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Interdisciplinary Research Project

Individual Report

Is Lincolnshire road verge biomass a suitable feedstock for anaerobic digestion?

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Abstract

Roadside verge biomass cuttings represent an underutilised feedstock for the generation of renewable energy through anaerobic digestion (AD). Generating energy from these grass clippings could provide a source income for Lincolnshire County Council. The energy output, or biomethane potential of the grass must be greater than the energy input for the system to be economically feasible. Nine Lincolnshire roadside verge samples were studied alongside four current AD feedstocks; straw, grass silage, rye grass and maize. The average theoretical bio methane potential (BMP) for the verge samples was 148 mL CH_4/g VS, similar to that of the current feedstocks. The verge grasses also displayed suitable characteristics for use in AD; pH, C:N and solubility of organic matter in the process water following thermal hydrolysis pre-treatment. These promising theoretical BMPs and feedstock characteristics provides evidence for future study of the grass cuttings through laboratory-scale BMP experiments.

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Contents

Nomenclature

AD – Anaerobic digestion

AMPTS – Automatic methane potential test system

BMP – Bio methane potential

BMPthBo – Bio methane potential derived from the Boyle's equation

BMPthBu – Bio methane potential derived from the Buswell equation

C:N – Carbon:Nitrogen ratio

COD – Chemical oxygen demand

FC – Fixed carbon

H1 – Hydrolysis 1

H2 – Hydrolysis 2

M - Moisture

Rpm – Revolutions per minute

TH- Thermal hydrolysis

TOC – Total organic carbon

TVS – Total volatile solids

VFA – Volatile fatty acid

VM – Volatile matter

VS – Volatile solids

1 Introduction

Growing socioeconomic and environmental pressures have reiterated significance of developing technologies for the generation of energy from sustainable sources (Luque et al., 2008). Following the 2009 Renewable Energy Directive, the UK has been set a target of 15% of total energy consumed to be generated from sustainable sources by 2020 (DECC). Alongside this the UK's Climate Change Act (Parliament, 2008) provides a UK target to reduce greenhouse gas emissions to 80% of the levels released in 1990 by 2050. Subsequent to these targets, there is becoming increasing interest in the development of technologies and strategies for renewable energy generation across the UK. A current area of interest is the utilisation of bioenergy, particularly from feedstocks with high lignocellulosic compositions (Rowe et al., 2009) which do not compete for land with arable crops. Such crops can produce biogas through anaerobic digestion. Biogas is a versatile product which can generate heat, electricity, or be used as a transport fuel; following processing. Currently, the UK Government offers incentives to anaerobic digestion plants. These incentives include; feed-in tariffs (FITs) and the renewable heat incentive (RHI). FITs are in place for sites which produce electricity greater than 5 MW_e of renewable electricity and RHI sites producing heat from biomass combustion (<200 kW_{th}) or through injection of biomethane into the national grid (POST, 2011). A combination of Government incentives and increasing demand for renewable energy gives scope for anaerobic digestion technologies to develop and succeed.

The UK county of Lincolnshire encompasses a large road network; 6,173km of which can be defined as 'rural' (Cheffins, 2015). Grass verges run parallel alongside these roads. The verges are annually cut by the council to comply with the Local Highways Authority. Maintaining the grass prevents overgrowth becoming a dangerous obstruction for pedestrians and drivers, especially around road junctions. Lincolnshire County Council currently cut 1.1m visibility strips along the verges using a flail mower. Across Europe, common practice for roadside verge maintenance is to leave the grass cuttings *in situ*; which undergoes a mulching process (Piepenschneider et al., 2016). These grass cuttings represent an underutilised potential feedstock for the generation of biogas through anaerobic digestion (Meyer et al., 2014). Through bioenergy generation from a waste material, Lincolnshire County Council could provide a source of income to contribute to balancing the cost of the roadside maintenance budget. However, collection and processing of the grass has to be both economically and environmentally viable. A significant factor for the economic feasibility of collecting grass for energy generation is the energy output; or bio methane potential that can be attained from the grass. Hence, roadside verge grass must produce competitive levels of bio methane to justify the substitution of current anaerobic digestion feedstocks, with verge grass. Grass clippings from public spaces as a feedstock is becoming an ever more common occurrence (Cadavid-Rodríguez and Bolaños-Valencia, 2016, Hidaka et al., 2013). This includes use of roadside verge grass (Meyer et al., 2014, Meyer et al., 2016, Piepenschneider et al., 2016, Salter et al., 2007), each of which indicate an economically feasible system of producing renewable energy from biogas. These promising conclusions suggest the utilisation of road verge biomass may also be feasible across Lincolnshire.

Collecting the road verge clippings can also impact the biodiversity of local flora and fauna species. Cutting and removing grass clippings can increase plant biodiversity (Parr and Way, 1988) as there is reduced smothering of plant seedlings from the cuttings. Road verges can be classified as an ecosystem, therefore increased plant biodiversity will encourage diversification of animal species; including important ecosystem engineers. Hanley and Wilkins (2015) reported twice the abundance of bumblebees along road verges compared to adjacent agricultural-land. Road verges have the potential to act as transportation corridors to connect fragmented areas of habitat (Marcantonio et al., 2013). This could increase biodiversity across a larger area; beyond the expanse of Lincolnshire.

1.1 Aims

This particular study aims to calculate the bio methane potential (BMP) of grass samples cut from the Lincolnshire area. From these results, an experimental protocol to validate BMP through laboratory-scale digesters is developed. The characteristic suitability of the grasses for use in digestion were also assessed. This includes; pH, carbon to nitrogen ratio (C:N) and solubility of organic matter in the process water following pre-treatment. All of the parameters studied assess the feasibility of substituting current anaerobic feedstocks with verge grass, with the aim of maximising potential biogas production; therefore profitability of the system.

2 Literature Review

2.1 Anaerobic Digestion Process

Anaerobic digestion (AD) is the degradation of biomass through a consortium of microorganisms in the absence of oxygen, resulting in the production of biogas (Ward et al., 2008). The microbial population within an anaerobic digester is diverse and complex, (Yu and Schanbacher, 2010) containing a multitude of bacteria, *Archaea*, fungi and protozoa species. The sequential pathways of microbial metabolic activity can be split into four stages of AD, displayed in Figure 2.1.1: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Vavilin et al., 2008)

Each stage of anaerobic digestion is associated with the colonisation of a specific range of microorganisms. Hydrolysis is the initial step of AD, involving the degradation of complex organic polymers; such as carbohydrates, proteins and lipids, into their constituent monomers or oligomers; monomeric sugars, amino acids and fatty acids, respectively (Rafieenia et al., 2016). Hydrolytic bacteria carry out hydrolysis of organic polymers through the release of extracellular enzymes (Yu and Schanbacher, 2010). These monomers then undergo a further degradation reaction, through acidogenic bacteria, producing a range of substrates (Bharathiraja et al., 2016); including acetate, a volatile fatty acid (VFA), alcohols and long chain fatty acids. Acetate can be immediately utilised in methanogenesis. The other substrates produced during acidogenesis are oxidised by acetogens to acetate, through intermediates such as hydrogen and carbon dioxide (Bharathiraja et al., 2016). The final stage of biogas production is methanogenesis, mediated through specialised *Archea* (O'Flaherty et al., 2006). Following the four microbial processes, biogas is the main product. However, nutrient rich process water and solid digestate are also produced, which can be applied as a natural fertiliser (Moller et al., 2009).

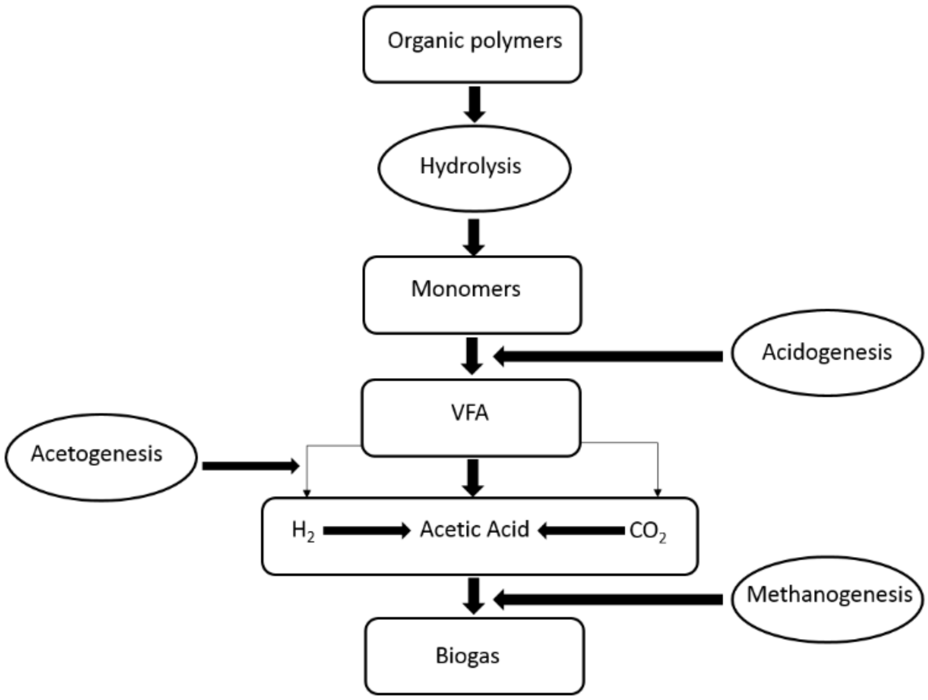


Figure 2.1.1: The process of biogas production from anaerobic digestion, adapted from Bharathiraja et al. (2016).

Formerly, AD technology was a method to stabilise waste materials, including sewage sludge. Currently, however there is growing interest in the use AD to produce biogas as a cost-effective source of energy (Lv et al., 2010). Weiland (2010) described biogas as a form of renewable energy, with the potential versatility for replacing fossil fuels in electricity and heat generation. Biogas can also be upgraded to biomethane, to be used as a transport fuel. Alongside this, biogas production has been described as one of the most energy-efficient forms of energy generation from biomass (Hublin et al., 2014).

