-digestion.

The subject of synergistic effect has been questioned by some researchers. Nevertheless, evidence of synergism during co-digestion has been well documented (Wan et al., 2011; Xie et al., 2017; Nielfa et al., 2015), as well as antagonistic effect (Xie et al., 2017).

Basically, the co-digestion of organic substrates can potentially bring about a synergistic effect or antagonistic/competitive effect. Synergistic effect usually refers to scenarios where an additional methane yield is obtained for co-digestion samples over the weighted average of the individual substrates in the mixture. Whereas antagonistic/competitive effect means a lower methane yield in the co-digestion substrates when compared with the expected yield (Nielfa et al., 2015).

Furthermore, synergism may occur from contribution of additional alkalinity, buffering capacity, trace elements, nutrients, enzymes, or any other improvement which a single substrate by itself may lack, and could therefore result in an increase in substrate biodegradability and consequently improve the biomethane production. It could also manifest in terms of increased hydrolysis rate constant, process kinetics improvement, accelerated degradability and solubilization, pH balance or even a combination of these factors (Ebner et al.,2016; Xie et al., 2017). Competitive effects on the other hand may result from factors such as pH inhibition, ammonia toxicity or high volatile acid concentration.

Table 5-3 presents the results of the synergistic and antagonistic index from various co-digestion mixtures considered in this study. The results from Table 5-3 highlights the benefit of ACo-D and shows that BMP is a useful screening tool for co-substrate evaluation. Considering the digestion of TWAS alone, the results indicate that CH_4 yield can be enhanced through a few carefully selected co-digestion scenarios. While five of the nine scenarios showed evidence of synergism, four indicated antagonistic/competitive effects. Going by the $CY_{calculated}$ in the trinary mixtures of SS with TWAS and OFMSW, the trend was to expect an increase in experimental methane yield with increase in the OFMSW content (Xie et al., 2017; Grosser, 2018), however results shows that synergism only occurred in 20%SS: 50%TWAS: 30%OFMSW (α = 1.2), 20%SS: 10%TWAS: 70%OFMSW (α = 1.05) and 40%SS : 10%TWAS : 50%OFMSW (α = 1.09). This underscores the importance of conducting experimental work in order to determine the actual BMP of substrates and co-substrates rather than relying on theoretical methods. The highest synergistic effect involving TWAS was in 20%SS: 50%TWAS : 30%OFMSW (α = 1.2) where the net CMY exceeded the $CY_{calculated}$ by 20%, thus proving that synergism does exists in co-digestion. Despite similar net CMY, the synergistic index was higher in 40%SS:60%TWAS (α = 1.13) compared to its corresponding trinary mixture 40%SS: 10%TWAS: 50%OFMSW (α = 1.09).

A competitive effect was also observed during co-digestion of the trinary LB group of 20%SS LB in 20%:10%LB:70%OFMSW (α = 0.9), since the reactor failed to perform as expected in terms of CH_4 yield. One reason could have been the composition of the mixture as well as the lower LB content in the mixture. On the other hand, synergism occurred in the other mixtures of LB groups as seen in Table 5-3. The greatest effect of synergism was observed in the ratio 20%SS: 70%LB: 10%OFMSW (α = 1.24), when the net CMY was 24.5% than the expected/calculated value. This mixture produced the highest methane yield in all the co-digestion ratios considered in this study. Within the group, net CMY was observed to increase with increasing %LB content, thus suggest the LB content played a role in the methane improvement. The above results demonstrate the dual benefit of co-digestion due to positive synergism as well the benefit of leachate blending.

5.4.3 Process Performance Indicators

5.4.3.1 Total VFA (TVFA) to TA ratio, pH and TAN

TVFA/TA ratio is an essential and an early warning indicator of imbalance or stability during AD (Onwosi et al., 2019). This parameter reflects the metabolism of the digesting system and imbalance that could result from VFA production and consumption. Figure 5-4a shows the average TVFA/TA in both mono and co-digestion modes. A TVFA/TA < 0.3 was suggested as the normal range for a stable AD process during the co-digestion of papermill sludge (Poggi-Varaldo et al., 1997). Li et al. (2014) later suggested a VFA/TA ≤ of 0.35 was a normal range during the AD of FW. On the other hand, Feng et al. (2013) identified three critical stages in assessing AD; stable (<0.4), some instability (0.4-0.8) and significant instability (>0.8). However, no universal value for TVFA/TA or consensus exists since AD systems vary significantly even when the same substrates are treated (Li et al., 2014). Even with the same parameter, multi-thresholds exist (Li et al., 2014). Figure 5-4a shows some of the reactors were initially slightly above TVFA/TA of 0.4 and therefore at a threshold of some instability or apparent stress at the initial stage except the 20%SS trinary TWAS group.

