

How Can Renewable Energy Reduce Methane Emissions from the Irish Dairy Herd to Safeguard Future Production?

*A Thesis Presented as part fulfilment for the Award of
Master of Science in Food Business Management and
Technology*

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**For Research Carried Out Under the Guidance of Cal
McCarthy**

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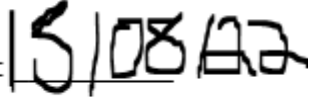
DECLARATION

I hereby certify that the material, which I now submit for assessment on the program of study leading to the award of MSc Food Business Management and Technology., is entirely my own work and has not been taken from the work of others save to the extent that such work has been cited and acknowledged within the text of my own work. No portion of work contained in this thesis has been submitted in support of an application for another degree or qualification to this or any other institution.

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Student Name

AODHAN BRENNAN

Date: 

I hereby certify that the unreferenced work described in this thesis and being submitted for the award of MSc Food Business Management and Technology is entirely the work of my own, Aodhan Brennan. No portion of the work contained in this thesis has been submitted in support of an application for another degree or qualification to this or any other institution.

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A special word of thanks to my thesis supervisor, Cal McCarthy. The knowledge, encouragement and advice provided throughout the process proved crucial in the delivery of this thesis.

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Sincere gratitude to all involved.

Abstract

Ireland must reduce its methane emissions by 30% from Agriculture by 2030. The purpose of this Thesis is to explore how Renewable Energy can reduce Methane Emissions from the Dairy Herd to safeguard future production. This is in line with legislation derived from the Paris Agreement and COP 26 and further supported by indigenous policy. Methane is one of the most significant Green House Gases derived from the Dairy industry in Ireland. It is a colourless and odourless gas with a significant global warming potential surviving in the atmosphere for up to twelve and a half years. In the absence of sufficient remedial action, a national cull and loss of production will present the only means of meeting these targets currently at an increase of 3.8%. The link between Renewable Energy sources and reduced methane emissions provides a means to help reach national emission targets whilst maintaining ongoing production with additional benefits to the economy. Anaerobic Digestion, in the conversion of biodegradable biomass to biogas observed benefits to reduce methane production by 85% when stored as Digestate. Feasibility of construction is also observed in herds comprising of over 100 cows typical of an Irish Herd scenario, particularly where external investment is attained in the production of energy. Pyrolysis, the decomposition of waste material facilitates the reduction in Methane through the beneficial production of biochar. Biochar is observed to reduce methane through its addition to stockpiled manure facilitating a reduction of 79%, its potential as physical barrier as a Biocover and Fertiliser as a saving of chemical fertiliser. Farmers, the primary producers, who are central to the implementation of remedial strategies portray a willingness to partake in sustainable practices and associate such practices as that of a good farmer. Further guidance, education and financial incentive is required to ensure ongoing participation.

Abbreviations

| | |
|----------|---|
| Acyl-CoA | Acyl Coenzyme A |
| AD | Anaerobic Digestion |
| ADP | Adenosine Di Phosphate |
| ATP | Adenosine Triphosphate |
| BC | Biochar |
| BET | Brunauer Emmett Teller |
| bLS | Backward Lagrangian Stochastic |
| C02 | Carbon Dioxide |
| CAP | Common Agricultural Policy |
| CH4 | Methane |
| CHP | Combined Heat and Power |
| CM | Centimeter |
| COP 26 | United Nations Climate Change Conference |
| DM3 | Cubic Decimeter |
| EEG | Renewable Energy Sources Act |
| EPA | Environmental Protection Agency |
| eq | Equivalent |
| EU | European Union |
| F1 | Farmer 1 |
| F2 | Farmer 2 |
| FC650 | Douglas Fir Biochar Gasification |
| FTIR | Fourier Infrared Spectroscopy |
| GHG | Green House Gas |
| GWh | Gigawatt Hour |
| GWP | Global Warming Potential |
| H2 | Hydrogen |
| H2S | Hydrogen Sulphide |
| HF600 | Douglas Fir Biochar Slow Pyrolysis |
| IRR | Internal Rate of Return |
| J KG | Joule Per Kilogram |
| Kg | Kilograms |
| kW | Kilowatt |
| LCA | Life Cycle Assessment |
| MMB | Micrometeorological mass balance |
| MSS | Multi Species Sward |
| MT | Million Tonnes |
| MW | Megawatt |
| N2 | Nitrogen |
| N2O | Nitrous Oxide |
| NAD | Nicotinamide adenine dinucleotide |
| NADP | Nicotinamide Adenine Dinucleotide Phosphate |

| | |
|-----------------|---|
| NAP | Nitrogen Action Program |
| NDC | Nationally Determined Contribution |
| NH ₃ | Ammonia |
| NH ₄ | Ammonium |
| nm | Nanometer |
| NMR | Nuclear Magnetic Resonance Spectroscopy |
| NPV | Net Present Value |
| NV2 | Nitrate Vulnerable Zones |
| OECD | Organisation for Economic Cooperation and Development |
| OH | Hydroxide |
| pH | Potential of Hydrogen |
| PRG | Perennial Ryegrass |
| Red II | Renewable Energy Directive |
| REFIT | Renewable Energy Feed Tariff Program |
| S2 | Scenario 2 |
| SB1383 | Short Lived Climate Pollutant Reduction Law |
| SEM | Scanning Electron Microscopy |
| SSAD | Small Scale Anaerobic Digestion |
| SVFA | Short Chain Volatile Fatty Acids |
| TGA | Thermo Gravimetric Analysis |
| TWh | Terawatt Hours |
| UNFCCC | United Nations Framework Convention On Climate Change |
| VS | Volatile Solids |
| XRP | X Ray Diffraction |

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Chapter 1: Introduction

1 Overview

Work presented in this thesis investigates how Renewable Energy can reduce methane output from the Dairy animal to safeguard future production. The focus of this thesis is to assess Renewable Energy processes and their by-products to help mitigate methane emissions from the Dairy animal for sustained production. For the purpose of this study, the two methods of Renewable Energy studied include Anaerobic Digestion and Pyrolysis and their by-products of Energy Production. Digestate and Biochar were studied in terms of their efficacy to reduce methane, their feasibility and overall benefit to the circular economy. The introductory chapter will set out the landscape of the Irish Dairy Industry, its expansion and its consequence in light of environmental targets facing the industry. This chapter will provide background on the impact of methane on the planet and why its reduction is necessary to safeguard future production in Irish Agriculture, specifically in the Dairy sector.

1.1 Methane

Methane is a greenhouse gas pollutant which is odourless and colourless with potential to survive in the atmosphere in excess of twelve and a half years, posing a significant challenge to global warming (Figure 1.1) (Myhre *et al.*, 2013). It is the second most abundant GHG (Green House gas) (Hellig *et al.*, 1994). It is highly potent and has the ability to increase the global temperature more than 21 times that of CO₂ by trapping infrared radiation in the atmosphere (FAO, 2006). Methane is responsible for 30% of Global Green House Gas Emissions (Teagasc, 2021). From an animal performance standpoint, methane is reported to be responsible for 2-12% of gross energy loss through eructation (Lascano *et al.*, 2010).

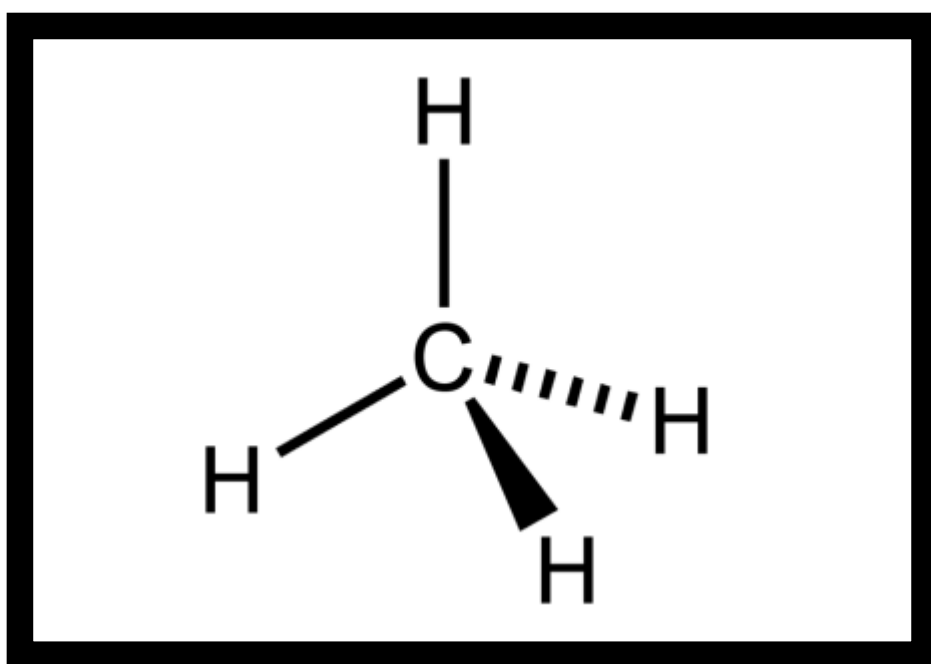


Figure 1.1 Methane Molecule (Taken from Lynch,2019).