Anaerobic digestion occurs across different reactor designs throughout industry and is closely linked to the type of feedstock digested. Anaerobic digestion can be broadly grouped into two temperature ranges; mesophilic 25°C – 40°C (Pullen, 2015) and thermophilic, around 55°C (De la Rubia et al., 2002). AD reactors designs can also be classified as one-stage or two-stage digesters. One-stage digestion is a more traditional design, where all digestion processes (Figure 2.1.1) occur simultaneously in one unit. A two-stage digestion is comprised of two units; one unit contains the hydrolysis process. Following hydrolysis, the contents are transferred to the second unit for continuation of digestion. Two-stage digesters are generally considered to be more efficient in the production of biogas. (Schievano et al., 2014).

2.2 Biogas Composition and Uses

Raw biogas is comprised mainly of a combination of methane and carbon dioxide (Leung and Wang, 2016), with traces of other gases, as shown in Table 2.2.1.

Table 2.2.1: Typical raw biogas composition from anaerobic digestion of organic matter. Table adapted from (Bedoya et al., 2013).

Gas	Chemical Formula	Compositional range of raw biogas (%)
Methane	CH_4	50-70
Carbon Dioxide	CO_2	25-50
Hydrogen	H_2	1-5
Nitrogen	N_2	0.3-3
Hydrogen sulphide	H_2S	Trace

The methane concentration of the biogas is crucial, as methane is associated with the economic value of the fuel produced (Khanal, 2008). Carbon dioxide represents a large proportion of the raw biogas, yet, is inert in combustion; reducing the calorific value of the fuel (Tippayawong and Thanompongchart, 2010). Biogas can be upgraded to biomethane to improve its quality as a fuel. Upgrading involves removing un-necessary components; such as CO_2, to improve the gas calorific value (Sun et al., 2015). The upgrading of biogas to a higher standard of fuel allows capacity for direct injection into the national grid, or use as a transport vehicle fuel (Weiland, 2010). Biogas composition is influenced by the type of feedstock used during AD, as shown in Table 2.2.2.

Table 2.2.2: The biogas yields and proportional methane content of various agricultural feedstocks in AD, adapted from Weiland (2010).

Crop	Biogas yield (Nm^3/t VS)	Methane Content of biogas (%)
Grass	530-600	54
Maize	560-650	52
Rye grain	560-780	53
Wheat	650-700	54
Red clover	530-620	56

2.3 The Bio Methane Potential (BMP) of Grasses

Bio methane potential (BMP) is the theoretical calculation of methane yield from a feedstock. The calculations are quick, inexpensive and invaluable (Nallathambi Gunaseelan, 1997) in determining the suitability of a feedstock for biogas production (Browne et al., 2013). Quantifying the BMP is a crucial parameter in implementing a large scale AD system (Angelidaki et al., 2009); influential to economic and management decisions to maximise bio methane yields (Nizami et al., 2012).

BMP of a feedstock can be derived stoichiometrically from the elemental composition (Raposo et al., 2011, Smith and Ross, 2016) or through laboratory-scale digesters (Salter et al., 2007). The results of BMP can be extrapolated to give an energy output value, which can be applied to models which assess the feasibility of using a specific feedstocks (Meyer et al., 2014, Salter et al., 2007, Smyth et al., 2009). The literature presents a wide range of predictions for BMP of grasses (Tables 2.3.1 and 2.3.2). This range of BMP values reflects the variability of experimental methodology and the structural composition of grass. BMP figures are often expressed as volume of methane per mass of volatile solids, due to the considerable variability of moisture contents across biomass feedstocks (Kenney et al., 2013).

Assessing the feasibility of roadside grass for use as a feedstock is a concept, only recently being explored. As a result of this there are few results presented in the literature (Table 2.3.1) to BMP predictions of grasses based on elemental stoichiometrical analysis.

Table 2.3.1: Theoretical methane yield of grasses, based on applied stoichiometrical equations following elemental analysis.

Sample of grass	Theoretical methane yield (mL CH_4/g VS)	Reference
Roadside grass	490	(Meyer et al., 2014)
Switchgrass	448	(Li et al., 2013)
Grass silage	443	(Wall et al., 2013)

Prediction of BMP through elemental analysis can be viewed as the maximum potential methane yield (Browne et al., 2013). BMP determination through this method is advantageous as it is quick compared to other BMP tests (Lesteur et al., 2010). Biodegradability of feedstocks during AD is not accounted for in the elemental BMP equations (Nizami et al., 2012), consequently assuming complete degradation. Theoretical methane potentials based on these yields are often an over-estimation of practical methane yields. A higher degradation rate is linked to higher methane yield (Liu et al., 2015) as a larger percentage of particles are solubilised in the AD liquid phase, increasing the efficiency of microbial metabolism (Khanal, 2008). The biodegradability during AD is variable across feedstocks; the practical methane yield of grass represent a range between 45-80% of theoretical yield (Meyer et al., 2014), though biodegradability has been shown to be as low as 24% for switchgrass (Labatut et al., 2011). Biodegradability of a feedstock in AD is a complex parameter to predict as it is dependent on the physiochemical composition of the feedstock, in combination with the conditions of the AD unit. Subsequently, identifying BMP of grasses through laboratory-scale digesters is more common across the literature (Table 2.3.2); which autonomously encompass the degree of biodegradability.

Table 2.3.2: Methane yields of grass samples following laboratory scale-digestion.

Sample of grass	Methane potential ($mL\ CH_4$/ g VS)	Reference
Roadside grass	270	(Salter et al., 2007)
Grass from public space	327	(Cadavid-Rodríguez and Bolaños-Valencia, 2016)
Fresh grasses	310-360	(Mahnert et al., 2005)
Grass silage	350-493	(Nizami et al., 2012)

The BMP results for grasses obtained through laboratory digesters (Table 2.3.2) are displayed across a wider range than the range of stoichiometrical BMP predictions (Table 2.3.1). The range of BMP predictions can be associated with variability of the biomass. However, the predictions of BMP using a laboratory-scale digester are difficult to compare, due to the variability of parameters within the methodologies. Parameters, including; temperature, pH, ratio of inoculum to feedstock, source of inoculum, pressure and time of digestion can differ between experimental protocols. As a result of these varying parameters, BMP values are difficult to compare across the literature (Nizami et al., 2012). The variability of protocols highlights the requirement for a standardised BMP protocol (Triolo et al., 2011).

There are many types of digester reactor. Figure 2.3.1 displays a number of reactors for the AD of grass silage. The variability of AD reactor type reiterates the issue of comparing BMP results.

Cadavid-Rodríguez and Bolaños-Valencia (2016) incubated the samples at 37°C for 60 days with a substrate concentration of 2g VS/L in closed one-stage digestion system. Mahnert et al. (2005) also used a one-stage digestion system, but at different temperature conditions; 35°C, a shorter incubation period of 28 days and a loading rate of 1.5 kg of inoculum to 0.05 kg of fresh grass. Again, this reiterates the complexity of comparing BMP results from experimental digesters. Nizami et al. (2012) calculated the BMP of grass silage through a range of laboratory digesters (Figure 2.3.1) to indicate the variability of BMP tests. Methane yields varied by 143 mL CH_4/ g VS across the various BMP tests. The large BMP apparatus displayed in Figure 2.3.1 showed a methane potential of 483-493 mL CH_4/ g VS and the small SMP apparatus a methane yield of 355-419 mL CH_4/ g VS.