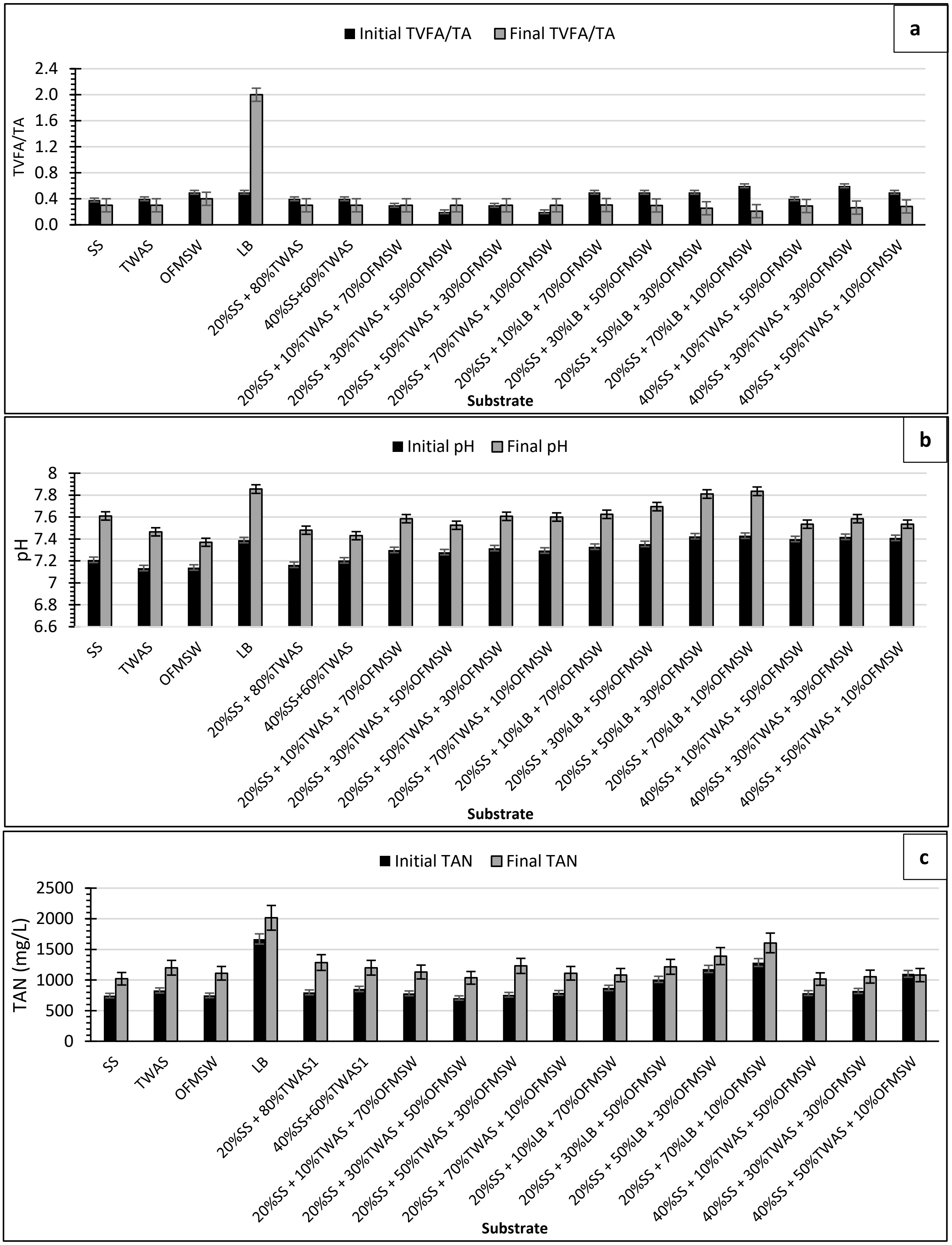

Figure 5-4: A) Average initial and average final TVFA/TA ratios in all the reactors. B) Average initial and average final pH values in all the reactors. C) Average initial and final total ammonia nitrogen (TAN) concentration in reactors.

The threshold instability relates to the unique nature of the various mixtures, high concentration of biodegradable organic matter as well as the onset of acidolysis in the reactors. The trend shows presence of LB and OFMSW exerted huge influence on the mixture. However, the reactors functioned normally since the initial pH (shown in figure 5-4b) remained stable and within recommended range of 6.5 – 8.2 for AD (Wang et al., 2013; Franke-Whittle et al., 2014). It is most likely because sufficient presence of inoculum provided the required buffer to prevent further pH drop during acidogenesis in both mono and co-digestion reactors.

Furthermore, figure 5-4c shows initial TAN levels were also generally within acceptable ranges in AD. When present in high concentrations, ammonium can directly inhibit biogas production during AD (Adghim et al., 2021). Various studies have cited different inhibitory thresholds for TAN since it depends on the factors such as substrate composition, temperature, pH, alkalinity, and acclimation period (Akindele and Sartaj, 2018). Final values of TAN reached an average of 2000mgL^{-1} in LB while 20%SS:70%LB:10%OFMSW was an average value of 1670mgL^{-1}. Final pH values were also with the prescribed range for methanogenesis. Since multilevel thresholds exits for TVFA/TA ratio in various systems, a final value of 2 in the LB reactor cannot be adjudged as unstable because CH_4 concentration was within an average of 61.5% (Table 5-3) in this reactor which shows methanogenesis proceeded undisturbed.

5.4.3.2 COD mass balance and anaerobic biodegradability

Table 5-4 and Figure 5-5 shows the relationship between the experimental methane yield (per gVS), calculated methane yield (per gCOD) and biodegradability of the various substrates in the mono and co-digestion experiments of this study. The basis of the calculated yield was on the amount of COD destroyed ($gCOD_d$) during the experiment. Generally, the $mLCH_4/gCODd$ of single substrates and co-digestion mixtures is consistent with the trend of methane production data except in few cases.

Table 5-4: Experimental methane data, COD mass balance and biodegradability analysis

Substrate	$mLCH_4/gVS$	$COD_{CH4}(g/L)$	$mLCH_4/gCOD_d$	%Mass Balance	% Biodegradability
SS	625.0	2.9	315.9	93.9	90.3
TWAS	184.6	0.8	136.3	81.4	39.0
OFMSW	252.3	1.2	203.1	87.6	58.0
LB	344.0	1.6	71.4	65.9	20.4
20%SS + 80%TWAS1	290.5	1.3	179.2	82.8	51.2
40%SS+60%TWAS1	407.6	1.9	255.8	94.3	73.1
20%SS + 10%TWAS + 70%OFMSW	335.3	1.5	235.2	90.2	67.2
20%SS + 30%TWAS + 50%OFMSW	255.6	1.2	205.76	81.1	58.8
20%SS + 50%TWAS + 30%OFMSW	351.6	1.6	241.40	89.1	69.0
20%SS + 70%TWAS + 10%OFMSW	244.5	1.1	207.73	85.0	59.4
20%SS + 10%LB + 70%OFMSW	301.6	1.4	190.78	50.5	18.5
20%SS + 30%LB + 50%OFMSW	398.9	1.8	131.19	55.0	26.4
20%SS + 50%LB + 30%OFMSW	445.0	2.0	103.16	68.0	41.8
20%SS + 70%LB + 10%OFMSW	486.7	2.2	104.55	94.9	88.0
40%SS + 10%TWAS + 50%OFMSW	408.4	1.9	177.94	75.6	50.8
40%SS + 30%TWAS + 30%OFMSW	374.0	1.7	125.56	61.6	35.9
40%SS + 50%TWAS + 10%OFMSW	356.4	1.6	98.17	55.0	28.0

The biodegradability provides more information about the nature of the substrates and the extent of degradation when compared to standardized conditions. In the mono-digestion, the higher value of $315mL.gCOD^{-1}$ from the SS is related to its high methane yield of $625mL\ gVS^{-1}$. This explains the reason for its high biodegradability of about 90%. The high biodegradability of FOG waste has been documented in the literature (Grosser, 2018; Salama et al., 2019). TWAS as a single substrate had a yield of $136.3mL\ gCOD^{-1}$ with 39% biodegradability. This was quite expected due to the low organic content in this type of substrates. Similarly, LB as a single substrate had a lower yield of $71.4\ mL\ gCOD^{-1}$ and a biodegradability of 20.4%, which could be related to the higher fraction of old leachate in the sample.