1.3 The Digestive Process

Dairy animals are categorised as ruminants comprising of the order Artiodactyl alongside sheep, beef animals and goats (Hackmann *et al.*,2010). Their primary source of nutrition is derived from plant material through grazing of forage or harvested crops produced by the farmer. The digestion process is carried out by a specialised process of complex interactions with symbiotic microorganisms in the conversion of food to energy (Tseten *et al.*, 2022). Four compartments of the animal's digestive system work in tandem during this process and are known as the Rumen, Reticulum, Omasum and Abomasum (Clauss *et al.*, 2014). Within the rumen, a large amount of microorganisms is present including bacteria, fungi, protozoa and methanogenic archaea which form a symbiotic relationship with the animal during the fermentation process. Complex macromolecules from the animals feed are broken down through enzyme synthesis to short volatile fatty acids (SVFA) and crude microbial protein. Here, the symbiotic relationship is complete as the animal receives a vital source of energy and protein whilst the microbes with an adequate environment to survive and grow (Cammack *et al.*, 2018).

There are three main sources of SVFAs in the rumen: Acetate accounting for circa 65% of total SVFAs, Propionate (20%) and butyrate (15%). The three combined provide circa 80% of total energy required by the animal (Tseten *et al.*, 2022). Methane is then produced as a result of anaerobic fermentation by methanogens present in the gastrointestinal tract (Janssen,2008).

1.4 Methane Formation Process

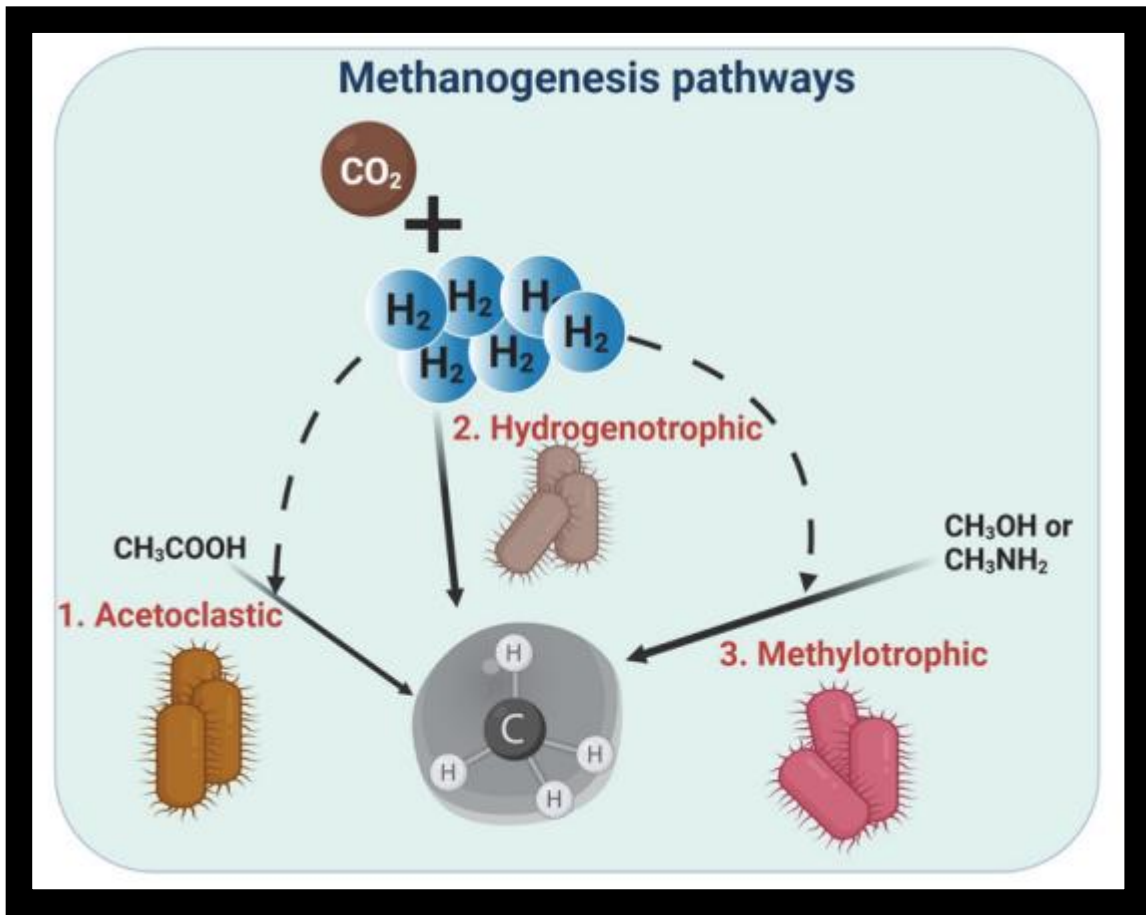


Figure 1.2 Methanogenesis Pathways (Taken from Tseten *et al.*, 2022).

Methanogens are described as bacterium which produce methane of which they can be divided into three clades based on the substrate it exploits: methylotrophic, hydrogenotrophic or acetoclastic as seen in Figure 1.2 (De la Fuente *et al.*, 2019). Hydrogenotrophic Methanogenesis provides the primary route for the disposal of hydrogen through the substrate H_2 and CO_2 as it performs as a hydrogen sink in the absence of oxygen (Thaeur *et al.*, 2008).

Alternatively, sulphate and nitrate may also perform as a hydrogen sink and is also more temperature favourable. However, its concentration within the rumen is low, deeming electron flow to the sulphate/nitrate pathway of reduction limited resulting in the bulk of H_2 destined for methane formation (Van Zijderveld *et al.*, 2010). Therefore, Methanogenesis provides the most effective means to abolish hydrogen in the rumen whilst allowing fermentation to continue (Tseten *et al.*, 2022).

1.5 The Paris Agreement

In 2015, 191 parties came together at the Conference of Parties to form the Paris Agreement to the United Nations Framework Convention on Climate Change (UNFCCC). The agreement formed a policy with 2 primary objectives:

1. Temperature Objective:

Maintain global temperature to no more than 2 degrees Celsius in excess of pre-Industrial levels.

2. Adaption Objective:

Provide an increased focus surrounding the adaption of unfavourable effects of climate change, promote resilience and growth of reduced greenhouse gas emissions with minimal impact to the production of food (EPA,2022).

The Intergovernmental Panel on Climate Change accredited methane with the responsibility of half of the 1.1-degree increase in the global temperature average on pre-industrial records. Most significantly for Agriculture, 37 % of Irish emissions is of Agricultural origin. Data from the Environmental Protection Agency indicates 80 per cent of emissions from farming are directly attributed to methane. The agreement requires each part to provide a Nationally Determined Contribution (NDC) to achieve. This is communicated and reviewed every 5 years to the UNFCCC. Irelands NDC was determined by the European Union (EU) in 2016. This commitment details a 40% reduction in emissions across the EU member states in comparison to that of 1990 levels (Government of Ireland, 2020).

1.6 COP 26

COP 26, the United Nations Climate Change Conference took place in October 2021 and follows on from Targets set about by the Paris Agreement (Teagasc, 2021). Within the Conference, specific targets relating to Methane emissions were set out. A global methane reduction target of 30% was agreed by 2030, partnering with 80 countries in total including America in reducing Methane emissions. In Ireland, the plan outlined includes a 2.5% reduction each year until 2025 to assess progress through the uptake of technologies and best practices to achieve this target which Ireland heralds at 22-30% (Teagasc, 2021).

1.7 The Climate Action Plan

The Government of Ireland introduced a number of policies to align their national objectives on GHG emissions with that of the Paris Agreement. The culminate action plan policy sets out a roadmap to halve emissions by 2030 and reach net zero no later than 2050.

41 actions in total are referenced in the policy with specific objectives for the Agricultural industry including:

1. Reduction of overall emissions from 23 to 16-18 MtCO₂ eq by 2030
2. Liaise with the waste sector to produce 1.6TWh of Biomethane indigenously each year to the gas grid by 2030.
3. Implement an action plan to the reduction of emissions to include: Land Diversification, Carbon Farming and the use of feed additives to reduce methane in pasture based systems (KPMG,2021).

1.8 Progress in Meeting the Targets

Thus far, national results aligned with previous European Union targets (2020 Climate and Energy Package) have been largely unsuccessful. Here, the expectation to reduce Green House Gas emissions by 1% was not met and was instead met with a 3.8% increase in overall emissions between 2005 and 2019 (EPA,2020). This largely contradicts the countries National policy ambition to reach carbon neutrality in the Agricultural sector by 2050.

Furthermore, figures from the Central Statistics Office indicate that emissions from agriculture is set to increase further from 21.15 Mt CO₂ eq in 2019 to an increase of 9% by 2030 based on 2005 levels (EPA,2020). From an Agricultural standpoint, this has largely been attributed to a rise in dairy cow numbers post abolition of the milk quota and rising demand in fertiliser and associated inputs as a result (Lanigan *et al.*, 2018). KPMG 2021, in a national farm survey predicted that if there is no methane reduction achieved with the Agricultural sector, a 18% cull in the National herd is required based on average methane produced per animal. On a national scale this equates to 1.3 million animals across each livestock category in Ireland.

1.9 Impact of Abolition of the Milk quota

Historically, regarding the European Union, Ireland was considered one of the most environmentally friendly producers of milk along with Austria in terms of CO₂eq per kg of milk (Leip *et al.*,2010). This is largely attributed to the style of management system in Ireland which predominately allows the Dairy herd in Ireland to produce milk from grazed grass. From this model Green House Gas Emissions per tonne of fat and protein corrected milk (FPCM) is attributed to be 15% lower in comparison to indoor systems (O'Brien *et al.*,2012). This competitive advantage is also mirrored in terms of cost of milk production within Europe and the greater world, which again I attributed to the economic value of grazed grass (Thorne *et al.*,2017). Recent figures quoted by Glanbia in conjunction with Teagasc indicate, even with inflated prices of inputs such as fertiliser in 2022, grazed grass is still a far more economical

option with one tonne of grass per dry matter costing approximately €70 and ensiled grass silage exactly double (Glanbia,2022). Lower production costs centre around Irelands temperate climate allowing grazed grass to be in the cow's diet for up to 305 days per year from early spring into the autumn (Läpple *et al.*,2012).