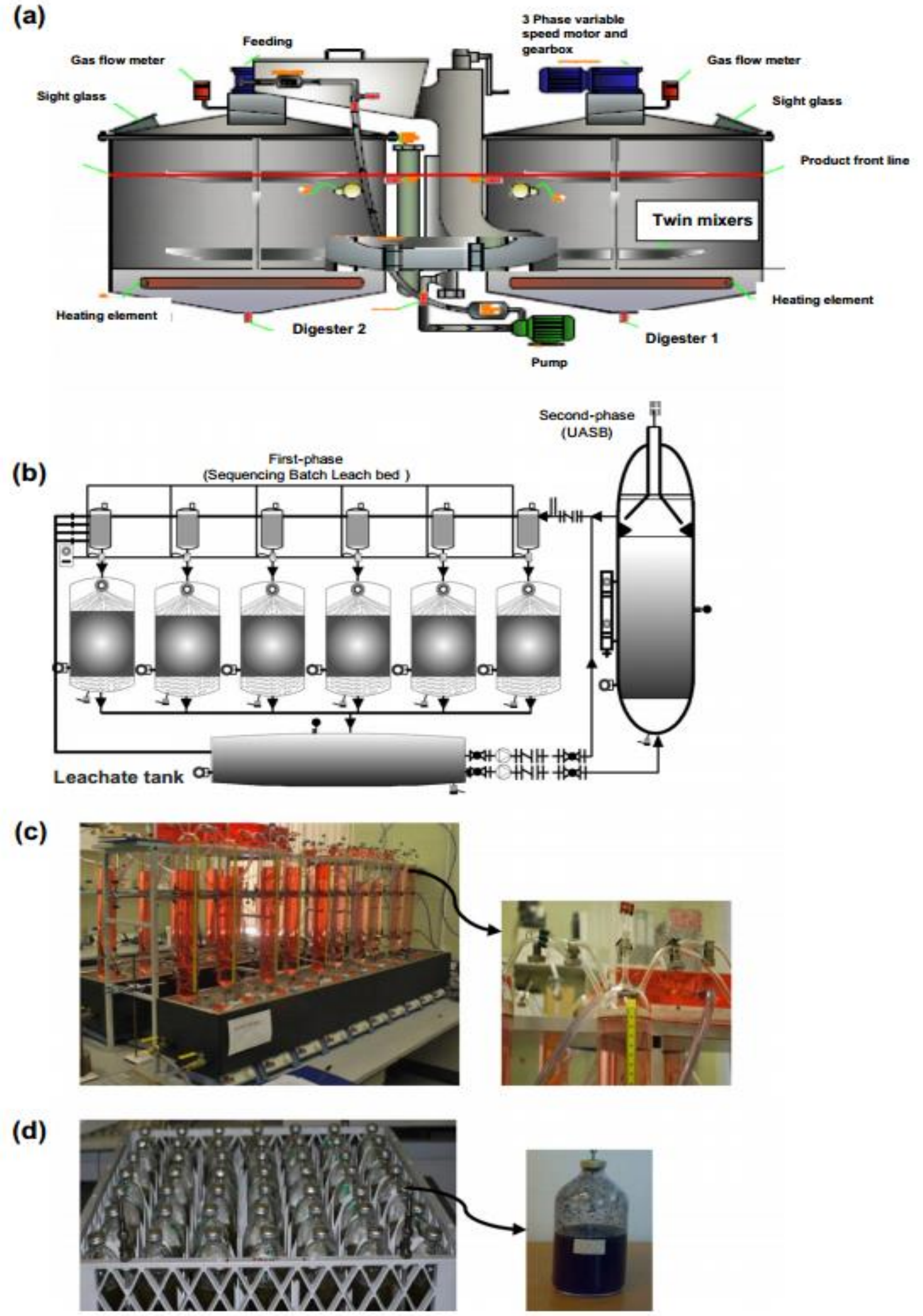


Figure 2.3.1: taken from Nizami et al. (2012). Various grass digestion systems including; (a) 2-stage continuously stirred tank reactor, (b) sequencing batch leach bed with up flow anaerobic sludge blanket reactor, (c) large BMP digester apparatus, (d) small BMP digester apparatus. Nizami et al. (2012) compared the BMP of grass silage using the reactors shown, as well as others.

2.4 Effect of Grass Structural Composition on Anaerobic Digestion

The use of grasses as an AD feedstock is of growing interest across many European countries, mainly due to the large quantity of grass available. With 91% of agricultural land in Ireland covered in grassland (Smyth et al., 2011). Digesting grass for the production of biogas; a bioenergy source is able to relieve pressure of arable land to produce energy crops (Murphy and Power, 2009). Lignocellulosic biomass has recently gained particular interest as a feedstock; as the sources of this biomass do not directly compete with the food or feed industries; which is previously associated with conventional energy crops (Sawatdeenarunat et al., 2015).

2.4.1 Composition of Grass

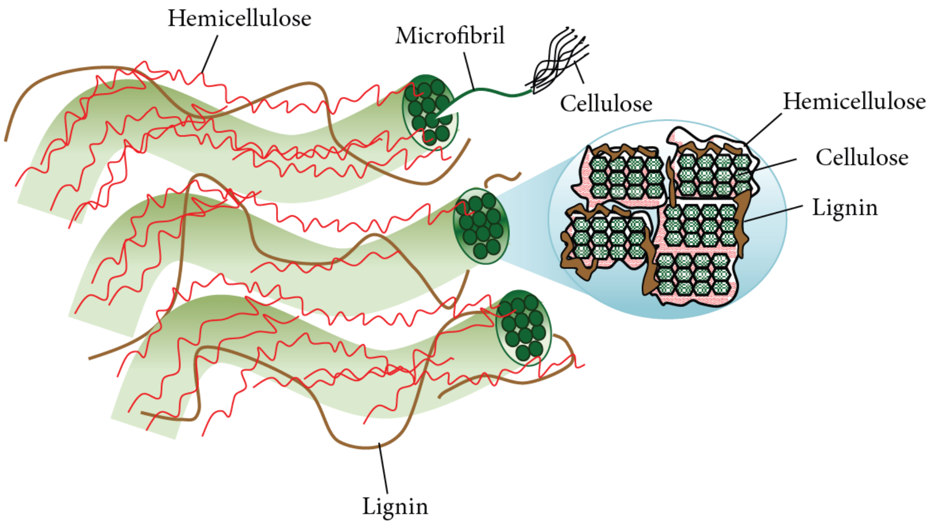
Lignocellulosic biomass is a complex structure, largely comprised of cellulose, hemicellulose and lignin (Sawatdeenarunat et al., 2015) each of these complex polymers interacts to provide structural rigidity to the feedstock. Table 2.4.1 displays the typical lignocellulosic composition of grass.

Table 2.4.1: The typical lignocellulosic composition of grass, adapted from Nizami et al. (2009).

Lignocellulose Polymer	Composition (%)
Cellulose	25-40
Hemicellulose	15-50
Lignin	10-30

Cellulose is a polymer of glucose units, linked by a β(1-4) glycosidic bond comprising a crystalline structure, highly resistant to enzymatic hydrolysis (Ioelovich and Morag, 2011). Hemicellulose is a constituent of plant secondary cell walls; it is a heterogeneous polymer comprised of hexoses, pentoses and in some cases urgonic acids. Hemicellulose interacts with cellulose, covering the cellulose polymers, effectively shielding it from enzymatic degradation (Mood et al., 2013). Lignin is a cross-linked phenolic polymer which provides mechanical support to plant cell walls as well as hydrophobicity properties (Sawatdeenarunat et al., 2015). Lignin also binds cellulose, further encapsulating cellulose, increasing the resistance to degradation (Isikgor and Becer, 2015). The structure of lignocellulose is depicted in Figure 2.4.1.

Figure 2.4.1: The structure of lignocellulose, taken from Lee et al. (2014)



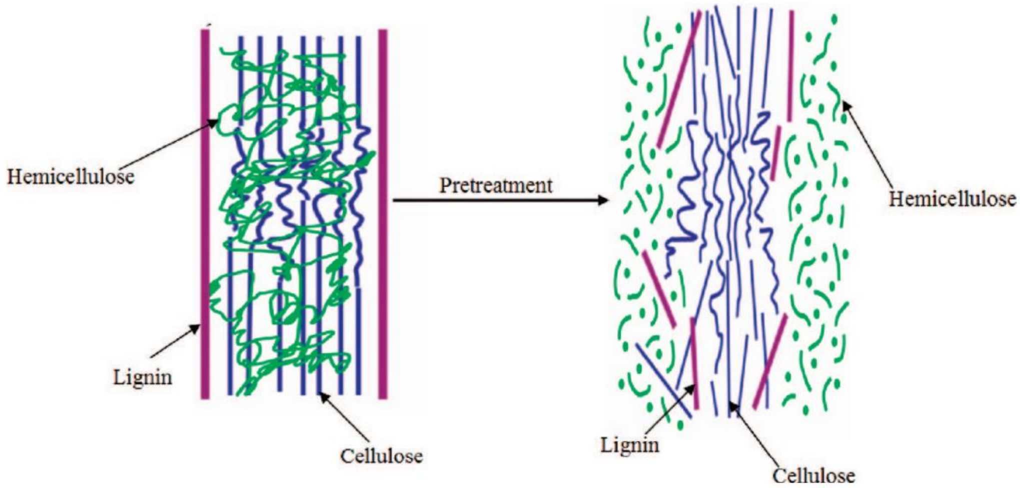
The lignocellulosic composition of grasses not only varies between species, but within species. The degree of maturity of grasses during harvesting may have an impact on the potential methane yield (Piepenschneider et al., 2016). High maturity of grasses often results in reduced methane yield (Surendra and Khanal, 2015), due an increase in the lignocellulosic fibre concentrations in the cell wall of the plant.

2.4.2 Hydrolysis of Lignocellulosic Biomass

The initial degradation, or hydrolysis of a lignocellulosic feedstock is described as rate limiting step of AD (Ariunbaatar et al., 2014, Fu et al., 2015). Efficient hydrolysis solubilises particulate matter, increasing substrate availability for microbial utilisation; increasing biogas yields (Carlsson et al., 2012). A slow hydrolysis rate is financially costly, as the retention time of the feedstock within the AD unit increases; with resulting implications on biogas yield. The complex physiochemical structure of lignocellulosic has potential to reduce hydrolysis rates in AD through a range of characteristics: cellulose structure, lignin content, moisture content and the surface area of the biomass particle (Hendriks and Zeeman, 2009). A significant factor in the initial breakdown of lignocellulosic biomass is the lignin content (De Moor et al., 2013, Klimiuk et al., 2010), which binds to cellulose microfibrils; reducing access to microbial degradation (Xie et al., 2011).

Attempts to increase hydrolysis rates have been developed through a range of pre-treatment methods. The aim of pre-treatments is to alter the physical and chemical structure of lignocellulosic biomass, allowing hydrolysis to occur at an increased rate (Kumar et al., 2009), as depicted in Figure 2.4.2. Pre-treatment methods can be broadly grouped into four sections; mechanical, thermal, chemical and biological (Ariunbaatar et al., 2014) each can be used individually or in combination with another treatment. Pre-treatment of biomass feedstock could become standard practice across the industry; with recent emphasis towards maximising all bioenergy potential from all of the available feedstock (Khanal, 2008).

Figure 2.4.2: The effect of pre-treatment on cellulose, hemicellulose and lignin, taken from Kumar et al. (2009).



Thermophilic hydrolysis is the heating of feedstocks in an aqueous environment to release nutrients into the process water, increasing the efficiency of microbial degradation. This pre-treatment is implemented into the two-stage digesters as the initial stage. Orozco et al. (2013) found that pre-treating grass silage through thermophilic hydrolysis at 55 °C improved the biodegradability, therefore bio methane production by 30% compared to the non-treated grass silage. Thermophilic hydrolysis can be encompassed under a broader term of thermal hydrolysis. Thermal hydrolysis treatments increases the accessible surface area of cellulose for hydrolytic enzymatic action of AD microflora (Chandra et al., 2012). These treatments can reach temperatures of up to 210°C (López González et al., 2014). However, high temperature thermal hydrolysis treatments can be associated with a large energy input to maintain high temperatures (Yao et al., 2016). Thermal hydrolysis processes are often implemented to two-stage commercial AD units (Section 3.1).

Sufficient hydrolysis is required to increase the solubilisation of organic particulate matter; therefore the chemical oxygen demand (COD) in the process water (Nizami et al., 2009). The COD is an indirect measurement of the organic matter within a solution, measured by the amount of oxygen used to oxidise available organic matter. The BMP can be determined from the COD content leached into the process water. With Hamilton (2012) suggesting 1g COD removed ≈ 400mL CH_4 produced. This prediction of methane yield is not exact, as not all of the COD is organic matter is able to be digested by microbes and does not account for utilisation of COD for microbial growth (Lesteur et al., 2010), though it gives an indication on how a feedstock will perform in AD.