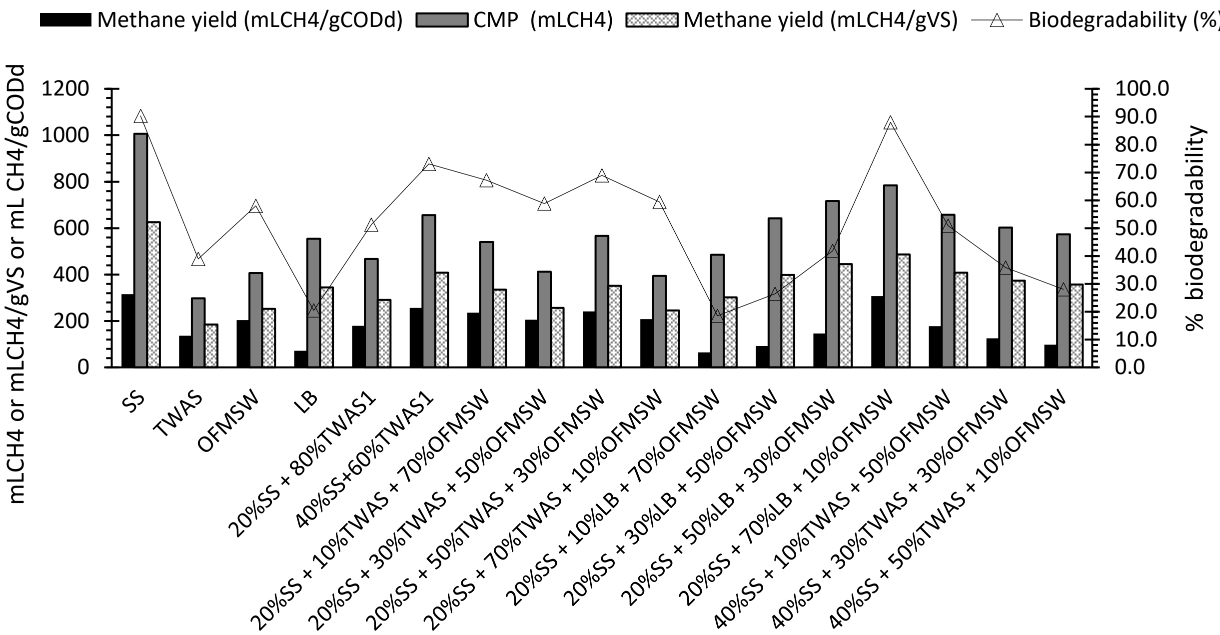

Figure 5-5: Average biodegradability and methane yield from both mono and co-digestion experiment.

In the co-digestion cases, the co-digestion of TWAS with 20%SS and OFMSW improved the biodegradability to above 80% compared to digestion of TWAS alone as seen in Figure 5-5. This could mean co-digestion can help improve biodegradability. Within the 20%SS group containing TWAS, biodegradability remained stable. Although the yield improved in the 40%SS group, the biodegradability did not improve concurrently. This could be because of the presence of a higher fraction of the non-biodegradable COD in the co-digestion mixture.

Furthermore, the LB presence had a greater influence on the LB co-digestion mixtures as biodegradability improved with increasing content of LB. When LB was co-digested with 20%SS and OFMSW, the influence of the LB is quite visible as well as the biodegradability of the mixtures generally increased with increase in LB content. This again shows that codigestion of LB with other substrates can improve biodegradability and thus lead to improve yield on a COD basis. As stated earlier, LB was a mixture of 67%old leachate and 33%new leachate. Old leachate has a higher content of refractory components but also a stabilized methanogenic consortium (Nair et al., 2014). Leachate blending can therefore improve methane recovery in the presence of other organic co-substrates.

The trend of the mass balance in Table 5-4 shows most of the COD in the single substrate and co-digestion were accounted for from the input, CH_4 and digestate. Unaccounted losses could have occurred during measurements, volatilization, and CO_2 in the biogas. These factors are suggested to be responsible for the huge losses in some of the reactors.

Overall, the analysis raises questions the reliability of COD data as a metric in analyzing methane yields and mass balances in a complex process involving AD and ACo-D. A high level of discrepancy is often encountered in the measurement of COD most especially when solids are involved (Raposo et al., 2011).

5.4.3.3 Kinetics Model result and comparison

Table 5-5 shows the parameters estimated using the FO, MG and LF. Figure 5-6a-c shows the plot of single substrate digestion and the co-digestion of 20%SS and OFMSW with the various LB and TWAS ratios. While FO gave an R^2 value of 0.967 – 0.999, a range of 0.947 – 0.999 was obtained for MG, while the LF gave a range of 0.936-0.999. These ranges show the selected models can simulate the principal kinetic patterns of biomethane production. However, to better compare the estimated values, the difference between the predicted value and the experimental value (Δ%) was derived as seen in Table 5-5. While the FO exhibited a higher upper value (Δ% = 0.5 - 24.7%), while MG (Δ% = 0.2 – 9.3%) and LF (Δ% = 0.6 – 9.8%) had less than 10% deviations, which shows the ability of MG and LF to provide a more accurate estimation than FO.

Table 5-5: Comparison of the parameters estimated from the various models.

Sample	Measured CH_4	First Order Model				Modified Gompertz Model					Logistic Function				
		β_o	k	R^2	Δ%	β_o	Rm	λ	R^2	Δ%	β_o	Rm	λ	R^2	Δ%
	mL/gVS	mL/gVS	hr^{-1}			mL/gVS	mL/gVS.hr	hr			mL/gVS	mL/gVS.hr	hr		
Single substrate Experiment															
SS	625.0	689.8	2.92E-03	0.985	9.4	614.3	1.81	61.6	0.999	1.7	604.0	1.82	71.7	0.997	3.5
TWAS	184.6	174.1	6.67E-03	0.978	6.0	168.9	0.76	0	0.947	9.3	168.1	0.7	0	0.936	9.8
OFMSW	252.3	239.0	6.67E-03	0.984	5.6	231.8	1.08	0	0.956	8.9	230.6	1	0	0.945	9.4
LB	344.0	351.1	4.17E-03	0.999	2.0	328.8	0.98	0	0.994	4.6	325.0	0.93	0	0.987	5.8
Co-digestion Experiment															
20%SS : 80%TWAS	290.5	283.7	5.00E-03	0.983	2.4	275.3	0.93	0	0.982	5.5	273.3	0.87	0	0.977	6.3
40%SS:60%TWAS	407.6	401.0	5.83E-03	0.998	1.6	391.0	1.49	0	0.990	4.2	388.4	1.39	0	0.984	4.9
20%SS : 10%TWAS : 70%OFMSW	335.3	401.2	1.67E-03	0.970	16.4	355.6	0.5	0	0.972	5.7	348.2	0.47	0	0.977	3.7
20%SS : 30%TWAS : 50%OFMSW	255.6	270.6	2.50E-03	0.983	5.5	261.2	0.53	81.5	0.998	2.1	251.7	0.55	102.4	0.999	1.5
20%SS : 50%TWAS : 30%OFMSW	351.6	385.4	2.08E-03	0.967	8.8	379.0	0.53	0	0.984	7.2	356.2	0.55	19.95	0.988	1.3
20%SS : 70%TWAS : 10%OFMSW	244.5	243.2	4.33E-03	0.997	0.5	234.5	0.71	0	0.990	4.3	232.4	0.67	0	0.985	5.2
20%SS : 10%LB : 70%OFMSW	301.6	327.2	2.50E-03	0.993	7.8	301.0	0.59	0	0.990	0.2	295.9	0.55	0	0.990	1.9
20%SS : 30%LB : 50%OFMSW	398.9	390.9	5.00E-03	0.990	2.0	378.6	1.29	0	0.969	5.4	376.7	1.19	0	0.959	5.9
20%SS : 50%LB : 30%OFMSW	445.0	554.1	1.67E-03	0.985	19.7	471.0	0.72	0	0.990	5.5	452.9	0.69	0	0.993	1.7
20%SS : 70%LB : 10%OFMSW	486.7	620.0	1.67E-03	0.985	21.5	490.7	1.05	69.1	0.998	0.8	475.2	1.08	87.4	0.998	2.4
40%SS : 10%TWAS : 50%OFMSW	408.4	438.8	2.92E-03	0.996	6.9	406.4	0.89	0	0.998	0.5	398.6	0.86	3.68	0.996	2.5
40%SS : 30%TWAS : 30%OFMSW	374.0	496.9	1.67E-03	0.981	24.7	387.4	0.72	55.4	0.994	3.5	371.9	0.75	81.4	0.997	0.6
40%SS : 50%TWAS : 10%OFMSW	356.4	-	-	-	-	353.3	1.19	292.2	0.998	0.9	347.5	1.14	294.2	0.997	2.6

Based on the results of this study, Table 5-5 shows that the β_o ($mLgVS^{-1}$) which is the ultimate methane production was observed to be under-estimated more by LF (14 cases out of 17cases) than the MG (11 cases out of 17cases). Over-estimation occurred in LF in 3 cases compared to MG which occurred in 6 cases.