Due to milk quota, a limit on the amount of milk produced per farm was in place. As a result, the number of Dairy Cows remained stable with an average growth of 1.3% per year from the period 2206 to 2013 (Läpple *et al.*, 2020). In April 2015 this quota was removed and brought about a significant increase in cow numbers to the Island of Ireland averaging a growth of 5.8% per year from 2014 to 2017(Figure 1.3) (Läpple *et al.*, 2020).

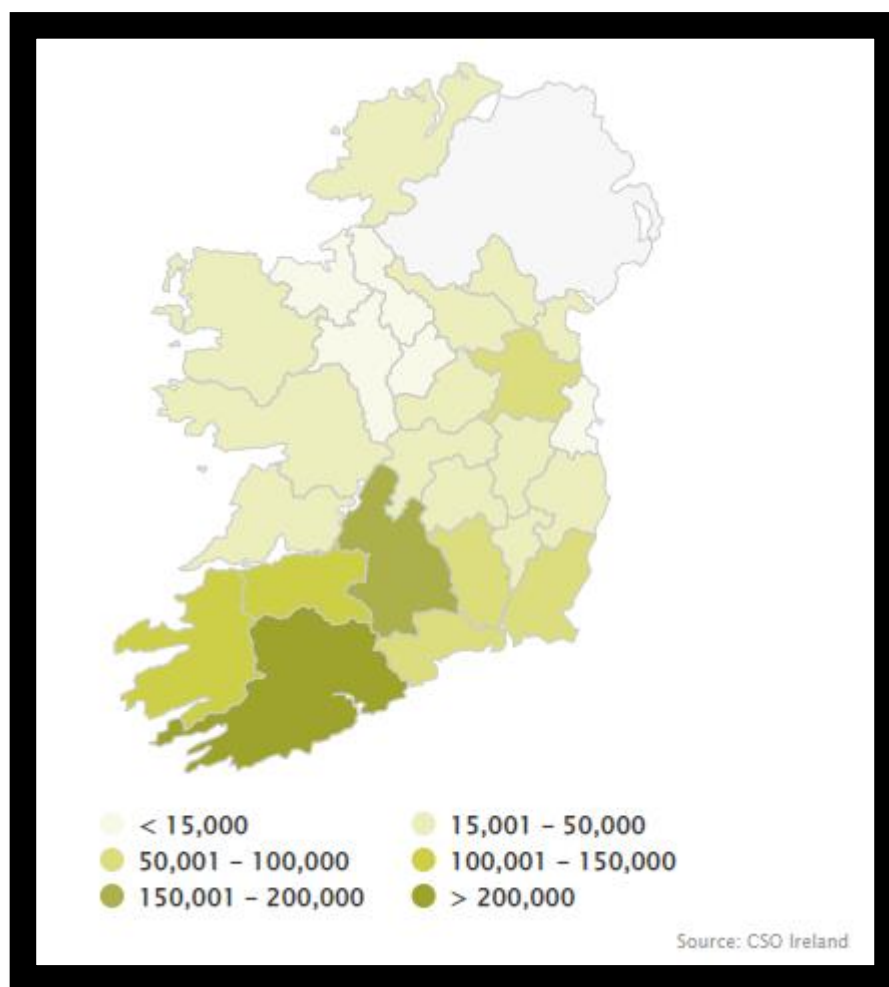


Figure 1.3 Dairy cows by county, taken from CSO,2020.

Dairy cow numbers seen an increase of 34.8% from 2013 to 2020 with 1,567,700 cows recorded by the Central Statistics Office, an increase of 3.4% on the previous year (CSO,2020). As a result, milk produced has increased by 50% since 2010(Figure 1.4) (CSO,2020).

Moreover, an increase in farm productivity is negatively correlated with Green House emission intensity such as methane (Läpple *et al.*, 2012). Despite Ireland's comparative advantage in milk production model, this large increase has now seen a narrowing of its competitive advantage and leaves the industry under pressure to reduce intensities without seeing a decrease in cow numbers. Data from a study carried out by KPMG found that in order to meet a reduction in greenhouse gas emissions of 35% (30% target), the Dairy livestock numbers would have to reduce by 45% from 2,126,421 in 2018 to 1,176,240 by 2030 (KPMG, 2021).

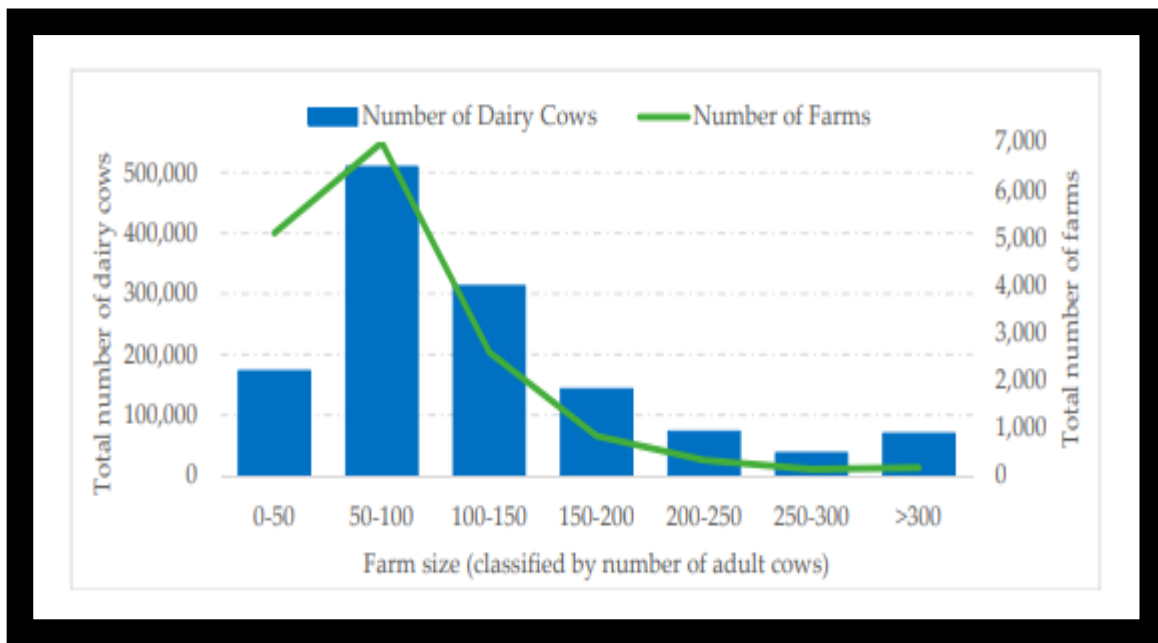


Figure 1.4 Farm numbers and distribution, taken from O'Connor *et al.*, 2020.

1.10 Importance of Dairy Industry to Irish Economy

The Irish Dairy industry is of key importance to the Irish economy employing over 60,000 people both directly through the primary producer and indirectly through linked practices (Glanbia, 2020). There are over 18,000 farms producing over 7 billion litres across the year destined for production by 1 of 24 production sites across the island of Ireland (Figure 1.5)



Figure 1.5 Overview of Dairy milk suppliers in Ireland, taken from Dairy Industry Ireland 2022.

2021 saw Irish Dairy exports reach 5 billion euro for the third year in a row from a product portfolio across powders, cheese and butter to 147 markets worldwide (BordBia 2021). Most significantly, KPMG in their study predict that if this methane target is reached through culling, then the impact could see a loss of 4 billion euro to the Irish Economy and a loss of over 56,000 jobs through Direct and Indirect employment (KMPG,2021).