2.5 Co-Digestion

Co-digestion is the use of a combination of feedstocks within AD, which can have a positive impact on biomethane yield (Ward et al., 2008).

2.5.1 Carbon to Nitrogen Ratios

The use of a variety of feedstocks broadens the macronutrient profile available to the microbes; which includes, nitrogen (N) and phosphorus (P) (Li et al., 2016, Valdez-Vazquez et al., 2016) alongside carbon (C). These macronutrients are essential for maintaining the population of microorganisms, particularly by maintaining an optimum C:N ratio (Ward et al., 2008). Sustaining a thriving microbial population is influential to the stability of biogas production; crucial in maintaining system economics. An ideal C:N ratio for microbial proliferation is between 20-30:1 with 25:1 being the optimum ratio (Yan et al., 2015). Nizami et al. (2009) found the C:N ratio to be 24:1 in grass silage and (Xie et al., 2011) 26:1, also for grass silage, both close to the optimal. Lignocellulosic feedstock often have a high C:N; greater than 50:1 (Ge et al., 2016), which can reduce biogas yield, due to a deficiency of nitrogen (Hussain et al., 2015) required for microbial protein biosynthesis (Vintiloiu et al., 2012). As a result of this it is suggested that lignocellulosic feedstocks are often co-digested with other feedstocks.

A particularly low C:N ratio is also not desirable. Biological degradation of nitrogenous constituents of a feedstock, such as; proteins, nucleic acids and nitrogenous lipids results in the production of ammonia (Kayhanian, 1999) which is inhibitory to AD (Chen et al., 2008).

Liu and Sung (2002) suggested that total ammonia nitrogen has inhibitory effects on the methanogenic *Archea* fundamental to biogas production.

2.5.2 Feedstock Characteristics

Each feedstock has differing BMP levels across the literature (Table 2.5.1) as well as individual characteristics which may impact the AD process (Yu and Schanbacher, 2010) such as varying lignocellulosic composition shown in Table 2.5.2.

Table 2.5.1: Typical theoretical BMP values for feedstocks based on laboratory-scale digestions.

Biomass Feedstock	**Bio methane potential mL CH_4/g VS**	**Reference**
Grass	286-324	(Sawatdeenarunat et al., 2015)
Maize	291-338	(Sawatdeenarunat et al., 2015)
Straw	297	(Kaparaju et al., 2009)
Grass Silage	350-493	(Nizami et al., 2012)
Rye grass	300-320	(Salter et al., 2007)

Table 2.5.2: Typical lignocellulosic compositions of various agricultural feedstocks.

Feedstock	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**	**Reference**
Grasses	25-40	15-50	10-30	(Nizami et al., 2009)
Grass silage	39	26	9	(Raud et al., 2015)
Wheat straw	35-39	23-30	12-16	(Isikgor and Becer, 2015)
Rye grass	43	28	7	(Raud et al., 2015)
Maize [a]	36	26	19	(Schwietzke et al., 2009)

[a]lignocellulose composition in the maize stover.

Grassland biomass is a useful feedstock for AD, especially for small-scale farm AD sites across Europe. However, in order to guarantee a continuous supply of good quality grass a common practice is to ensile the grass after harvesting (Nizami et al., 2009). Ensiling creates lactic acid through the microbial fermentation of free sugars; in turn this lowers the pH of the feedstock, preventing growth of bacteria which may spoil the grass (McEniry et al., 2014).

2.5.3 Management of Co-digestion

Though co-digestion of grasses with other feedstocks can overcome some of the issues associated with mono-digestion, the process has to be carefully managed. This may involve including a source of trace elements and alkalinity (Thamsiriroj et al., 2012); especially with grass silage, which contains high levels of lactic acid (McEniry et al., 2014); inhibitory to acetogenesis. Hidaka et al. (2013) found methane yield reduced from 0.2 NL/g VS to 0.09 NL/g VS following co-digestion of grass from public spaces with sewage sludge, at a ratio of 10:1 respectively. Piepenschneider et al. (2015) suggested that grass has a lower methane yield due to a higher dry matter content, which can cause mechanical issues with the AD plant. This reiterates that many factors must be considered when selecting a feedstock for use in AD.

3. Methodology

3.1 Site Visit to Scrivelsby Farm

In November 2016, a site visit to Scrivelsby farm was carried out to gather information about the on-site AD unit. The site was used as a model to base experimental design for this project and future work. If the verge grass is suitable for digestion Scrivelsby farm will digest the grass cuttings in January 2017.

Scrivelsby farm, located in Horncastle, Lincolnshire, UK is a family owned, arable farm complete with an anaerobic digestion unit with four operational areas. The anaerobic digestion process begins with two separate thermal hydrolysis pre-treatment units (Figure 3.1.1). The first (H1) at 51°C, with a 22-hour holding cycle and the second (H2) at 53°C; following each holding cycle 50% of the content of H1 is transferred to H2. The loading rate is 22 tonnes of feedstock in volume of 137m^3 liquid phase.

Figure 3.1.1: Scrivelsby farm hydrolysis 1 (H1) and hydrolysis 2 (H2) units.

The main AD unit, is maintained at 45°C with a 35-day retention time. The final unit is a storage unit, here the digestate is passed through a screw press; the liquid phase is recirculated back to H1 and the solid digestate is extracted.

Scrivelsby AD unit co-digests agricultural residues (Figure 3.1.2). It is important to note that laboratory experiments were carried out using fresh road verge clippings, should they be deemed suitable for AD Scrivelsby farm will ensile the grass to prolong storage retention time.

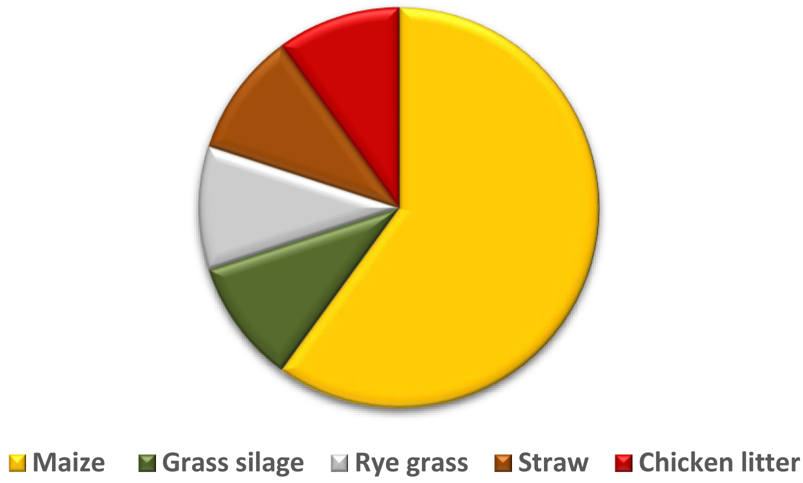


Figure 3.1.2: The proportions agricultural residue feedstocks used in AD by Scrivelsby farm.

3.2. Collection of Samples

Representative samples of roadside verge grass were collected in May 2016 by Lincolnshire County Council. Each was labelled with the specific sample site number S_n corresponding to the location it was collected across Lincolnshire county; for example, S1 was collected from ‘site 1’. Figure 3.2 shows the site locations the road verge grass was collected. The samples were also given an $H_{x.y}$ code, with ‘x’ equivalent to the harvest number; all samples used for this report were collected in harvest number 1 (May 2016). The ‘y’ value of the $H_{x.y}$ code corresponds to the swath of the verge the sample was cut from; H1.1 meaning harvest site 1, swath 1 and H1.2 meaning harvest site 1, swath 2. The roadside verge samples are as follows: S1/H1.1, S1/H1.2, S2/H1.1, S6/H1.1, S9/H1.1, S9/H1.2, S10/H1.1, S10/H1.2 and S11/H1.1.

Alongside the road verge grass samples, four current feedstocks used in AD at Scrivelsby farm were provided by Dr Nick Cheffins of Peakhill Associates, from site; straw, grass silage, rye grass and maize. All samples were placed into a -18°C freezer until analysis, with the assumption freezing and thawing would have no effect on the moisture content of the samples.

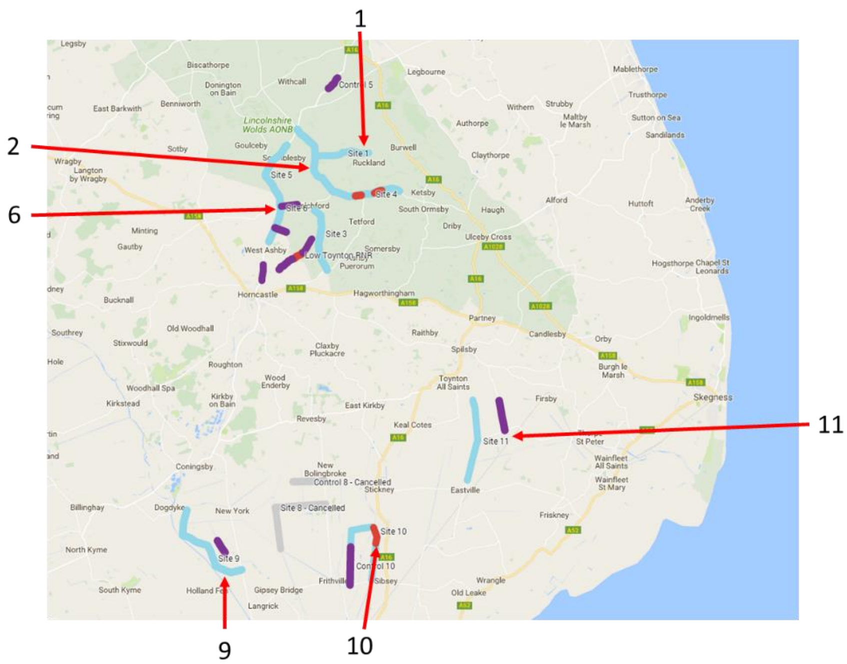


Figure 3.2: The site locations of the verge grass harvests across Lincolnshire. The numbering correspond to the site numbers used in sample labelling.