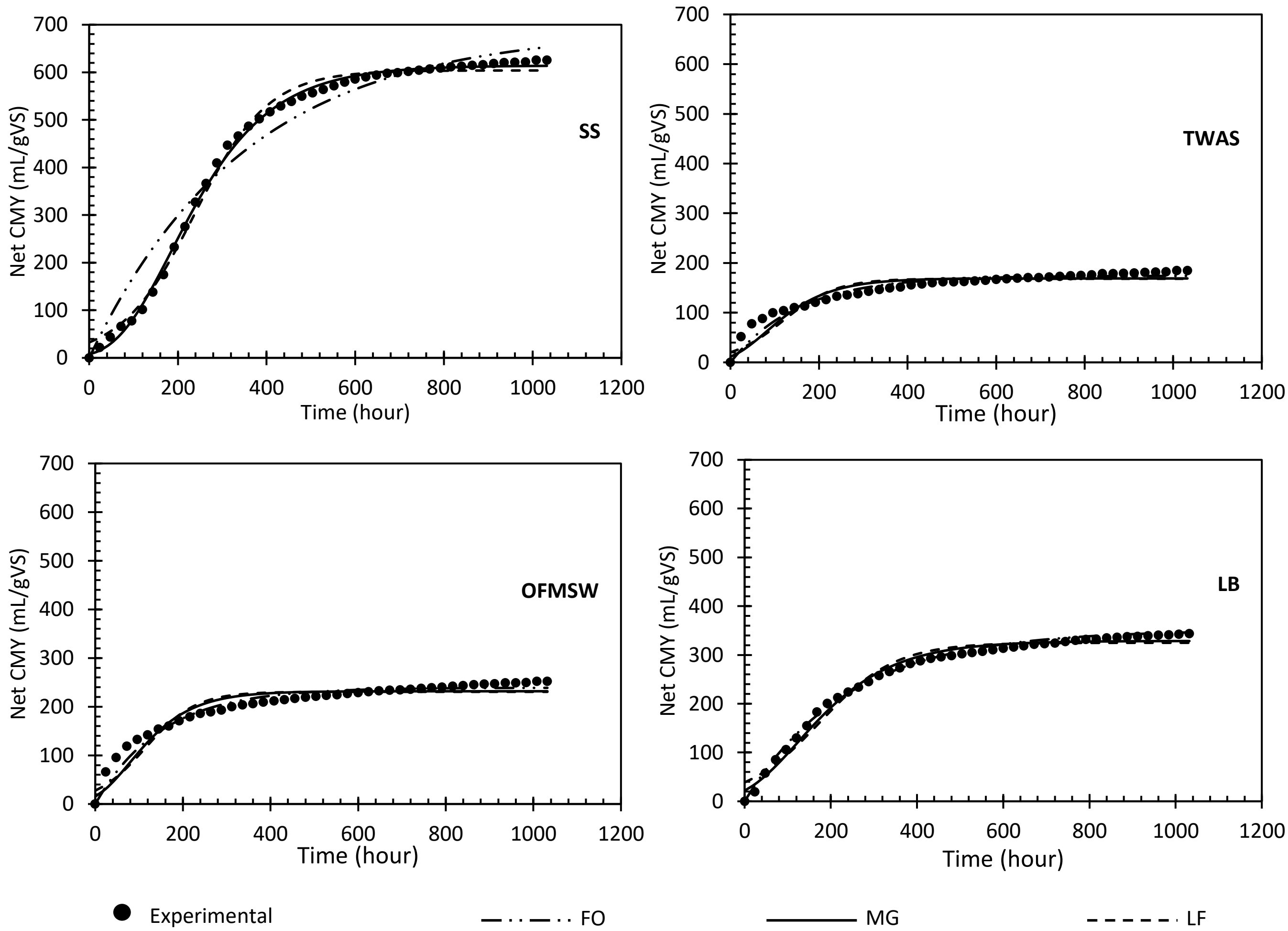

Figure 5-6a: Model graphs of the net cumulative methane yield from mono-substrate digestion in this study.

The FO is mostly applied in order to estimate the hydrolysis constant, k (day^{-1}) of a substrate. Hydrolysis is considered the rate limiting step in AD (Angelidaki and Sandars, 2004). k is a measure of the biodegradability of substrates. A higher k value is more desirable since this usually indicates a higher degradation rate (Aromolaran and Sartaj, 2021a). Considering the estimated parameters for k in the mono-digestion, TWAS (k = 0.16day^{-1}) and OFMSW (k = 0.16day^{-1}) are easily labile and