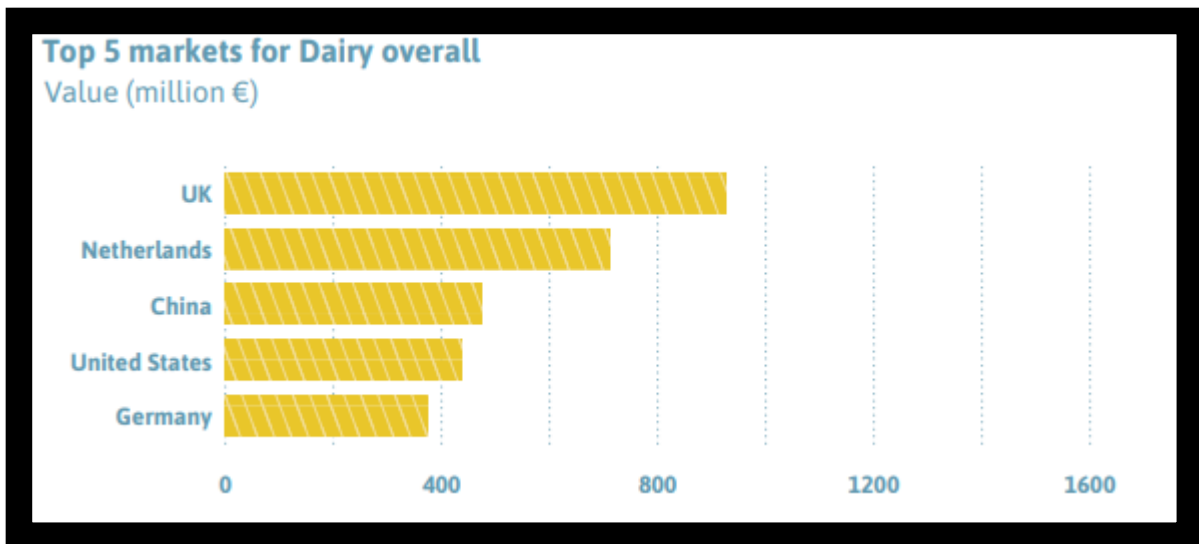


Figure 1.6 Top 5 Dairy Destinations 2021, taken from Bord Bia 2021

1.11 Methane in Slurry Storage

Faecal matter produced by the dairy animal is a waste product which poses an environmental risk through the loss of methane to the environment. On Intensive farms, livestock manure is typically in liquid form or slurry comprising of urine and straw or other bedding material less than 15% solids. During the storage of this material, the formation of a crust develops which in turn creates anaerobic conditions. Microbes present in this environment break down the organic matter within the slurry into simpler forms by a fermentation process with bacteria. During this process methane is produced by methanogenic archaea (Dalby *et al.*, 2021). Depending on the age and management approach, dry matter of liquid manure ranges from 1.7 to 9% Dry Matter (Kupper *et al.*, 2020). An average of 75% of this Dry matter is volatile solids (VS) and pH of 7-8. This makes liquid slurry derived from ruminants an excellent source of substrate for microorganisms present. Microbial oxidation describes the process of which microbe's uptake and convert methane to carbon dioxide inside the crust of the slurry. This formation of this crust essentially seals the liquid slurry in place and slows down the rate of gaseous emissions to the environment. methane oxidation is reported to cease with a crust of 1.5cm as oxygen can no longer penetrate the crust (Yun-Feng *et al.*, 2017). The storage and subsequent temperature of the stored storage also contribute to the amount of methane which is emitted from the slurry (Baral *et al.*, 2018). Therefore, without ongoing measurement it can be difficult to quantify the exact methane losses from slurry as shown in Fig 1.4 comparing cattle and pig slurry emissions (Peterson *et al.*, 2016).

Table 1.1 Emissions from cattle and pig slurry, taken from Peterson *et al.*, 2016

| Table 4. Methane production rates (MPR) corresponding to the temperature in slurry channels at the time of collection. Data shown are mean and 95% confidence limits (C.L.) of six replicates, and coefficients of variation (C.V.). | | | | |
|---|--------------------|-----------------------------------|--|-----------------|
| Sample ID | Slurry type | Ambient slurry temperature | MPR (mg CH₄ kg⁻¹ VS h⁻¹) | C.V. (%) |
| 2 | Pig | 16.9 (-1.1) * | 12.7 (9.1–16.2) [§] | 14 |
| 3 | Pig | 18.4 (-0.3) | 44.3 (38.2–50.3) | 7 |
| 5 | Pig | 14.8 (0.4) | 25.4 (15.2–35.5) | 21 |
| 9 | Pig | 18.4 (1.2) | 116.4 (106.6–126.2) | 4 |
| 10 | Pig | 17.5 (0.3) | 90.5 (76.1–104.8) | 8 |
| 11 | Pig | 19.4 (-0.6) | 115 (105.2–124.8) | 4 |
| 12 | Pig | 20.1 (0.1) | 130.4 (92.3–168.4) | 15 |
| 13 | Pig | 22.3 (2.3) | 231.9 (213.6–250.1) | 4 |
| 14 | Pig | 20.2 (0.2) | 92 (62.2–121.7) | 17 |
| 15 | Pig | 17.7 (-2.3) | 39.3 (14.4–64.1) | 32 |
| 16 | Pig | 21 (1) | 70.8 (46.6–94.9) | 17 |
| 17 | Cattle | 5.5 (-3.5) | 3.7 (2.9–4.4) | 12 |
| 18 | Cattle | 9.1 (0.1) | 13 (4.1–21.8) | 35 |
| 19 | Cattle | 9.4 (0.4) | 14.3 (11.1–17.4) | 11 |
| 20 | Cattle | 10.5 (1.5) | 39 (32.5–45.4) | 8 |
| 21 | Cattle | 9.3 (0.3) | 12.2 (5.3–19) | 28 |
| 23 | Pig | 20.6 (-1.4) | 65.6 (25.6–105.5) | 31 |
| 24 | Pig | 21.4 (-0.6) | 79.1 (67.7–90.4) | 7 |
| 25 | Pig | 22 (0) | 147.6 (116.4–178.7) | 11 |
| 26 | Pig | 20 (-2) | 99.3 (91.8–106.7) | 4 |
| 27 | Pig | 18.1 (-3.9) | 28.9 (10.4–47.3) | 32 |
| 28 | Pig | 18.6 (-3.4) | 83 (71.2–94.7) | 7 |
| 29 | Cattle | 7.4 (-1.6) | 6.5 (-3.4–16.4) | 24 |
| 30 | Cattle | 8.8 (-0.2) | 7.1 (0.8–13.3) | 11 |
| 31 | Cattle | 9.7 (0.7) | 17.1 (14.7–19.4) | 7 |
| 32 | Cattle | 9 (0) | 29.3 (26.5–32) | 5 |
| 33 | Cattle | 10.7 (1.7) | 2.3 (0.7–3.8) | 32 |
| 34 | Cattle | 20.6 (-1.4) | 28 (24.8–31.1) | 6 |
| 36 | Pig | 18.9 (1.9) | 57 (54.8–59.1) | 2 |
| 37 | Pig | 19.4 (2.4) | 84.8 (68.1–101.4) | 10 |
| 38 | Pig | 16.4 (-0.6) | 25.3 (18.8–31.7) | 13 |

Generally, livestock liquid manure is richer in substrate nutrient as shown in Table 1.2.

Table 1.2 Cattle liquid slurry vs Pig in terms of Dry Matter and Volatile Solids, taken from Kupper *et al.*, 2020.

| Animal category | DM ^a | VS ^a |
|--------------------------------|-----------------|-----------------|
| Cattle lagoon | 17 | 3.7 |
| Cattle tank | 67 | 48 |
| Pig lagoon | 9.7 | 4.5 |
| Pig tank | 42 | 37 |
| Cattle solid liquid separation | 39 | 29 |
| Pig solid liquid separation | 29 | 23 |

The timely use of stored manures is core to efficiency and loss of emissions to the environment. However, slurries in Ireland and other such countries within the European Union are stored for a prolonged period of time in between spreading periods. This is in line with the nitrates directive which dictates spreading periods and can result in storage periods of up to 22 weeks (91/676/EEC). During this period of storage harmful greenhouse gases are emitted to the environment. Furthermore, this loss of gas to the environment also lowers the nutrient value of the slurry as a fertiliser for crop usage thereafter (Thorn *et al.*, 2022). Nitrogen is lost via NH₃ volatilisation which in turn increases the need for chemical fertiliser which is not only a cost to the producer but a further cause of damage to the environment in its production and use. Typical nutrient value of 1000 gallons of Dairy cow slurry comprises of 6 units of Nitrogen, 5 units of Phosphorus and 30 units of Potassium depending on variables such as timings and application method detailed in Fig 1.6 (Teagasc, 2022)

Table 1.3 Typical slurry nutrient value, taken from Teagasc, 2022.

| Typical N, P and K fertiliser replacement values of cattle slurries with varied levels of dilution | | | | | | |
|--|--------------------------|-------------|--------|---|---|----|
| DM% | Application Dilution | Application | | Fertiliser Value (units/ 1000 gallons) | | |
| | | Timing | Method | N | P | K |
| 7 | None | Spring | SP* | 6 | 5 | 30 |
| | | | TS/BS* | 10 | | |
| | | Summer | SP | 3 | | |
| | | | TS/BS | 6 | | |
| 5 | 1/3 water, 2/3 slurry | Spring | SP | 5 | 4 | 28 |
| | | | TS/BS | 7 | | |
| | | Summer | SP | 2 | | |
| | | | TS/BS | 5 | | |
| 3 | 2/3 water, 1/3 slurry | Spring | SP | 3 | 2 | 17 |
| | | | TS/BS | 4 | | |
| | | Summer | SP | 1 | | |
| | | | TS/BS | 3 | | |
| *SP = Splash Plate | | | | | | |
| *TS/BS = Trailing Shoe/Band Spreader | | | | | | |

1.12 Policy considerations

As a result of the Paris Agreement and more recent COP 26, there has been a number of key policies introduced at both a National and European level to aid its successful implication. Policies of relevance noted relate to addressing Natural and Synthetic means to reduce methane and associated GHG emissions from the Dairy herd.

1.13 European Union: Farm to Fork Deal

On the 11th of December 2019, the European Commission announced the Farm to Fork Strategy as part of the European Green Deal with the aim of addressing Climate Change and associated challenges related to the Environment. An Action plan was devised for the period 2020-2024 and includes the following targets of relevance:

- Production of food with positive or Neutral Environmental impact.
- European Union Strategy on Carbon Farming- introduced Green strategies to allow the sequestration of Carbon from the Food Chain
- The Promotion of a bio based circular economy
- Strategy to reduce excessive pesticide use and nutrient losses by 2030
- Reduce nutrient losses by 50% without adverse effect on soil health
- 20% reduction in the use of Chemical Fertiliser
- Increase of 25% in Organic Farming by 2030 (European Commission, Farm to Fork Strategy,2020).

1.14 Methane Strategy

As the second most significant contributor to Climate change, methane has its own Strategy specific to its mitigation within the European Union. It presents both legislative and non-legislative actions to help cut Methane Emissions. Specifically, regarding Biogas the following strategy points are outlined:

- Benefits of Biogas in Reducing Methane losses to the Environment
- Rural Development and Potential Revenues associated with Biogas Production
- The role of Digestate in displacing chemical fertiliser utilising fossil fuels in its production.
- Digestate as a mechanism to improve soil fertility
- Ultimately, provide information and support through policy to increase the development of a market for Biogas from sustainable feedstock such as Slurry or organic waste (European Commission,2020).