3.3 Preparation of Feedstock Samples

Samples were roughly divided into three sections; the first was kept in the freezer for storage. The second section was freeze dried for use in future experiments (see section 5.4). The third was air-dried at room temperature for a minimum of 24 hours, with the moisture loss recorded through mass difference. Following air-drying the samples were oven dried in a 60°C drying oven for a minimum of 24 hours, with moisture loss recorded. The oven-dried samples were used in the analysis described through this report. Each sample was milled using a NutriBullet 1000 series for use in proximate analysis. Following this, a section of each sample was cryomilled using a SPEX 6770 Freezer/Mill and passed through a 150µm sieve to achieve a more homogeneous sample; gaining a more representative ultimate (CHNS) analysis.

3.4 Calculation of Theoretical BMP

3.4.1 Proximate Analysis

Proximate analysis of the verge grasses and current feedstocks were performed in duplicate, according to British Standards; BS EN ISO 18134-1:2015, BS EN 15402:2011 and BS EN 14775:2009. Moisture (M) values of samples were derived from mass balance difference following drying in a Carbolite moisture oven set at 105°C for a minimum of 4 hours in a nitrogenous environment. Volatile matter (VM) was calculated through mass difference following the reaction of samples in a 900°C Carbolite AAF 1100 furnace for 7 minutes. Ash values were calculated through mass balance difference following reaction in a Carbolite furnace. The temperature was evenly raised to 250°C over 30 minutes and maintained for 60 minutes, thereafter, temperature was raised evenly to 550°C over 30 minutes and maintained for 120 minutes. Fixed carbon (FC) was calculated through difference as shown in Equation 1.

$$(1)\ FC = 100 - M - VM - Ash$$

3.4.2 Ultimate Analysis

Ultimate analysis, also known as elemental analysis was carried out on each of the cryomilled verge grass samples and current feedstocks, in duplicate, according to the British Standard BS EN 15104:2011. An EA112 Flash Analyser (CHNS) was used to determine the percentage composition of Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) in the samples.

Combustion of samples occurred at 900°C, the resulting elemental gases were detected using gas chromatography. The percentage Hydrogen composition was corrected for moisture to organic Hydrogen (Equation 2) and Oxygen (O) calculated by difference (Equation 3).

$$(2)\ Organic\ H\ content = \%H\ - \left(\%Moisture\ \times \left(\frac{2}{18}\right)\right)$$

$$(3)\ \%O = 100 - \%moisture - \%ash - \%C - \%organic\ H - \%N - \%S$$

Following ultimate analysis, the higher heating value (HHV) of the samples were calculated using Equation 4 (Friedl et al., 2005).

$$(4)\ HHV = 3.55C^2 - 232C - 2230H + 51.2C \times H + 131N + 20{,}600$$

3.4.3 Calculation of Theoretical BMP through Elemental Analysis

Results from proximate and ultimate analysis was converted from an 'as received' to a 'dry' basis, using the example conversion displayed in equation 5. The empirical formula was derived ($C_cH_hO_oN_nS_s$) through dividing the % mass of the element by the molecular weight (g/mol) of the element. The molar ratio number ($_{c,h,o,n,s}$) were applied to the BMP calculations (Equations 6, 7& 8). Calculations of theoretical biomethane yields were calculated using the Buswell equation (BMPthBu); Equation 6 and the Boyle's equation (BMPthBo); Equation 7 (Raposo et al., 2011).

$$(5)\%C\ (dry) = \left(\frac{\%C(as\ received)}{100 - \%moisture}\right) \times 100$$

$$(6)\ BMPthBu = \frac{22\ 400\ \left(\frac{c}{2} + \frac{h}{8} - \frac{o}{4}\right)}{12c + h + 16o}$$

$$(7)\ BMPthBo = \frac{22\ 400\ \left(\frac{c}{2} + \frac{h}{8} - \frac{o}{4} - \frac{3n}{8}\right)}{12c + h + 16o + 14n}$$

The theoretical proportions of methane in the biogas derived from each sample were calculated using a modified Buswell equation (Buswell and Mueller, 1952); Equation 8.

$$(8)\ CH4\,\% = \frac{\left(\frac{c}{2}+\frac{h}{8}-\frac{o}{4}\right)}{\left(\frac{c}{2}+\frac{h}{8}-\frac{o}{4}\right)+\left(\frac{c}{2}-\frac{h}{8}+\frac{o}{4}\right)}$$

Biodegradability factors for low, medium and high theoretical BMP scenarios were applied; with 0.3, 0.5 and 0.7 respectively.

3.5 Process Water Analysis

The aim of process water analysis was to identify the solubility of the feedstocks and the acidity of the process water environment, following pre-treatment.

3.5.1 Thermal Hydrolysis (TH) Pre-treatment

Thermal hydrolysis treatment was carried out on two road verge samples; S1/H1.1 and S2/H1.1, as well as the four current feedstocks. Samples were sieved to a particle size of 500µm. A 10g sample in 100mL of distilled water was placed in a 51°C water bath for 24 hours, then 53°C for a further 24 hours; as per the conditions of Scrivelsby farm (section 3.1). The samples were washed with 10mL distilled water and centrifuged at 4000Rpm for 5 minutes using a SIGMA 4-5L centrifuge. The liquid phase was filtered using a Büchner funnel and filter paper. Centrifugation and filtration was repeated twice, each time with a 50mL distilled water wash. The filtered liquid volume was made up to 250mL using distilled water in a 250mL volumetric flask. The pH of each sample was recorded using a Hach pH meter.

3.5.2 Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD)

The TOC and COD of the sample process water following thermal hydrolysis were calculated in duplicate. TOC was calculated using a HACH IL 550 TOC-TN analyser, here total carbon (TC) and inorganic carbon (IC) was identified, with TOC calculated by difference. COD was measured following BS 6068-2.34 using ferrous ammonium sulphate solution and ferroin indicator solution.

Each of the TOC and COD results were multiplied by a factor of 2.5 to account for the dilution of the washes during filtration. The methane yield derived from the process water was determined on the assumption 1g of COD ≈ 400ml CH_4 (Hamilton, 2012) using the proportion of TOC to COD as conversion factor (Equation 9), for example 49% = 0.49.

$$(9)\left(\frac{TOC}{COD}\right) X\ 100$$

4 Results

4.1 Proximate and Ultimate Analysis

4.1.1 Proximate Analysis

The results of the proximate analysis on an as received basis are displayed in Table 4.1.1. The average moisture for the grasses was 5.1% higher than all of the current feedstocks. The grasses also showed higher ash contents compared to the current feedstocks. The average ash content of the verge grasses was 17%; more than double that of the grass silage, rye grass and maize. The average volatile matter (VM) content of the verge grasses, was 63.6%; lower than all the current feedstocks which all had a VM content higher than 70%.

4.1.2 Ultimate Analysis

Table 4.1.2 displays the ultimate analysis of all feedstocks tested. The roadside grass samples all had a lower C:N and HHV (calorific values) compared to the current feedstocks. The %C and %H values were higher in the current feedstocks and yet despite this, %O was also higher in the current feedstocks.

Table 4.1.1: Proximate analysis results of all verge grasses and current feedstocks on an as received basis ± the SE. Values presented as a percentage (%) weight of the sample.

Sample	% Moisture (AR)	% VM (AR)	% Ash (AR)	% FC (AR)
S1/H1.1	4.4 ± 0.0	61.7 ± 0.1	19.4 ± 0.7	14.6 ± 0.6
S1/H1.2	3.7 ± 0.4	63.8 ± 0.5	17.1 ± 0.1	15.4 ± 0.2
S2/H1.1	5.6 ± 0.1	67.3 ± 0.2	13.1 ± 0.3	14.0 ± 0.2
S6/H1.1	3.1 ± 0.2	67.7 ± 0.2	15.6 ± 0.6	13.6 ± 0.6
S9/H1.1	4.6 ± 0.3	63.0 ± 0.5	17.6 ± 0.0	14.8 ± 0.2
S9/H1.2	8.2 ± 0.1	61.5 ± 0.2	15.8 ± 0.1	14.5 ± 0.2
S10/H1.1	5.3 ± 0.1	64.4 ± 0.0	17.4 ± 1.7	12.9 ± 1.8
S10/H1.2	5.3 ± 0.1	61.4 ± 0.2	18.4 ± 0.1	14.9 ± 0.2
S11/H1.1	5.7 ± 0.0	61.4 ± 0.1	18.4 ± 0.2	14.5 ± 0.3
Straw	2.9 ± 1.2	75.3 ± 1.2	9.8 ± 3.2	12.0 ± 3.2
Grass Silage	2.1 ± 0.2	73.1 ± 0.3	7.1 ± 0.0	17.7 ± 0.1
Rye grass	4.6 ± 0.2	70.5 ± 0.5	7.2 ± 0.3	17.6 ± 0.3
Maize	1.7 ± 0.0	78.7 ± 0.2	3.4 ± 0.0	16.3 ± 0.3

SE= standard error ($\sigma_{\overline{x}}$). AR = as received. VM= volatile matter. FC= fixed carbon.

Table 4.1.2: Ultimate analysis of verge grass and current feedstocks on a dry basis ± the SE. Values presented as a percentage (%) weight of the sample.