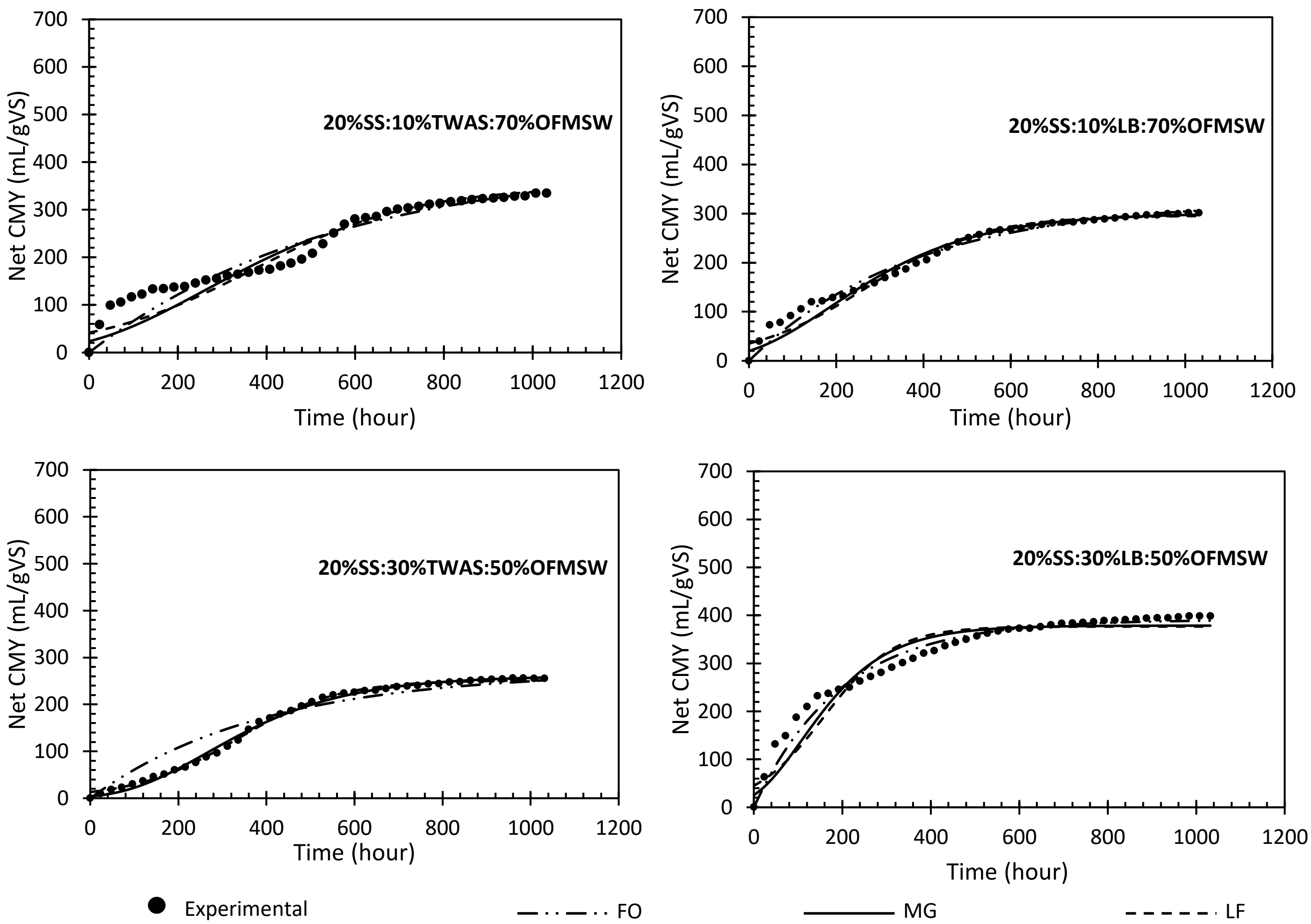

Figure 5-6b: Model graphs of the net cumulative methane yield from some co-digestion groups in this study.

as expected, showed the fastest hydrolysis rate before LB (k =0.1day^{-1}). On the other hand, SS which had the highest methane yield had the least k value of 0.07day^{-1}. One reason could be because FOG from most WWTP is FOG has been considered to be a slowly biodegradable particulate organic matter (sbpCOD) (Metcalfe and Eddy, 2003). The k value of SS translates to the fact that low hydrolysis can also promote high methane yield (Wang et al., 2021).

The estimation of the k value becomes a little challenging in the co-digestion mixtures due to the varying fractions of SS, OFMSW, TWAS and LB. Relative to TWAS alone and OFMSW alone, k value reduced in all co-digestion mixtures, suggesting a hydrolysis became slower due to multiple organic components needing more time for hydrolysis. Hydrolysis however occurred faster in the binary combinations (k = 0.12day^{-1} in 20SS:80TWAS and k=0.14day^{-1} in 40SS:60TWAS) compared to the corresponding ternary mixtures. Relative to LB alone, hydrolysis occurred faster in only one mixture with k = 0.12day^{-1} in 20%SS: 30%LB: 50%OFMSW and much slower in 20%SS: 50%LB: 30%OFMSW (k=0.04day^{-1}) and 20%SS: 70%LB: 10%OFMSW (k=0.04day^{-1}).

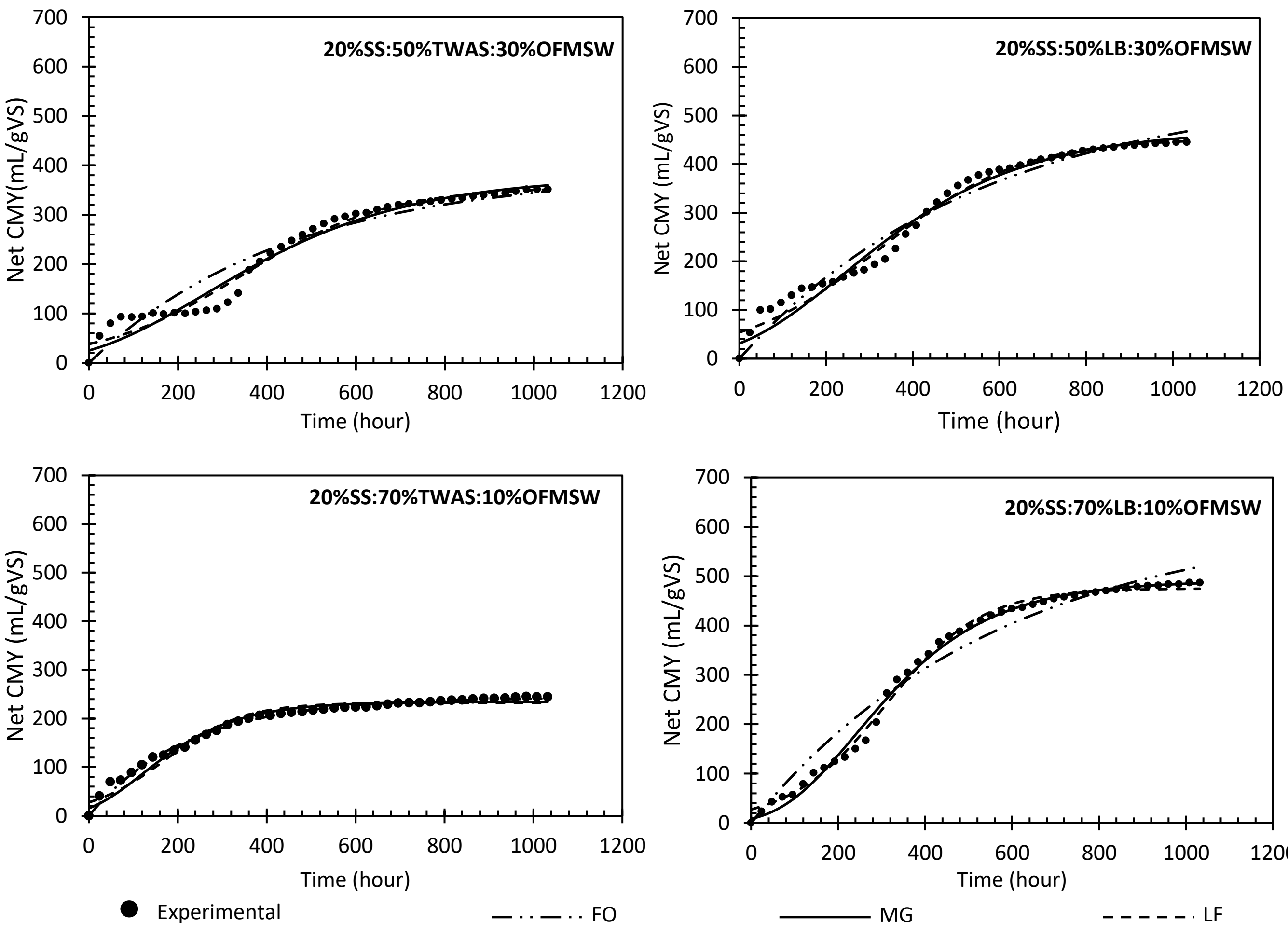

Figure 5-6c: Model graphs of the net cumulative methane yield from some co-digestion groups in this study.