1.15 Circular Economy Action Plan

The European Union Circular Economy Action Plan was released in tandem with the EU Farm to Fork Strategy with the aim to develop the European economy away from linear value chains to a circular with the following objectives:

- Promotion of sustainable practices.
- Support a circular economy through the Bio Economy Action Plan
- Create a potential Regulatory framework to certify Carbon Removal through an accounting process to facilitate ongoing removal and verification of processes (European Commission, 2020).

1.16 Programme for Government

Each year the Government of Ireland sets out its strategy for the year ahead. In 2022, the Irish Government consisting of a coalition of Fianna Fail and Fianna Gael documented the following plan of Interest regarding Renewable Energy in the Agricultural Industry:

- Investigate Anaerobic Digestion as an opportunity for the Agri- sector
- Reduce the proportion of chemical fertiliser applications on land incrementally to 2030.
- Pursue a reform a restructure of the Common Agricultural Policy (CAP) to incentivise sustainable practices to improve biodiversity, quality of water and air and the production of renewable energy.
- Promote Carbon sequestration and environmentally beneficial practices.
- Promote farmer investment in infrastructure in the creation of renewable energy (Government of Ireland, 2022).

1.17 Common Agricultural Policy

The Common Agricultural Policy was first introduced in 1962 by six of the original founding countries with a view to create common guidelines in providing a steady supply of affordable, high quality and safe food for citizens within the EU. The CAP has undergone many reforms with the same goal dealing with differing environmental conditions each time. The period 2021-2022 presents a transitional policy regulation until the next agreed CAP is introduced for 2023-2027. The much anticipated document will set the future direction of

Farming within the EU with key areas summarised in Figure 1.7.



Figure 1.7 Objectives of CAP, Taken from European Commission 2022.

CAP reform agrees 25% of its funding to be allocated towards ECO-SCHEME farm payments.

Payments of relevance within this scheme include:

- Practices in the reduction of GHG from Farm activities
- Maintenance and development of carbon sequestration.
- Improvement of soil nutrients through a management plan
- Reduced nutrient losses
- Crop rotation to include those resilient to climate change such as Multi Species Swards
- Improved management of manure and storage facilities (KPMG,2021).

1.18 The Nitrates Directive and Derogation

European Directive 91/676/EEC sets out a limit to the amount of Nitrogen which can be applied to Agricultural land in each member state to 170kg of Nitrogen per hectare each year derived from livestock manure in nitrate vulnerable zones (NVZ). The resultant zones were decided by member states and Nitrogen Action Programmes (NAP) designed for each. In Ireland, the entire country has been designated to a vulnerable zone. The Nitrates Regulations make legal Ireland's programme of action for nitrogen usage.

Under this regulation, Ireland has been granted the right of derogation in 2018. This allows farms of intensive nature to operate at a higher stocking rate of livestock manure. Specifically, this is 250 kg of Nitrogen per hectare per annum. This is in accordance to compliance practices which allow the safe usage of this nitrogen. This programme was set to run out in 2021 but has since been further extended until 2025.

1.19 Directive II on Renewable Energy (RED II)

The European Union under the renewable energy directive have set out a number of guidelines for biofuel produced to be accepted as renewable. The Directive was reviewed and revised in 2018 and this new Directive is in play for the period 2021-2030. It sets out an ambition of energy produced from renewable sources of 32% by 2030. In relation to agricultural sets out the eligibility criteria for biofuel produced from agriculture to include:

- Agricultural feedstock must not be obtained from: Former Peat land, Land of high Biodiversity or Land of high carbon value such Wetlands or Forestry.
- Fuels used as an electricity source must facilitate a 70 saving of GHG, increasing to 80% where plants after 2026.

1.20 Thesis Outline

Therefore, this thesis sets out to explore how Renewable Energy can be utilised to reduce Methane emissions from the Irish Dairy herd. Background provided sets the precedence of its importance and how Renewable Energy sources such as Anaerobic Digestion and Pyrolysis may be utilised to reduce Methane and associated GHG emissions from the Dairy herd whilst also benefitting the circular economy. This will be explored at length throughout this thesis whilst acknowledging the important financial and political metrics involved in its implementation.

Chapter 2: Anaerobic Digestion and Digestate

2.1 Role of Biomethane

An energy rich gas, Biomethane gas is the by-product of anaerobic decomposition of biomass to produce a natural renewable energy source which can then be synthetically processed further to create energy. It consists mainly of methane (CH₄) and Carbon dioxide (CO₂) with smaller quantities of nitrogen (N₂), hydrogen (H₂), ammonia (NH₄) and hydrogen sulphide (H₂S) (Teagasc,2022). In Agriculture, the production of biogas plays a key role in securing sustainable farm practices. Methane, found in slurry and manure which would otherwise be lost to the atmosphere is trapped and converted into a renewable energy source. This not only reduces GHG emissions at farm level but also a potential commercial outlet for an otherwise negative by product of milk production from an environmental standpoint.

2.2 History of Anaerobic Digestion

The process and theory behind Anaerobic Digestion is not a new concept. First use of the process was first recorded over 1000 years BC where biogas created was used to create hot water in the bathhouses in Assyrian (Surendra *et al.*, 2013). Medieval alchemists were aware of the process creating pure Gas associated with digestion and putrefaction. However, it was the Scientist Alessandro Volta who looked at and isolated methane. This was on the back of previous studies by Bechamp, Pasteur, Soehngen, Bunsen and Hoppe-Seyler who recognised the metabolic pathways and microorganisms involved in the process of Anaerobic Digestion (King *et al.*, 1992).

The aforementioned Pasteur was the first scientist to suggest using the process of fermentation as a fuel source in 1884 with subsequent use to power the street lights in his native Exeter (Deublein *et al.*, 2011). Soon after one of the first Anaerobic Digestion plants was built in India acting a treatment facility for raw sewage which in turn provided power for a local leper asylum (Abbasi *et al.*, 2011). From here on, the concept grew in popularity, sparking the creation of many anaerobic ponds across the world.

The growth of Anaerobic Digestion was sparked in many areas of the world due to Global events. Two such events include World War 2 and the oil crisis of the 1970s where the process was seen as an alternative to fossil fuel generation. Here, agricultural waste was the predominant feedstock of choice (Lebuhn *et al.*,2014).

This trend has somewhat continued into the 21st century with ongoing global constraints of supply and climate pressures have brought about increased interest and growth in the industry. Today, the industry is posed for further growth and relevance as confidence in engineering

processing and technology have seen many government and private organisations promote the installation of the technology indigenously (Auer *et al.*,2021).

2.3 History of Anaerobic Digestion in Europe

2.4 Germany

Within Europe, Germany is the flagship for the use of Anaerobic Digestion, posing the highest production of Biogas with 8000 plants that produce in excess of four gigawatts of energy per annum (Auer *et al.*, 2021). The uptake of the technology has increased significantly since the 1990s where the first commissioned sites had a combined capacity of 300 megawatts. By 2006 production capacity had increased to over 3 gigawatts (Auer *et al.*,2021). Where Electricity is one of the most common end uses for Biogas, in Germany the majority of energy produced is destined for combined heat and power (CHP). Heat produced is destined for Industrial uses where CHP sites can create finished energy product with an efficiency of 750-900 J kJ-1 through the conversion of biogas (Zuber, 2012). Just 1.7% or 151 of German plants further process biogas to Biomethane.

Biogas plants produce in excess of 23 J kJ-1 of Germanys total energy output and a further 230 J kJ-1 from other renewable sources which accounts for 41.1 % of total Energy produced (Auer *et al.*, 2021). The growth in the uptake of Bio digestion in Germany is greatly attributed to the German Governments strategy in the support of renewable energy processes.in 2000, the Government introduced Feed in tariffs which guarantees an above average price for producers who supply the creation of renewable energy whilst guaranteeing a steady supply of feedstock for the plant. The EEG Renewable energy legislation guaranteed plants a stable and consistent fee for twenty years and given priority of supply to the National Grid (Gesetz für den Vorrang Erneuerbarer Energien, 2000). Priority was also given to Germanys “Smart Grid” technology which consisted of a power grid which was bi-directional, allowing private operators of medium and small size to feed any surplus power back to the grid (Aureur *et al.*,2021). From this legislation, a consistent construction phase of plants was created, averaging 240 plants per annum.

Further amendments to this legislation have further encouraged the construction of more plants in Germany. In 2004, farmers/producers who provided energy crops as feedstock were granted a bonus under a renewed EEG legislation for the CHP industry. Between 2004 and 2009, a further 450 plants were constructed each year in response to this legislation (Scheftelowitz *et al.*, 2015). 2009 brought about an increased focus on the Environment with bonuses paid the

use of manure as feedstock, uptake of new technologies and the reduction of emissions. This brought about an additional 1000 plants each year (Auer *et al.*, 2021).

Today's legislation in Germany looks to further develop its supply chain of feedstock and help diversify farming practices. This is encouraged through the construction of large Anaerobic Digestion facilities with a large capacity to hold feedstock, not just from animal manure but from energy crops such as Maize and other cereal crops. Typical substrates/ feedstock today consist of: Maize Silage, liquid manure, solid manure, grass silage, whole crop silage and derivatives of other cereal grain, fodder and rye. This has seen a switch of practice to many farms in Germany as although agricultural by products are fed into the system, many farmers are now growing crops specifically designed as feedstock to the system. Dedicated arable land to this practice is estimated to consist of 23 billion square meters of land or 1/5 of Arable land in Germany (Scheftelowitz *et al.*, 2015).