Sample	% C (DB)	% H (DB)	% N (DB)	% O (DB)	% S (DB)	C:N (DB)	HHV (MJ/kg) (DB)
S1/H1.1	39.2 ± 0.2	5.2 ± 0.1	2.4 ± 0.1	32.5 ± 0.1	0.4 ± 0.1	16:1	16.10
S1/H1.2	40.6 ± 0.0	5.5 ± 0.0	2.4 ± 0.0	33.4 ± 0.1	0.2 ± 0.0	17:1	16.51
S2/H1.1	43.3 ± 1.5	5.5 ± 0.3	2.5 ± 0.2	34.7 ± 2.0	0.1 ± 0.0	18:1	17.46
S6/H1.1	41.2 ± 0.1	5.7 ± 0.0	1.9 ± 0.0	35.1 ± 0.2	0.1 ± 0.1	22:1	16.63
S9/H1.1	41.3 ± 0.6	5.5 ± 0.1	1.9 ± 0.0	32.8 ± 0.8	Trace	22:1	16.70
S9/H1.2	41.7 ± 0.1	5.0 ± 0.1	2.0 ± 0.0	34.1 ± 0.1	0.1 ± 0.1	21:1	16.88
S10/H1.1	41.8 ± 0.2	5.5 ± 0.1	1.8 ± 0.0	32.6 ± 0.3	0.1 ± 0.0	24:1	16.85
S10/H1.2	40.6 ± 0.1	5.3 ± 0.0	1.9 ± 0.1	32.8 ± 0.1	Trace	21:1	16.48
S11/H1.1	40.4 ± 0.1	5.0 ± 0.1	2.4 ± 0.0	32.6 ± 0.2	0.1 ± 0.0	17:1	16.53
Straw	44.5 ± 1.0	6.0 ± 0.1	0.6 ± 0.0	38.8 ± 1.2	Trace	74:1	17.67
Grass Silage	44.1 ± 0.3	6.2 ± 0.0	1.2 ± 0.0	41.4 ± 0.4	Trace	37:1	17.60
Rye grass	47.0 ± 1.1	6.4 ± 0.1	1.8 ± 0.0	37.2 ± 1.3	Trace	26:1	18.92
Maize	45.2 ± 0.1	6.7 ± 0.0	1.3 ± 0.0	43.3 ± 0.2	Trace	35:1	18.11

SE= standard error ($\sigma_{\overline{x}}$). C= carbon. H= hydrogen. N= nitrogen. O= oxygen. S= sulphur C:N=carbon:nitrogen ratio. HHV= higher heating value/calorific value.

4.2 Bio Methane Potential

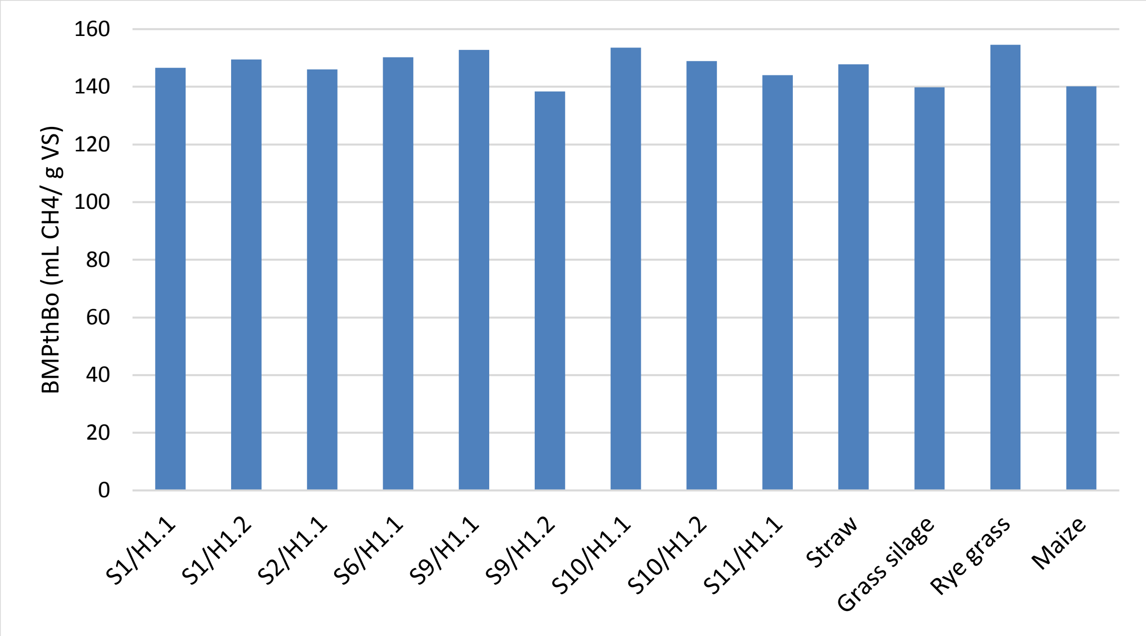


Figure 4.2: Theoretical BMP, derived from the Boyle's equation; BMPthBo (Equation 7) with a 0.3 biodegradability factor applied for verge grasses and current feedstock samples.

The BMP for the roadside grasses ranged from 138 mL CH_4/g VS (sample S9/H1.2) to 154 mL CH_4/g VS (sample S10/H1.1), with an average BMP of 148 mL CH_4/g VS (Figure 4.2). This average BMP for the verge samples is around 5% higher than the BMP values for grass silage and maize and is similar the BMP for straw (150 mL CH_4/g VS) . Rye grass had the highest BMP value of 155 mL CH_4/g VS; around 5% higher than the average BMP for the verge samples. Three of the sites (S1, S9 and S10) used to cut verge grass samples had two swaths cut; for S9 and S10 the second swath (H1.2) had a reduced BMP compared to the first swath (H1.1). However, for S1 the second swath had a higher BMP compared to the first swath.

The BMP results derived from the Buswell equations (Equations 1 and 3) are displayed in Table 4.2. The BMP results at the 0.3 biodegradability conversion are greater than those predicted than the Boyle's equation (Figure 4.2). The verge grasses show an average BMP of 157 mL CH_4/g VS derived from the Buswell equation with a 0.3 conversion factor. The verge grasses have higher predicted BMPs than all current feedstocks, except rye grass. Rye grass and verge sample S10/H1.2 have the highest BMP values of 538 mL CH_4/g VS as well as the highest theoretical proportion of methane of 55.5% in the biogas. The sample with the lowest BMP; S9/H1.2 also has the lowest methane proportion 52.6% with the biogas. The average predicted proportion of methane in the biogas produced by the verge grasses is 54.2%, higher than straw and rye grass and near equivalent to maize.

Table 4.2: Theoretical BMP predictions using the Buswell equation; BMPthBu (Equation 6) with the various biodegradability conversion factors applied. Alongside the predicted proportional methane composition of methane in biogas derived from Equation 8. All results presented on a dry basis.

Sample	BMPthBu (mL CH_4 / g VS)				Theoretical proportion of methane in biogas (%)
	Conversion Factor				
	None	0.3	0.5	0.7	
S1/H1.1	517	157	259	366	54.4
S1/H1.2	523	160	262	373	54.9
S2/H1.1	522	156	261	363	53.9
S6/H1.1	513	158	257	369	54.7
S9/H1.1	533	161	267	375	55.0
S9/H1.2	507	146	253	340	52.6
S10/H1.1	538	161	269	375	55.0
S10/H1.2	524	157	262	366	54.4
S11/H1.1	518	154	259	359	53.5
Straw	500	150	250	350	53.7
Grass silage	480	144	240	336	53.4
Rye	538	161	269	376	55.5
Maize	482	145	241	337	54.4

4.3 Process Water Analysis

The two road verge samples selected for analysis were S1/H1.1 and S2/H1.1. Sample S1/H1.1 has the lowest C:Ash ratio and S2/H1.1 has the highest C:Ash ratio.

The results of the process water analysis are displayed in Table 4.3, containing pH, COD and TOC values. COD is a measure of solubility of a sample and is defined as the amount of organic matter solubilised in a solution. TOC is a proportion of COD, which contains the carbon species, metabolised to generate methane. Once solubilised, TOC is easily accessible for microbial utilisation, so degrades at a much faster rate than the carbon species in the solid phase. It is assumed that 1g COD ≈ 400 mL CH_4 (Hamilton, 2012), but methane can only be generated from the TOC proportion. Therefore TOC proportion can be applied as a conversion factor (E.g. 49% = 0.49) to derive a more accurate representation of ML CH_4/ g COD (Figure 4.3).

The pH values for all samples process waters were acidic. Verge sample S1/H1.1 provided the least acidic environment of all feedstock with a pH of 6.71. The most acidic process waters were generated from rye grass and maize. S2/H1.1 produced a more acidic environment that straw and grass silage. The verge grass samples have an average pH of 5.91, where only grass silage is less acidic.

The verge grass samples had higher COD values than all the current feedstocks, except for rye grass (19.8 g/L). However, rye grass had lower TOC levels than S2/H1.1 and equivalent levels to S1/H1.1. The verge grass samples TOC values were among the highest of all the feedstocks. Straw had the lowest COD value (4.8 g/L) and TOC value (2.0 g/L). The verge grass samples had the highest proportion of TOC in COD, with an average of 50% and grass silage the lowest with 16%.

Table 4.3: Analysis of the samples process water following thermal hydrolysis. TOC is expressed as a proportion of COD (%).

Sample	pH	TOC (g/L)	COD (g/L)	Proportion of TOC in COD (%)
S1/H1.1	6.71	5.7	11.7	49
S2/H1.1	5.12	7.0	13.7	51
Straw	5.41	2.0	4.8	42
Grass silage	6.07	2.1	13.3	16
Rye grass	4.71	5.8	19.8	29
Maize	4.14	4.6	11.4	40

(TOC)= total organic carbon. (COD)= chemical oxygen demand.

Figure 4.3 displays the predicted volume of methane per gram COD. Both grass verge samples; S1/H1.1 and S2/H1.1 have the highest methane potential per gram of COD, producing 196 mL CH_4/g COD and 204 mL CH_4/g COD respectively. Straw and maize have a similar methane potential per gram of COD. Grass silage produces the least potential methane; 64 CH_4/g COD, 31% less than S2/H1.1 sample.