Despite lower hydrolysis rate, the methane yield was the higher in both 20%SS: 70%LB: 10%OFMSW (486.7mLgVS^{-1}) and 20%SS: 50%LB: 30%OFMSW (445mLgVS^{-1}), thus suggesting that lower hydrolysis can as well lead to early methanogenesis. The result of the FO also shows that effect of SS addition to co-digestion mixtures could either cause a faster or slower hydrolysis rate, depending on the mixture. Similar to the effect of TWAS addition in the binary and tertiary mixtures, hydrolysis occurred faster in the k = 0.12 in 20SS:80TWAS and k=0.14 in 40SS:60TWAS when compared to SS alone. A faster rate was also observed in some tertiary mixtures and the fastest was in 20%SS: 30%LB: 50%OFMSW where k was 0.12day^{-1}.

The lag phase shows how long it took for the microbial population to modify and take advantage of the new environment. Generally, the LF model estimated longer lag phases than the MG model. As expected, λ values of 0.0 days meant methane production was started off quickly in TWAS, OFMSW and LB, perhaps because faster hydrolysis implied the VFA was immediately bio-accessible to methanogens. On the other hand, the SS experienced a delay (λ = 2.6days (MG); λ=3days (LF), further confirming that hydrolysis was slower in SS. Grosser (2018) reported a longer lag phase in GTS (λ = 7.01 days (MG) and λ = 8.27 (LF)), possibly due to the varying properties of FOG rich wastes. The question therefore arises as to if the addition of SS, TWAS or LB affected the lag phase in the co-digestion mixtures evaluated in this study. Amha et al. (2017) had concluded FOG addition could reduce lag phase when the authors applied non-linear regression to methane production in tertiary codigestion of PS: TWAS: FOG and reported λ = 1.93 - 4.92 days. When FW was added as a quaternary component, the study reported λ = 3.54 – 4.75days. In this study, since TWAS, LB and OFMSW had no lag phases, λ was reduced to 0 in most co-digestion mixtures following the addition of TWAS/OFMSW/LB, for instance (40%SS:60%TWAS, 20%SS: 50%TWAS: 30%OFMSW, 20%SS: 10%LB: 70%OFMSW) which shows the lag phase of SS can be reduced through co-digestion depending on the content of co-substrates. On the other hand, a significantly longer lag phase was detected in 40%SS: 50%TWAS: 10%OFMSW (λ= 12.2 days (MG) and λ = 12.3 (LF)). Therefore, in order to avoid longer lag phases, the co-substrate of FOG wastes must be carefully selected. Compared to when the individual substrates were digested alone, the addition of FOG to the individual substrates led to an increase in lag phase of the substrates in the various mixtures considered in this study, even though the methane yield improved. This is similar to the experience of Alqaralleh et al. (2016).

The Rm value (mL.gVS^{-1}.day^{-1}) indicates the rate at which methane and methanogenesis occurs in the reactor. Fairly similar values were estimated by both MG and LF models. In Table 5-5, SS had the highest value of 43.44 mL.gVS^{-1}.day^{-1} (MG) and 43.68 mL.gVS^{-1}.day^{-1} (LF). Despite the long lag phase, this result shows that methanogens consumed the organic acids in this reactor, leading to a faster methane production rate and a higher methane yield as well. Grosser (2018) reported lesser values of 28.2 (MG), 31.67 (LF) for a GTS sample. The Rm values for OFMSW (25.92 mL.gVS^{-1}.day^{-1} (MG), 24mL.gVS^{-1}.day^{-1} (LF)) and LB (23.52 mL.gVS^{-1}.day^{-1} (MG), 23.32 mL.gVS^{-1}.day^{-1} (LF)) were closely related and more than the rate reported in TWAS (18.24 mL.gVS^{-1}.day^{-1} (MG), 16.8 mL.gVS^{-1}.day^{-1} (LF)). For OFMSW, Grosser (2018) reported higher values of Rm (MG=34.16 mL.gVS^{-1}.day^{-1}, LF= 33.86 mL.gVS^{-1}.day^{-1}) than what was obtained in this study. The same study showed sewage sludge had higher values (MG=24.88 mL.gVS^{-1}.day^{-1}, LF= 26.88 mL.gVS^{-1}.day^{-1}) than the TWAS Rm values estimated by the models. In the co-digestion scenario, the addition of TWAS led to an increased methane rate in the binary mixtures as Rm of the mixture increased to 22.32 mL.gVS^{-1}.day^{-1} (MG), 20.88 mL.gVS^{-1}.day^{-1} (LF) in 20%SS:80TWAS and 35.76mL.gVS^{-1}.day^{-1}(MG), 33.36mL.gVS^{-1}.day^{-1} in 40%SS:60TWAS. This shows co-digestion with SS and TWAS can improve the methane production rate. When it comes to the tertiary mixtures, Rm value improved highest in 40%SS: 50%TWAS: 10%OFMSW with 28.56 mL.gVS^{-1}.day^{-1} (MG), 27.36 mL.gVS^{-1}.day^{-1} (LF), thus confirming the earlier position that the addition of SS and OFMSW to TWAS can help improve the methane production rate during co-digestion. Whereas, the Rm values were not positively impacted when TWAS was added to tertiary mixtures of 20%SS: TWAS: OFMSW. The situation was very different when LB was added to 20%SS: LB: OFMSW. Table 5-5 shows that 20%SS: 30%LB: 50%OFMSW had the highest Rm value of 30.96 mL.gVS^{-1}.day^{-1} (MG), 28.56 mL.gVS^{-1}.day^{-1} (LF). This confirms that leachate blending can improve methane production rates in co-digestion mixtures.

5.4.3.4 Energy generation

Since the aim of engaging in AD and ACo-D is renewable energy through biomethane production, average energy implication of the methane yield obtained from the various substrates and co-substrates were derived and presented in Figure 5-7.