However, further change was necessary in 2011 to make a switch back to smaller plants as it became apparent that large scale plants may not be profitable without government aid which encouraged farmers to produce extra crops, increasing monocultures and reducing biodiversity. The resulting legislation discouraged large scale bio digestion through limiting supply. For example, processing plants must now use at least 60g kg feedstock as manure, limit energy crop Maize to 600g kg per annum or use at least 600 J Kj of the heat generated from the process. This new legislation has limited new plant construction to 340 per annum (Auer *et al.*, 2021).

The latest legislation updated in 2015 further echoes this requirement as new plants established since and including 2015 receive reduced feed in tariffs for large scale plants. New entrants to the Anaerobic Digestion Industry cannot exceed 100 MW per year. Furthermore, smaller scale plants which are smaller than 75kW and utilise manure as feedstock receive a higher subsidy above those of other plants. Today almost 10% of all power produced in Germany derives from the Anaerobic Digestion process (Auer *et al.*, 2021). Therefore, the drive of Anaerobic Digestion today is largely focused on the smaller plant which utilises natural feedstock such as Dairy manure as a by-product rather than Feedstock specifically grown for the process, reducing biodiversity in the process. (Auer *et al.*, 2021).

2.5 Ireland

In comparison to Germany, Ireland has not reached the same heights as the country is still very much reliant on imported energy to power the country circa 900 J Kj (Auer *et al.*, 2021). This is far from the 160 J Kj targeted for 2020 which the country has not met. In 2013, renewable

energy sources accounted for just 33 JkJ of total energy produced (28.53bn kWh in total). Of the renewable energy sources utilised in Ireland, wind energy holds the majority at 16 J kJ of total demand (Dineen *et al.*, 2015). Biomass energy inclusive of landfill, biogas and solid biomass was responsible for just 11 JkJ of consumed energy, mainly derived from landfill generators of gas (Auer *et al.*, 2021).

In 2006, the Irish Government through the Department of Communications, National resources and Energy developed a Renewable Energy Feed Tariff programme (REFIT) to support the growth of renewable energy sources (RE-FIT, 2006). Part 3 of the program indicated the fundamentals regarding a 15-year plan for Anaerobic Digestion. Here, an obligation was placed on the National Grid energy of renewable energy source at a set price. However, uptake was considerably low in comparison to Germany due to a lower rate of tariff offered and local constraints. In terms of economics, to break even Irish Anaerobic Digester plants needed to charge waste producers a gate fee from €50 to €80 for every 100kg of feedstock delivered (Singh *et al.*, 2010). Such a gate fee was seen as a significant deterrent for farmers who may simply chose to use the waste slurry as fertiliser. These fees also were not regulated, bringing further confusion to an already distorted market.

As a result, only 10 biogas plants exist in Ireland today accepting animal by products (31 in total). Anaerobic Digester feedstock in Ireland availability includes slurry and manure from agriculture as well as Silages both maize and grass, which are subject to a gate fee. Therefore, although the livestock potential to produce feedstock is high, uptake of Anaerobic Digestion utilisation is very low in Ireland. With the Irish Dairy sector alone accounting for in excess of 1.5 million animals, potential feedstock is plentiful.

Most recently, commenting on the 5th of July 2022, Teachta Dála Christopher O’Sullivan for Fianna Fail through their official website has proposed the drafting of a National Strategy for Anaerobic Digestion titled “Anaerobic Digestion Bill 2022” (Fianna Fail, 2022). The proposed bill which if ratified by government proposed to streamline the Renewable Energy sector removing the current obstacles in establishing and running an Anaerobic Digestion facility today.

2.6 Anaerobic Digestion

Anaerobic digesters pose the technology to create biogas on a commercial scale in Ireland (Figure 2.1). In this natural process, microorganisms convert biodegradable material into

biogas through the creation of an anaerobic environment. Microorganisms present include hydrolytic, acetogenic, fermentative and methanogenic bacteria (O'Connor *et al.*, 2020).

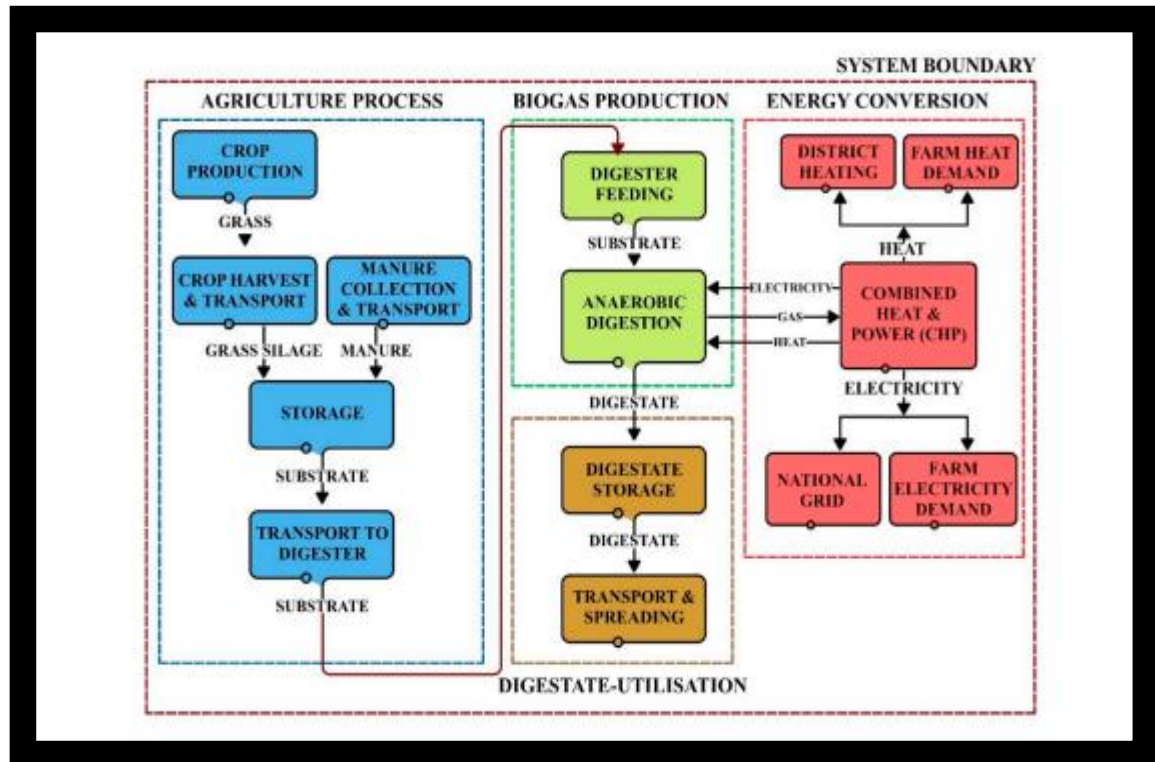


Figure 2.1 Applications of Anaerobic Digestion to Ireland, taken from O'Connor *et al.*, 2020.

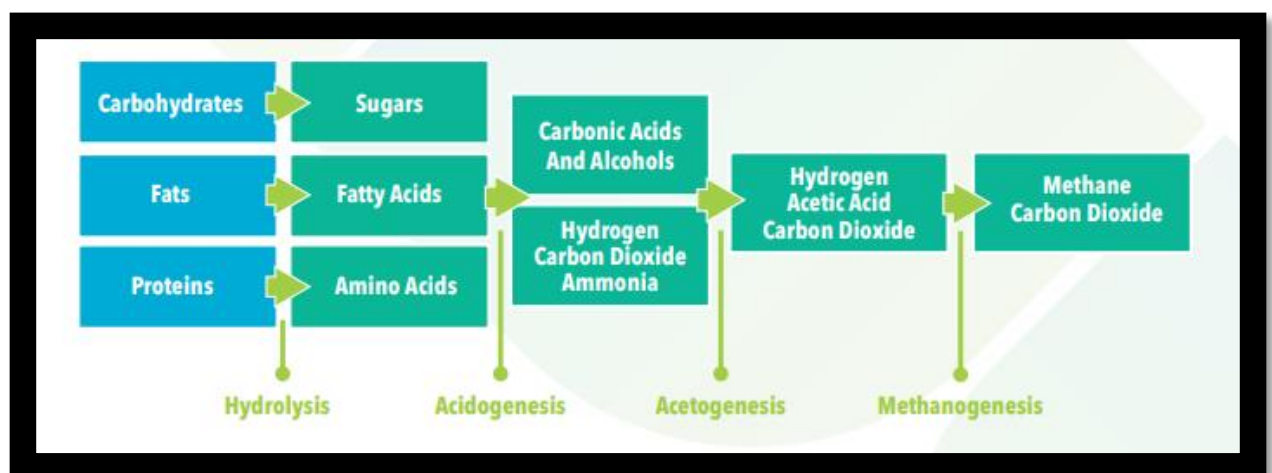


Figure 2.2 Four stage process of Anaerobic Digestion, taken from Weinrich *et al.*, 2021

2.7 Hydrolysis

Hydrolysis is the first stage of Anaerobic Digestion in which molecular polymers consisting of those such as Carbohydrates, Protein and fats are broken down into their simplest form (Figure

2.2). This is achieved through the action of the enzyme hydrolase which catalyses hydrolytic cleavages of the chemical bonds. The portion of amino acids, sugars, glycerine and long-chain fatty acids will depend on the substrate available during the process (Sanders *et al.*, 2001). Substrate availability and usage will also determine the time it takes for hydrolysis to occur. Dairy cow manure which is a dissolved organic compound is available for direct use in fermentation process. Where more complex substrates are present, the rate of hydrolysis has been noted as the most limiting factor to the rest of the process (Weinrich *et al.*, 2021). Thus, correct substrate choice is of vital importance. Hydrolysis therefore facilitates the degradation of dissolved intermediates and makes them available for absorption in the cell membrane of microorganisms where further processing can then take place (Pavlostathis *et al.*, 1991).