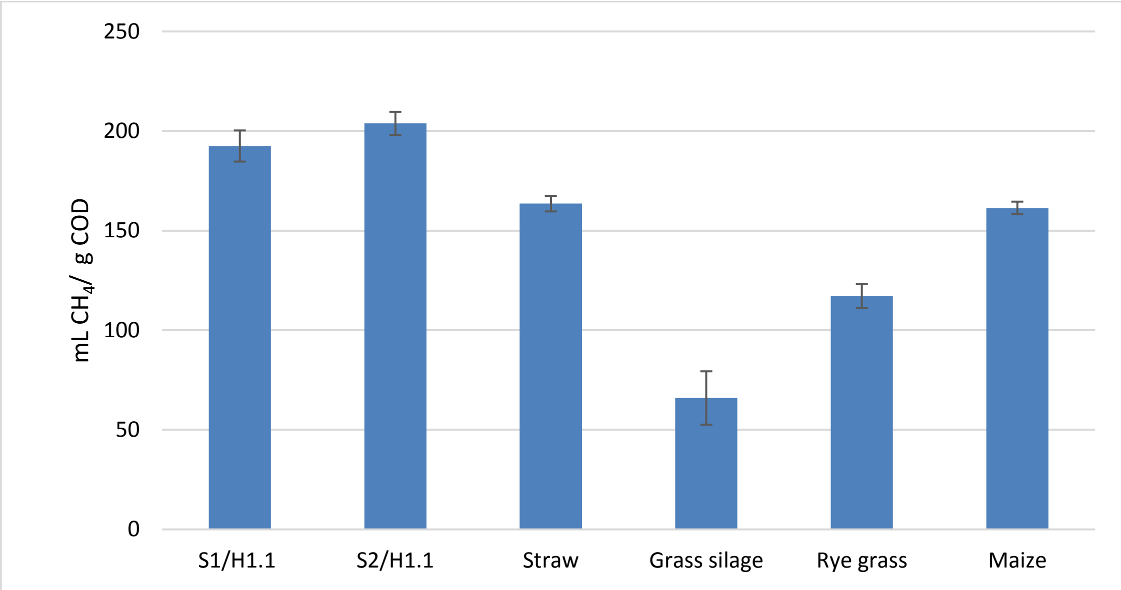


Figure 4.3: The theoretical methane yield per gram of COD in the sample process water following thermal hydrolysis, with standard error bars. Calculated from the assumption that 1g COD ≈ 400 ML CH_4 with the applied corresponding TOC conversion factor (Table 4.3).

5 Discussion

5.1 Theoretical BMP from Elemental Analysis

The Boyle's equation can be viewed as a more accurate representation of BMP prediction compared to the Buswell equation. The Boyle's equation incorporates the nitrogen fraction of biomass; giving a prediction for the theoretical ammonia content in biogas; giving a closer representation of the methane content (Achinas and Euverink, 2016). The average BMP of the verge grasses was 148 mL CH_4/g VS, around 70% lower than predicted by Meyer et al. (2014); 490 mL CH_4/g VS. Meyer et al. (2014) is the study which most closely represents the analysis of theoretical BMP in this report; using the Boyle's equation on oven-dried roadside verge grass. When determining the net energy gain of using grass as a feedstock Meyer et al. (2014) used a 0.45 degradation conversion factor. In this report a lower conversion factor of 0.3 was applied, closer to the value Labatut et al. (2011) suggested with switchgrass. This conservatively low biodegradability factor value was applied to avoid over-estimation of energy output as BMP prediction through these methods does not account for feedstock degradation or microbial energy demand. The assessment of the accuracy of this conversion factor will be validated through laboratory-scale digestions (Section 5.4) Assuming 100% degradation for the verge grasses tested in this report gives an average BMP value of 492 mL CH_4/g VS; similar that of Meyer et al. (2014). To assume 100% degradation would not be feasible, for lignocellulosic biomass in particular (Labatut et al., 2011).

The average theoretical BMP value for the verge grasses (148 mL CH_4/g VS) was also lower than those found by Li et al. (2013); 448 mL CH_4/g VS and Wall et al. (2013); 443 mL CH_4/g VS. These studies also calculated BMP through elemental analysis with no applied biodegradability factor, but of switchgrass and grass silage, respectively. Li et al. (2013) applied the Buswell equation to calculate BMP; which should provide a further overestimation of BMP compared to the Boyle's equation. Li et al. (2013) found the degradability of switchgrass to be between 54-55%, much higher than the 25% degradability found by Labatut et al. (2011). This again reiterates that biomass is highly variable, therefore difficult to predict degradability, hence in this report a conservative biodegradability factor was applied to prevent over-estimation of energy output.

The average BMP for the verge grasses in this study also recorded lower theoretical BMPs than those derived through laboratory-scale digesters, presented in Table 2.3.2. Salter et al. (2007) found the resultant BMP for the roadside grass studies in Wales was 270 mL CH_4/g VS. This figure could be achieved by the verge grasses studied in this report if the biodegradation was greater than 50%, predicted by the Buswell equation (Table 4.2). A biodegradability factor of 50% could be a realistic representation of the degradation in AD as Meyer et al. (2014) suggest grass biodegradability can range from 45%-80%.

The verge grasses appear to have similar BMP values to the current feedstocks already being used in the Scrivelsby AD plant. This suggests substituting current feedstocks with the verge grass would still have similar energy outputs. The average proportion of methane in the biogas of the verge grass samples (54.2%) is similar to that of maize (54.4%). Maize constitutes 60% of the total feedstock used by Scrivelsby farm, suggesting the verge grasses may act an efficient feedstock substitution. However the ash content of the verge grasses is, on average, almost double that of the current feedstocks. As a result of this, the current feedstocks have a higher proportion of volatile matter to be utilised during methanogenesis. This may indicate that digestion of the fresh grass could produce less methane (mL/ g fresh grass) than the current feedstocks. The grass clippings are collected through a cutting and suction method. During this process soil particulates, high in inorganic matter, may also be collected; potentially contributing the overall ash content of the verge grass feedstock.

5.2 Suitability of Roadside Verge Grass as a Feedstock

5.2.1 C:N ratio

An ideal C:N ratio to sustain the microbial population, therefore biogas stability, is between 20-30:1 with 25:1 being the optimum ratio (Yan et al., 2015). The average C:N ratio for the verge grass samples is 20:1; closer to the ideal ratio than the current feedstocks, except rye grass. This average C:N ratio is lower than those specified for grass silage by Nizami et al. (2009) and Xie et al. (2011). A select few of the verge grasses (S1/H1.1, S1/H1.2 and S11/H1.1) had low C:N ratios, this may negatively impact AD due to the build-up of ammonia; inhibitory to AD (Chen et al., 2008). However, if the decision is made to digest the grass, the cuttings will be co-digested with the current feedstocks utilised in Scrivelsby farm. Straw, grass silage and maize all display high C:N ratios which, will balance the overall C:N ratios to optimum levels.

5.2.2. pH

Optimal pH range for AD is between pH 6.8-7.2 (Ward et al., 2008), below this pH range methane production is reduced. The verge grass sample S1/H1.1 process water is the closest to this range (pH 6.71). Scrivelsby AD plant uses the currently uses the current feedstocks successfully, from this it can be assumed that the pH levels generated by the verge grasses will not affect the AD process as they are less acidic than the current feedstocks. The grass silage tested was surprisingly less acidic that the other current feedstocks tested (pH 6.07). During the ensiling process lactic acid is generated (McEniry et al., 2014) through microbial fermentation, preserving the grass. This lactic acid would be expected to generate a more acidic process water.

5.3 Solubility of Feedstocks and Theoretical Methane Yield from the Process Waters

The verge grass samples, particularly S2/H1.1 are predicted to have a higher methane yield per gram of COD within the process water compared all of the current feedstocks. The verge samples leach high levels of COD into the process water, of which a high proportion is the TOC fraction; suggesting a higher methane yield per gram of COD. High solubility of organic matter is important to maximising methane production; as this impacts the rate limiting step of hydrolysis. The degree of nutrient solubility of the verge grass supports the argument of their suitability in AD. The varying COD values of the feedstocks could be attributed to the varying lignocellulosic compositions. Though, as this was not directly measured in this report and due to the highly variable lignocellulosic compositions of feedstocks across the literature, it would be difficult to put this variance down to lignocellulosic composition alone.

It was unexpected that grass silage would produce such a low methane potential per gram of COD. It also produced a process water which was less acidic than the other current feedstocks. Ensiling grass has been shown to have now effect on methane yield compared to fresh grass (McEniry et al., 2014). Amon et al. (2007) suggest that ensiling maize would increase the methane yield by 25% compared to non-ensiled maize. During ensiling, nutrients become solubilised through a mild fermentation. The reduced COD and high pH could be due to the sample of grass silage which was collected. If the sample was exposed to adverse weather conditions, such as rain, these soluble nutrients and lactic acid would be washed from the sample and lost to the surrounding environment. The verge grass will be ensiled if deemed appropriate by Lincolnshire County Council as an AD feedstock, therefore the method and preservation of ensiling grass is critical to ensure maximal energy output.

5.4 Development of BMP Testing

Promising theoretical BMP results derived through elemental stoichiometric equations were shown for the verge grasses in this report. Future work with involve validation of these BMP values through laboratory-scale digester experiments. These experiments will provide the practical methane yields of the verge grasses, a more accurate representation of performance in AD, compared to theoretical methane yields. Freeze dried feedstock samples (Section 3.3) are to be used in these experiments.

Practical methane yields will be analysed using an automatic methane potential test system (AMPTS). The experiments are to replicate the AD conditions of Scrivelsby farm (Section 3.1) as close as possible. The experiments can be broken down into three separate runs of samples through AMPTS; process waters, process waters and solids and co-digestions. Each run will involve a thermal hydrolysis pre-treatment of 51°C for 24 hours and 53°C for a further 24 hours, with a loading rate of 10g in 100ml distilled water. During AMPTS samples will be loaded in specific ratios with the inoculum; to be collected from Scrivelsby farm, (specified in sections 5.4.1, 5.4.2 and 5.4.3) with a total volume of 400ml; leaving a 100ml headspace. Each sample will be run in duplicate. At the start of AMPTS volatile fatty acids (VFAs), COD, total volatile solids (TVS) and pH, will be measured and again at the end of the run. The samples will be flushed with nitrogen gas for 2 minutes, to ensure an anaerobic environment. The temperature will be maintained at 45°C through a 21-day incubation period. AMPTS equipment is shown in Figure 5.1. The AMPTS comprises of three units, a digester, a CO_2 removal system and a gas collection unit. The removal of CO_2 will be through a 3M solution of NaOH system as represented in the literature; (Maile et al., 2015, McEniry et al., 2014), enabling biomethane yield to be identified in the gas collection unit.