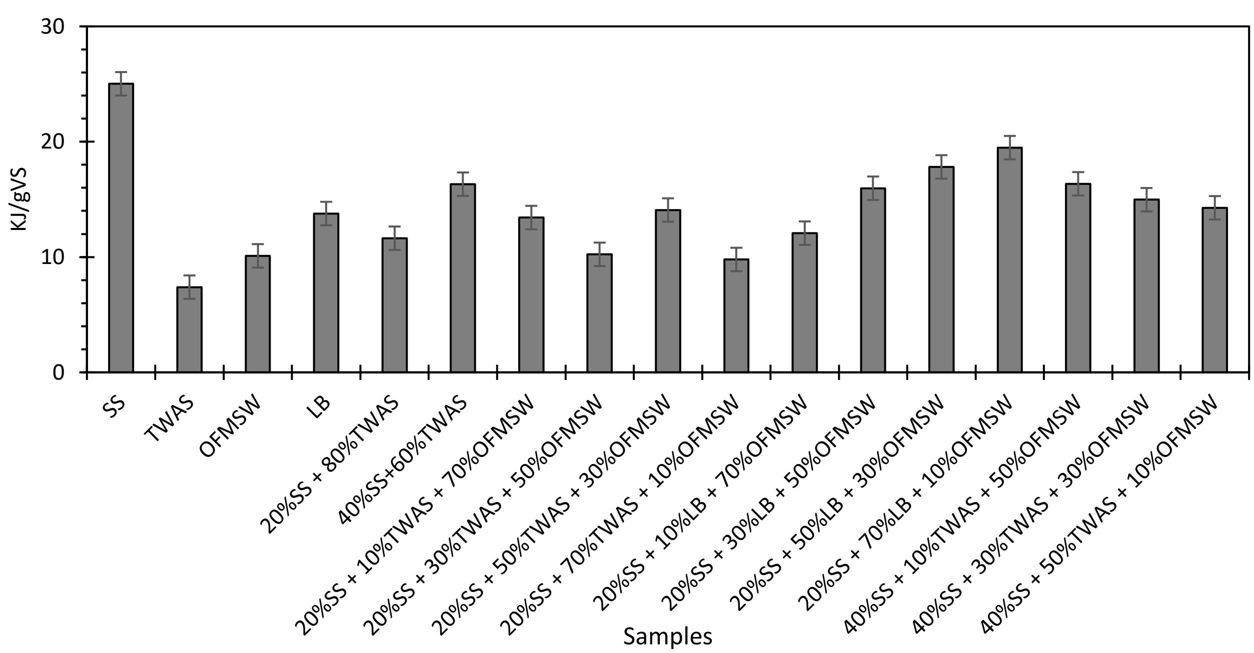

Figure 5-7: Energy generation from the methane yield obtained from the various samples.

A 5% standard error was applied in all cases. Figure 5-7 shows that the energy generation is consistent with the methane yield obtained from the various single digestion, binary and tertiary co-digestion. More importantly, the trend shows the energy is more improved in the co-digestion samples, compared to the single substrate digestion. For instance, the treatment of TWAS alone produced 7.4KJ/gVS while 20%SS:50%TWAS:30%OFMSW produced 14.1KJ/gVS, which translates to a 91% increase in energy generation. When it comes to the use of LB as a tertiary co-substrate, an increase of 36% in energy was achieved in 20%SS:70%LB:10%OFMSW over LB alone. The above scenarios emphasized the positive effect of co-digestion. Enhanced renewable energy generation reduces greenhouse gas emission. Consequently, existing WWTPs can consider the co-digestion of SS and OFMSW with TWAS to improve biomethane production and ultimately energy production. Likewise, bioreactor landfills can consider the addition of SS and leachate blending to the already present OFMSW, to enhance biomethane production and improve renewable energy supply.

5.5 Conclusion

This BMP study investigated the feasibility of trinary co-digestion of TWAS, OFMSW and sewage scum for use in a sewage treatment. This alternative scenario was also compared to the use of LB during trinary co-digestion of SS and OFMSW for use in bioreactor landfill. The conclusions are as follows:

- Compared to TWAS alone, biomethane yield and energy production was enhanced through co-digestion of TWAS with SS and OFMSW due to the benefit of co-digestion and positive synergism without operational difficulties. A mixing ratio of 40%SS:10%TWAS:50%OFMSW proved to be the best performing mixture.

- Biomethane and energy production from the trinary co-digestion of SS, LB and OFMSW enhanced energy production over the treatment of LB alone without operational issues. 20%SS:70%LB:10%OFMSW performed best in all the possible ratios investigated.
- The use of LB in a trinary mixture of SS and OFMSW led to a higher biomethane recovery over the use of TWAS in a similar trinary mixture. Also, methane concentration was also higher in the LB group.
- The application of the MG and LF kinetic models to the methane data indicated that the addition of TWAS or LB to their corresponding tertiary mixtures containing SS and OFMSW helped increase methane production rate.
- The application of the FO model showed that a slow hydrolysis rate resulted into a quick methanogenesis in SS, 20%SS:70%LB:10%OFMSW and 20%SS:50%LB:30%OFMSW. Also, the presence of SS in trinary co-digestion mixtures affects the hydrolytic rate.
- %VSR removal did not lead to increased methane production rate during the trinary co-digestion using TWAS or LB.
- Co-digestion improved the biodegradability of the mixtures over the single substrate digestion leading to improved methane yield.

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Chapter 6 - Synthesis, Integration and General Discussion of the Research Results

Biogas production during anaerobic biocenosis is a cost-effective and sustainable process for renewable energy generation. This process occurs in nature, anaerobic bioreactor landfill and anaerobic digesters. However, this process is often encumbered by toxicants, inhibitors and some environmental conditions in bioreactors and digesters, leading to poor biogas yield.

To promote an improvement in biogas production during organic waste treatment, leachate blending, and anaerobic co-digestion were utilized as strategies in three phases of laboratory experiments. Previous studies had established the fact that leachate blending (i.e., combining old and new landfill leachate together) could improve biogas production due to the properties of old leachate such as stabilized methanogenic consortia, high pH and high buffering capacity. It has also been reported that co-digestion improves biogas production due to dilution of toxicants and synergistic effects among other benefits.

Therefore, the first experimental phase answered the question of how leachate blending recirculation and mode of recirculation in anaerobic bioreactor landfills treating OFMSW in continuous mode could help boost biogas production. In the second phase, the question of how the co-digestion of sewage scum with either organic fraction of municipal solid waste or landfill leachate could help boost biogas production was investigated. Sewage scum was introduced as a co-substate during anaerobic co-digestion because it has a huge biogas potential and remains an untapped source till date. The third phase compared two alternatives and answered the question of whether the co-digestion of sewage scum and OFMSW performed best when either landfill leachate blend or thickened waste activated sludge is used a tertiary component. Major results from the phases are as follows:

6.1 Phase - Continuous Simulated Bioreactor Experiment

6.1.1 Recirculation of blended leachate to improve biogas production from organic fraction of municipal solid waste

This phase addressed the following issues:

1. How the recirculation of different leachate blends affects production of biogas.
2. How the recirculation mode (open vs. closed) affects biogas production.
3. The effect of recirculation of different leachate blends in addressing ensiling and lag phase.

In this phase, leachate blends (67%New:33%Old (2N1O), 33%New:67%Old (1N2O)) as well as 100%New (0N3O), and 100%Old(0N3O) were recirculated through laboratory scale bioreactors containing OFMSW. To investigate how the recirculation modes affects biogas production, 2N1O and 1N2O were operated as either open or closed loop. i.e 2N1O-OP, 2N1O-CL, 1N2O-OP, 1N2O-CL. Whereas 3N0O was operated as closed (3N0O-CL), 0N3O was operated as open (0N30-OP). A total of six bioreactors were used. The results showed that compared to the control reactor (100% New leachate, closed loop), biogas improved in the reactor recirculating a leachate blend of 33%New:67%Old. Furthermore, comparison of the results from open-loop and closed-loop operated bioreactors indicated that there was more biogas in open loop bioreactors due the occasional supplementation of the old leachate into the reactors. The model results show that Gompertz model produced a better fit than the first-order and Logistic Function models and leachate blending reduced the lag phase by almost half, thus help alleviating the ensiling during the start-up phase. The results are timely because most bioreactors can improve biogas generation by adopting the practice of recirculating blended leachate.

6.2. Phase II- Batch Experiment

6.2.1 Biogas production from co-digestion of sewage scum with OFMSW and leachate

Phase I had established the fact that recirculation of blended leachate could enhance biogas production and 67%old leachate;33%new (1N2O) had proven to be the best blend combination. Therefore, in this phase, the possibility of co-digesting the blend with other complimentary organic substrates to improve biogas generation was explored in anaerobic system. Among other possible substrates such as leachate and OFMSW, sewage scum was also tested. The reason is because sewage scum is a high strength FOG waste with a huge biogas potential and could serve as a useful co-substrate to enhance the co-digestion process.