2.8 Carbohydrates

Carbohydrates are formed through the linkage of monosaccharides to form complex oligosaccharides and polysaccharides (Mortimer *et al.*, 2007). From an Agricultural standpoint, the majority of carbohydrates present will be in the form of long chain polysaccharides such as cellulose and starch, the carbohydrate present in many forages including straw. During hydrolysis, these complex carbohydrates are broken down into their basic monomeric units (Fig 2.3).

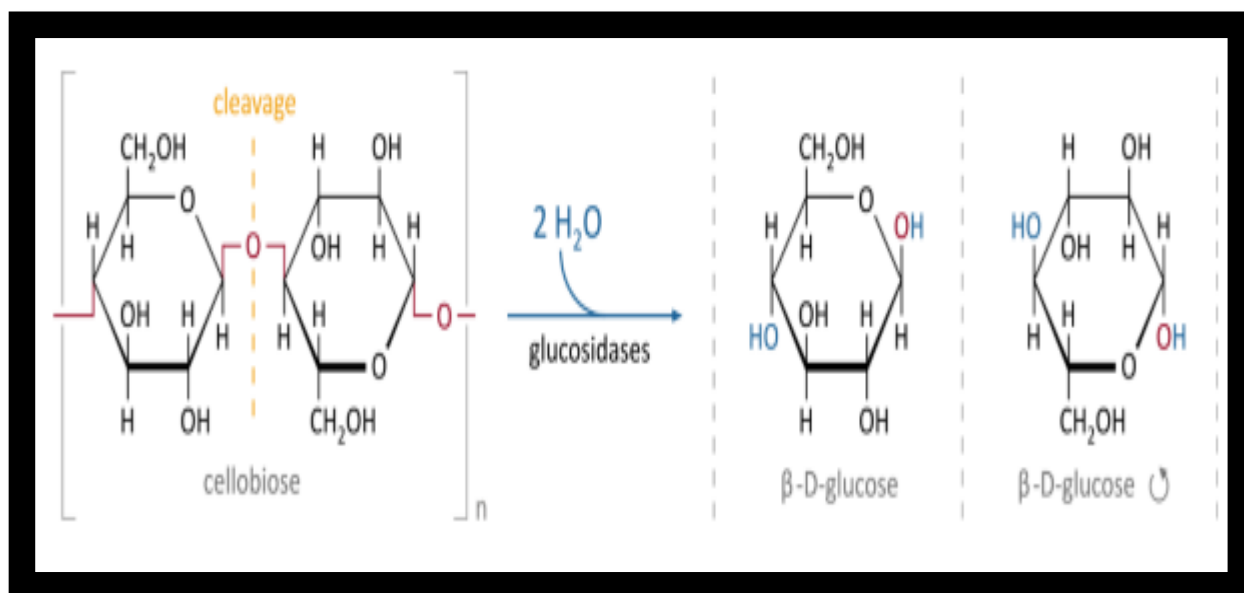


Figure 2.3 Hydrolysis of Cellobiose, taken from Weinrich *et al.*, 2021

Moreover, simple disaccharides such as maltose or sucrose can be broken down quickly. This is in contrast to many Agricultural substrates containing pectin or cellulose to which the process is considerably slower. Indeed, many products which contain compounds which are

lignocellulose cannot be completely hydrolysed, due to lignin's inability to be split anaerobically (Weinrich *et al.*, 2021).

2.9 Proteins

Proteins have been described as the building blocks of life formed through the linkage of amino acids. Amino acid sequence determines the type of protein formed in terms of structure and properties. Hydrolysis of proteins include the enzyme protease which acts on the protein to split it into amino acids and polypeptides (Fig 2.4) (Berg *et al.*, 2007). Similar to carbohydrates, the rate of breakdown is dependent on the type and structure of protein present.

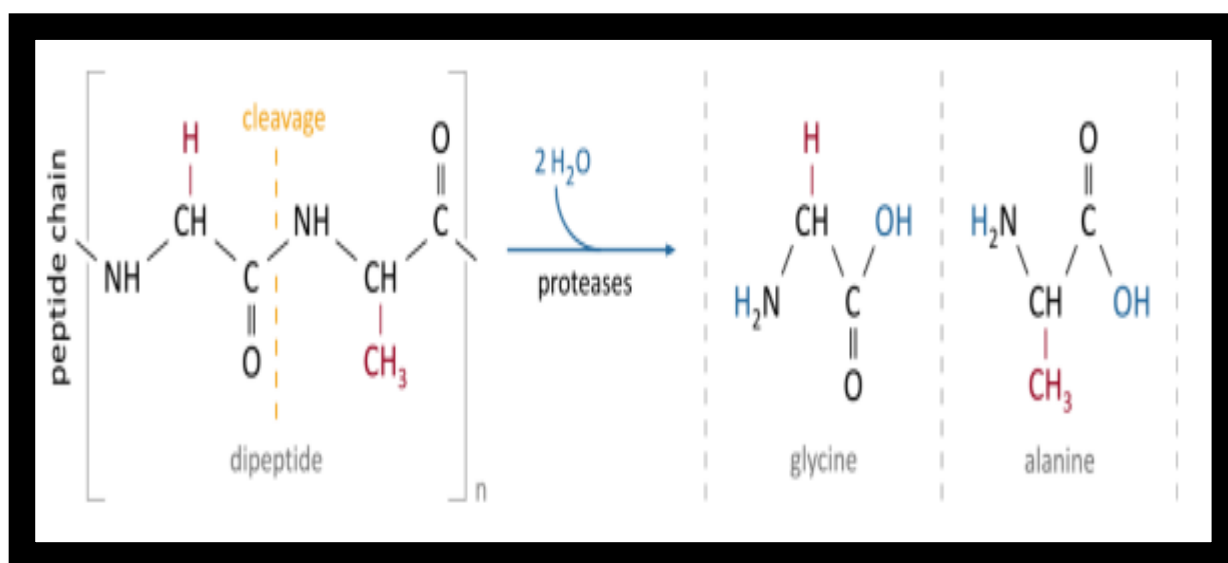


Figure 2.4 Hydrolysis of Protein, Taken from Weinrich *et al.*, 2021

2.10 Fats

Esters of Glycerol, fats consist of long chain fatty acids. The vast majority of natural fats in this context are a mix of triglycerides where each hydroxyl group of the glycerol is esterified with a fatty acid (Mortimer *et al.*, 2007). The enzyme lipase, splits the fat molecule into long chain fatty acids and Glycerol during hydrolysis (Fig 2.5). conversely to proteins, fats can be hydrolysed entirely at low decomposition rates (Weinrich *et al.*, 2021).

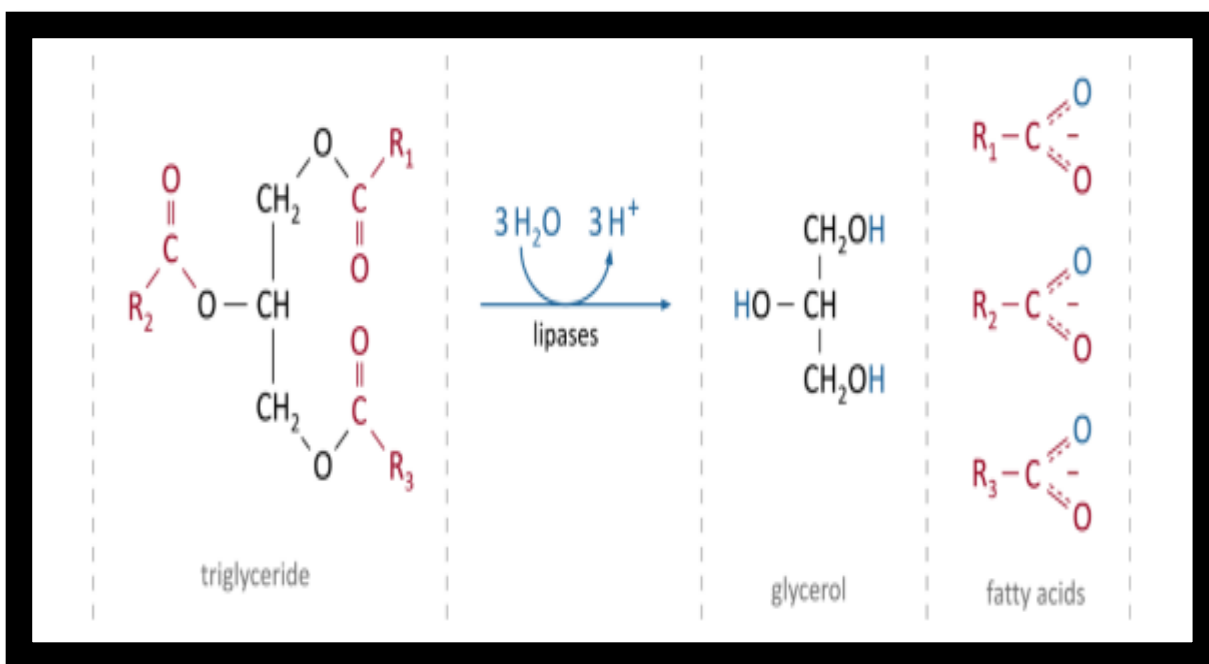


Figure 2.5 Hydrolysis of Fats, Taken from Weinrich *et al.*, 2021

2.11 Acidogenesis

Acidogenesis is the second stage in the biogas formation process. In this stage, products which have been hydrolysed are fermented by bacteria to produce carbon dioxide, short-chain organic acids, hydrogen, ethanol, hydrogen sulphide and ammonia. During this process, metabolic by products from prior degradation are converted to carbon dioxide, acetic acid and hydrogen. The rate and degree of degradation is determined by the environment present along each metabolic pathway. Such factors include temperature and hydrogen partial pressure.