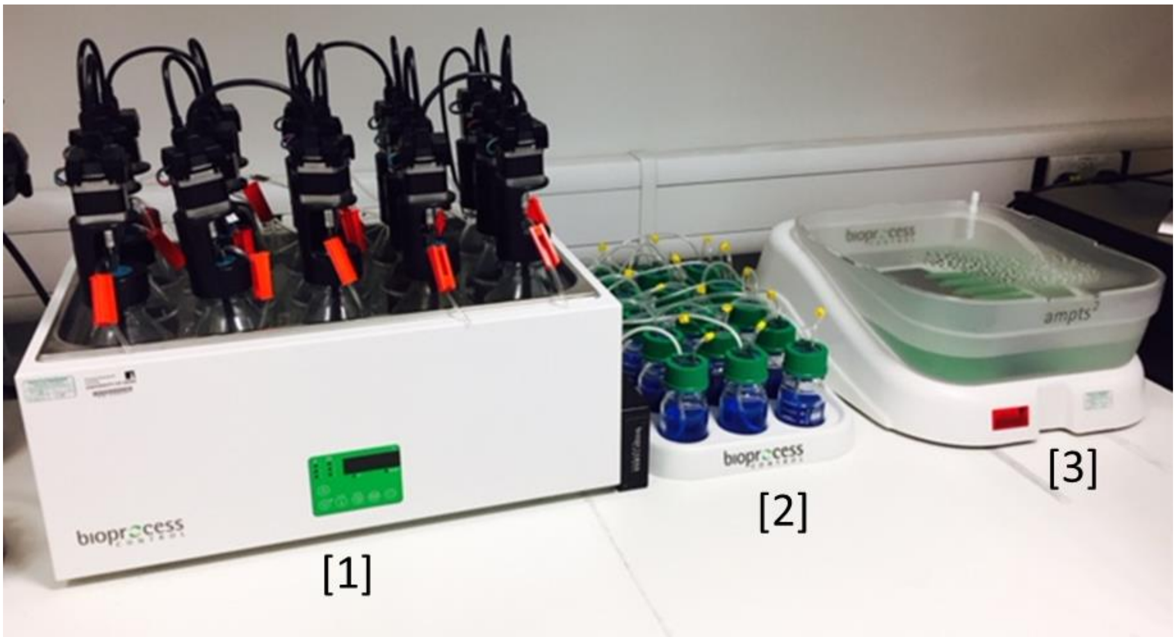


Figure 5.1: The AMPTS equipment to be used in the BMP tests. The equipment is made up of three units; [1] digester, [2] CO_2 removal system and [3] gas collection unit.

It is important to note that Climent Barba et al., 2016 found that sample S1/H1.1 contained Mercury levels that were beyond the limits deemed acceptable by UK legislation. Consequential information from Dr Nick Cheffins of Peakhill Associates found that sample site 1 (S1) had the road re-surfaced three days prior to the sample being taken. Therefore, the resulting aggregate from the road re-surfacing may have contaminated the verge grass samples located on site. Future work following this report was to test the BMP of S1/H1.1 using AMPTS. The process water of S1/H1.1 will undergo AMPTS, to identify if heavy metals influence the AD process. However, no further analysis of this sample will occur. Another grass verge sample S9/H1.1 will undergo characterisation (Sections 3.5.1 and 3.5.2) and BMP tests through AMPTS. This sample has a relatively high BMP derived from the Boyle's equation (Figure 4.2) and there is a large amount of sample in storage to analyse.

5.4.1 Process Waters

Practical BMP through AMPTS will be identified for the process waters collected during this report (Section 3.5). This will include the following samples: (verge grasses) S1/H1.1, S2/H1.1 and S9/H1.1, as well as; (current feedstocks) straw, grass silage, rye grass and maize. The volume ratio of inoculum:process water will be 1:1, each with 1000mg of COD.

5.4.2 Process Waters and Solids

The practical BMP of the whole product of thermal hydrolysis; process water and the solid phase is to be identified, following thermal hydrolysis. This is to include the following samples; S2/H1.1 and S9/H1.1, as well as the current feedstocks: straw, grass silage, rye grass and maize. The TVS ratio of inoculum:sample will be 1:1.

5.4.3 Co-Digestions

A control of the feedstock combinations currently digested at Scrivelsby farm (Figure 3.1.2), including 60% maize, 10% straw, 10% grass silage, 10% rye grass and 10% chicken litter will be used. The verge grass sample with the highest BMP (from the individual AMPTS runs) is to be selected to replace a proportion of the maize. A discussion with a local farmer (Climent Barba et al., 2016) suggests maize is the most expensive of the current feedstocks, therefore the most desirable to replace with roadside verge grass. Maize with 32% dry matter costs £32 per tonne, the next most expensive current feedstock; chicken litter, costs £15 per tonne. Scrivelsby farm has potential access to 723 tonnes of verge grass within a 5km radius of the farm; representing 7% of feedstock capacity and 2954 tonnes of grass within a 10km radius; representing 28% of feedstock capacity (Climent Barba et al., 2016). Assuming the roadside verges are cut once a year, these can give a low, medium and high situations for the proportions of verge grass cutting Scrivelsby can substitute maize; 5%, 15% and 25% of total feedstock respectively. A 15km radius of Scrivelsby farm gives a yield of 6421 tonnes of verge grass; 62% of feedstock capacity. However a local farmer expressed that the maximum amount of verge grass a farm would be inclined to digest is about 30% of the total feedstock proportion (Climent Barba et al., 2016). The combinations of co-digested feedstocks to be used in these experiments, displayed in Table 5.1.

Table 5.1: The proportions of feedstocks to be used in future AMPTS experiments. Maize is increasingly substituted for roadside verge grass, as maize is the most expensive current feedstock; so the most desirable to replace.

Feedstock	Proportions of individual feedstocks in co-digestion (%)			
	Control	5% verge grass substitution	15% verge grass substitution	25% verge grass substitution
Verge grass	0	5	15	25
Maize	60	55	50	35
Straw	10	10	10	10
Grass silage	10	10	10	10
Rye grass	10	10	10	10
Chicken litter	10	10	10	10

Thermal hydrolysis treatment is to be applied to each sample before an AMPTS run. This is to be applied to all co-digestion samples listed in Table 5.1. The process waters and solids of each sample will be studied and BMP analysed using the AMPTS method listed above.

Across the literature, a loading ratio of inoculum:substate is 2:1 TVS:TVS (Maile et al., 2015, McEniry et al., 2014). In the experiments planned here, a loading ratio of 1:1 (TVS:TVS) is to be used. This lower ratio is due to the loading rate of the Scrivelsby farm model (section 3.1); 50% of the contents of Hydrolysis 1 (H1) is transferred to H2 before the feedstocks are initially added at the start of a digestion cycle.

A schematic of the further laboratory work to be carried out is represented in Figure 5.2

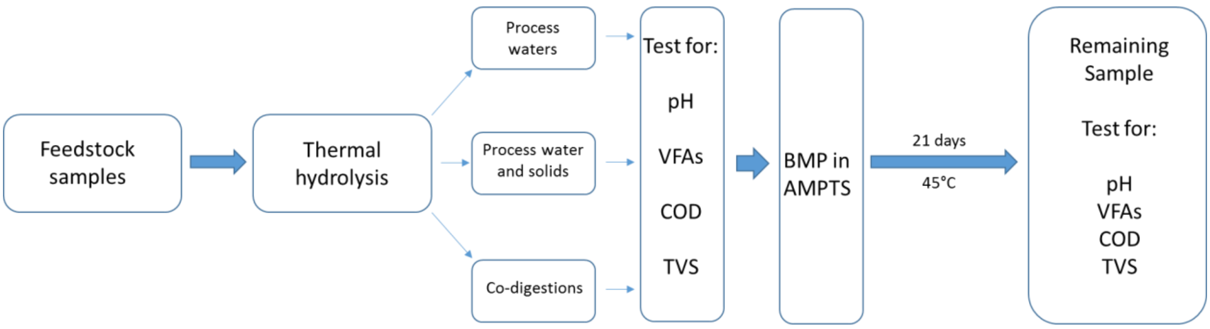


Figure 5.2: A layout of the future laboratory work to be achieved between January and May 2017.

6 Conclusion

The 9 roadside verge grass samples tested have shown encouraging initial results for the potential utilisation as a feedstock in anaerobic digestion. The grasses displayed an average BMP value of 148 mL CH_4/g VS derived from the Boyle's equation with a 0.3 biodegradability factor. This appears to be competitive with the BMP of feedstocks currently used in AD in farms in Lincolnshire; straw, grass silage, rye grass and maize. Though a more accurate BMP value is to be derived from future laboratory-scale digestion experiments, gaining a more accurate representation of biodegradability. The verge grass samples display promising feedstock characteristics related to; C:N, as well as the pH and solubility of organic matter in the process waters following thermal hydrolysis pre-treatment. However, the verge grasses have high ash content which may reduce the BMP of the fresh grass during digestion. The grass silage sample displays a low methane yield per gram of COD, therefore future work is required to ensure ensiling the grass samples would not have an effect on BMP if large-scale digestion of the grass was approved. The initial energy output results from the verge grass are sufficiently encouraging to allow further investigation.

6.1 Future work

Run the laboratory-scale digestions as described in Section 5.4. Collect a fresh sample of grass silage to test as a current feedstock, ensuring the sample was not exposed to rainfall.

Assess the lignocellulosic and biochemical composition of the verge grasses and current feedstocks to identify if a link is established to the COD values shown in this report.

Examine the resulting effect of BMP through ensiling the verge grass samples. The samples will be ensiled following collection if this scheme is to be established long-term.

Trial alternative systems of collecting the grass verge samples which eliminate collection of soil particulate matter, which may influence the overall ash content of the feedstock.

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