This phase addressed the following issues:

1. How the co-digestion of sewage scum and OFMSW affect biogas generation.
2. How the co-digestion of sewage scum and landfill leachate (young, old or blend) affect biogas production.
3. The effect of co-digestion on the biodegradability of the overall mixture.

During this mesophilic batch BMP experiment, 10%, 20% and 40% (VS) of sewage scum (volatile solids basis) were added to each of OFMSW, old leachate, new leachate and a leachate blend (67%old leachate and 33%new). In the single substrate digestion, the blend was the best performed in terms of biogas production while the sewage scum was severely inhibited due to LCFA accumulation. In the co-digestion group, the addition of 40% sewage scum improved the biogas production the highest compared to the 20% and 10% additions (VS basis). The co-digestion results also showed that there was positive synergism as the addition of 40% sewage scum to each of the co-substrates improved net cumulative bio-methane yield when compared to their respective mono-substrate digestion bio-methane yield. Quite noticeable was the fact that the reactors containing leachate blends consistently produced more biogas over other sets due to the effect of blending. The addition of sewage scum to the substrates showed that there was an improvement in the biodegradability of the mixtures which subsequently led to the improvement in biogas production. The results of kinetic modelling which was applied to the bio-methane production data proofed that modified Gompertz equation achieved a better fit compared to the logistic function. Also, co-digestion substantially reduced the lag time encountered during mono-digestion. Some of the weaknesses of this phase was the low inoculum to substrate ratio used in the reactors.

6.3 Phase III- Batch Experiment

6.3.1 Enhancing biomethane production through trinary co-digestion of sewage scum and municipal solid waste with thickened waste activated sludge and leachate blend addition

The results of phase II had established the fact that leachate blending can improve biomethane production even when co-digested with sewage scum. Also, the co-digestion of sewage scum with OFMSW was recognized as a potential method for improved methane production. Therefore, in this phase, the possibility of trinary co-digestion was further explored in order to investigate other ways digesters and bioreactors can further improve biogas production. Two possible scenarios were identified and compared i.e., a sewage treatment plants treating thickened waste activated sludge (TWAS), OFMSW and sewage scum versus a bioreactor landfill treating OFMSW, leachate blend and sewage scum. Since the 20% and 40% (VS) additions of sewage scum performed best in phase II, they were selected for this phase. Besides, less quantity of sewage scum is produced compared to the other substrates. Also, the blend combination of

1N2O (33%New; 67%Old) was considered here based on previous tests which showed it was the best performing combination. This phase consequently addresses the following issues:

1. How the co-digestion of sewage scum, OFMSW and TWAS affects biogas production.
2. How the co-digestion of sewage scum, OFMSW and leachate blend affects biogas production.
3. Are there any benefits in using TWAS or leachate blend as a tertiary co-substrate?

The results indicated that biomethane yield can be generally enhanced in trinary mixtures over the mono-digestion of the individual substrates except sewage scum. Specifically, the biomethane yield from the co-digestion of both 20% and 40% sewage scum (VS) addition to TWAS enhanced biogas production over the mono-substrate digestion of TWAS alone. The results also show that leachate blending was a factor in the process as there was an enhanced biogas production in trinary mixtures of leachate blends over similar trinary mixtures involving TWAS. Therefore, leachate blend is more beneficial for use as a tertiary co-substrate. Interestingly, the content of the mixtures did not directly affect volatile solids destruction in the reactors as there were instances where improved biogas production did not show a significant impact on the VS loss recorded. The trend of the biomethane production in the co-digestion mixtures showed a diauxic pattern suggested to be as a result of the adaptation of the microbes to the presence of multiple substrates. Overall, the results showed that a trinary co-digestion can be a beneficial method to improve biogas production in existing facilities without the need for additional expenditures. The application of kinetic models also showed that lower hydrolysis rates in some of the co-digestion reactors promoted faster methanogenesis in the reactors.

Chapter 7- Overall Conclusions and Recommendations

7.1 Conclusions

The results of the various experiments have shown that leachate blending and co-digestion through the addition of sewage scum are useful strategies that can be used to improve process efficiency, enhance biogas production as well as the methane concentration in anaerobic systems. The application of these strategies will vary and depend on the system under consideration. The main conclusions are follows:

i. Continuous recirculation of blends of new and old leachate in the proportion of 33%New and 67%old (1 new leachate part and 2 old leachate part) can improve biogas production between 77 and 193% over the recirculation of only young leachate or only old leachate when OFMSW is treated.

ii. Operating a real-life bioreactor as an open loop with occasional old leachate supplementation has the greatest benefits in terms of biogas production and alleviating ensiling compared with operating as a closed loop i.e., with no old leachate supplementation. From the results, up to 28 and 65% more biogas can be collected if the open loop strategy is adopted eventually.

iii. Another way to improve the biogas production in digesters is through the addition of sewage scum to the substrate. This can be done either in binary or trinary mixtures. In the binary, the addition of sewage scum to the different substrates (OFMSW, NL, OL and LB) showed that methane production improved over the mono-substrate digestion.

iv. In both binary and trinary co-digestion scenarios, leachate blending was observed to have played a major role in improving the net biogas production due to positive synergism and high methanogenic population present in old leachate.

v. When it comes to co-digesting OFMSW and sewage scum, leachate blend proved to be a better tertiary component over TWAS because biogas production improved by 38% when leachate blend is used co-substrate.

vi. Wastewater treatment plants can improve biomethane generation by 32 - 122% if TWAS is treated with sewage scum and OFMSW instead of treating TWAS alone. Also, bioreactors recirculating leachate blend can improve biomethane collection if they accept sewage scum to co-treat with OFMSW by 41% instead of treating leachate alone.

vii. Low biogas production was observed during the mono-substrate digestion of sewage scum in the second study possibly due to insufficient microbial load causing inhibition and poor biodegradability. Improving the amount of inoculum in the trinary scenario later showed to be a better option. However, overloading may be counterproductive due to possible inhibition of the substrate.

viii. The modified Gompertz and Logistic Function kinetic models was generally useful and produced a good fit for the methane data obtained from both continuous column and batch experiments.

7.2 Recommendations

I. Further studies exploring the idea of co-disposal of sewage scum and OFMSW in bioreactors recirculating leachate blends can be conducted in order to assess the benefit of this practice.

II. Scale up binary and trinary co-digestion of sewage scum with the various co-substrates should be conducted at mesophilic temperatures. Furthermore, thermophilic, and hyper-thermophilic conditions can also be done to assess the effect and benefits therein.

III. Pre-treatment of substrates and co-digestion mixtures have been identified as other strategies to improve the recovery of biomethane. Therefore, various methods of pre-treatment can be applied to the various substrates and co-substrates to assess the benefit of various pre-treatment methods available in the literature.

IV. It is recommended that further studies be carried out on the estimation of synergistic effect under suboptimal conditions such as low inoculum content.

V. Microbial analysis can be conducted in all experiments to understand the how the microbial population and diversity affects the stability and performance of the various co-digestion experiments.

Appendix

The picture below shows the experimental setup of Phase I.

A picture of the experimental setup of Phase I