2.12 Monosaccharides

Glucose is one of the most famous examples of a Monosaccharide and will be used for reference when speaking of Acidogenesis of Monosaccharides. This process requires Energy and is obtained through glycolysis where the substrate undergoes phosphorylation. The substrate is oxidised moving electrons along the carrier molecule NAD which generates energy necessary to regenerate ADP to ATP (Weinrich *et al.*, 2021). Figure 2.6 illustrates this process, catalysing the monosaccharide glucose to propionate, butyrate and acetate.

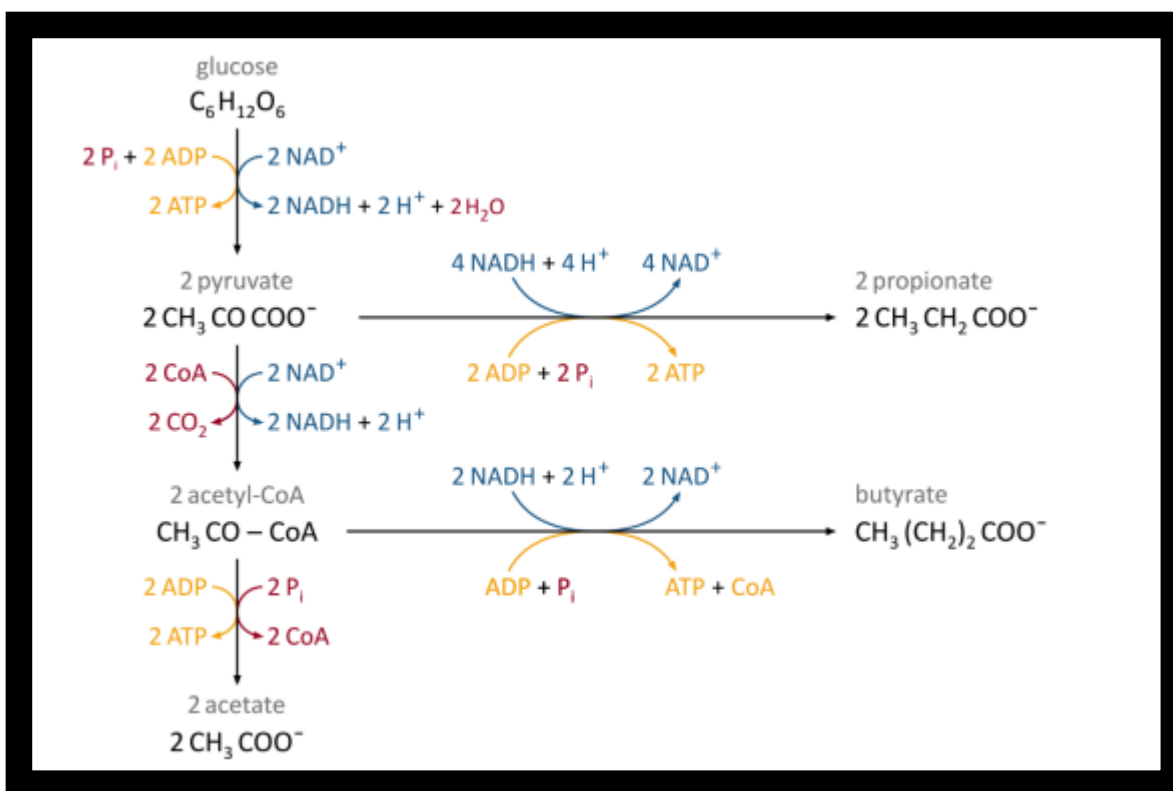


Figure 2.6 Fermentation of Glucose to form Propionate, butyrate and acetate, taken from Weinrich *et al.*, 2021

2.13 Amino Acids

The breakdown of amino acids by Acidogenesis takes place anaerobically in pairs through the Stickland reaction or solely through the dehydration of an amino acid via external electron acceptors (Ramsay *et al.*, 2001). As the Stickland method is a faster mode of degradation it is often favoured in the processing of biogas. Depending on the structure and concentration of the amino acids, varying short-chain fatty acids, hydrogen, ammonia, carbon dioxide and hydrogen sulphide, although less frequent can be produced.

The Stickland procedure is a redox reaction. An amino acid is oxidised and placed with a reducing amino acid. This is to allow different amino acids to participate during the process to act as electron acceptors or donors (Weinrich *et al.*, 2021). In a series of reactions, the amino acids undergo degradation via decarboxylation and deamination to create energy (ATP) as illustrated in Figure 2.6. During the oxidation process Carbon Dioxide and Ammonia are created along with carboxylic acid in degrading alanine to acetate. The amino acid which utilises hydrogen (Glycine Figure 2.7) is reduced down to ammonia and carboxylic acid in turning Glycine to acetate (Weinrich *et al.*, 2021).

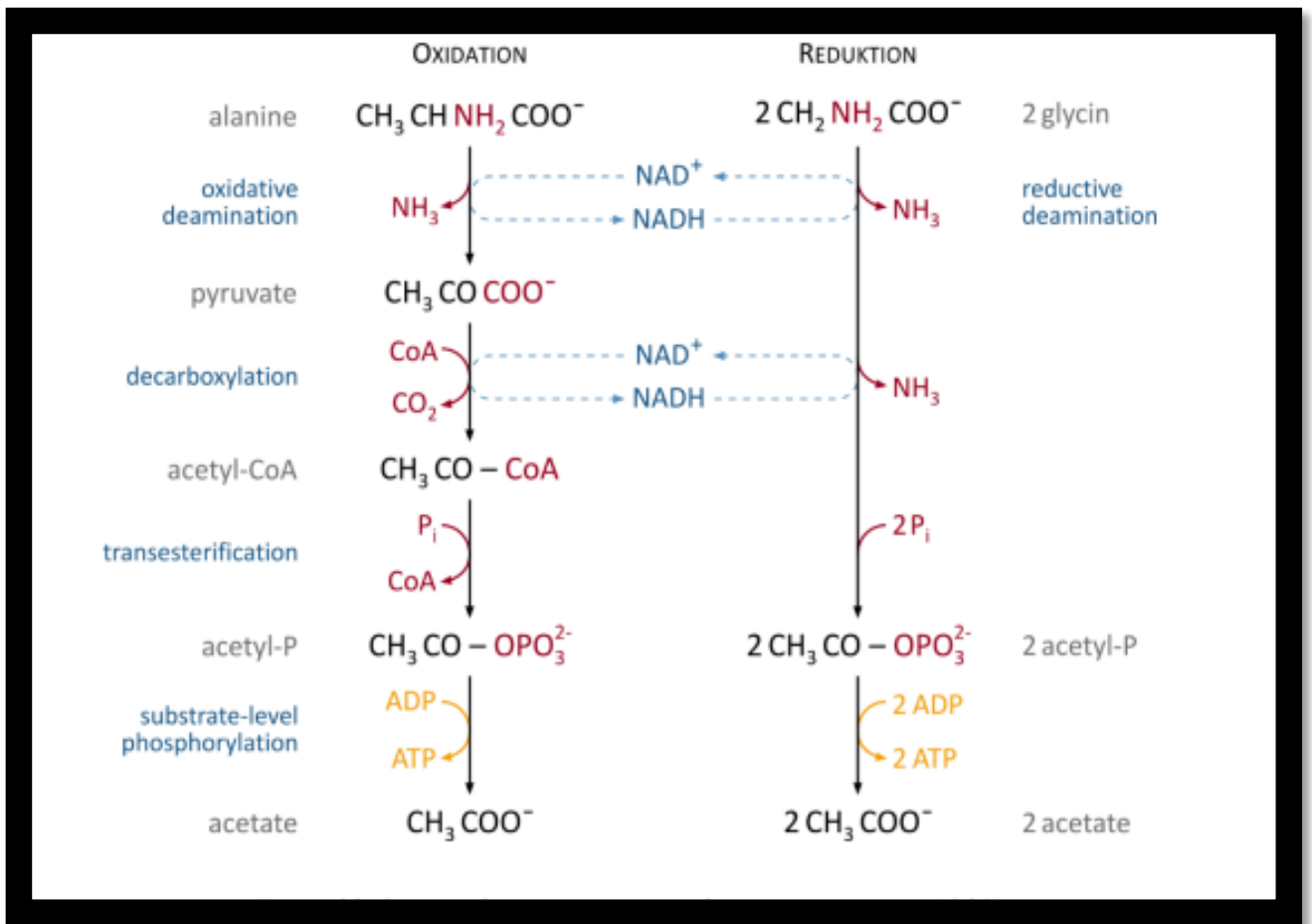


Figure 2.7 Stickland reaction of alanine and glycine to produce ATP, taken from Weinrich *et al.*, 2021

2.14 Long Chain Fatty Acids

Beta oxidation is used to break down long chain fatty acids via Acidogenesis. This process is depending on the number of carbon atoms and configuration of double bonds presented. Configuration will determine the compound formed. Where even chained fatty acids undergo Acidogenesis, acetic acid is produced. Whereas odd chains will produce propionic acid (McInerney *et al.*, 1981). To facilitate degradation of fatty acids by microbes, fatty acids are synthesised by catalytic Acyl-CoA to form an energy dense thioester bond with the carboxyl group from the fatty acid and Co Enzyme A which creates Acyl-CoA. In the process of beta oxidation, the fatty acids activated are decreased by two carbon atoms each reaction during the cycle via thiolysis, hydration and oxidation as seen in Figure 2.8.

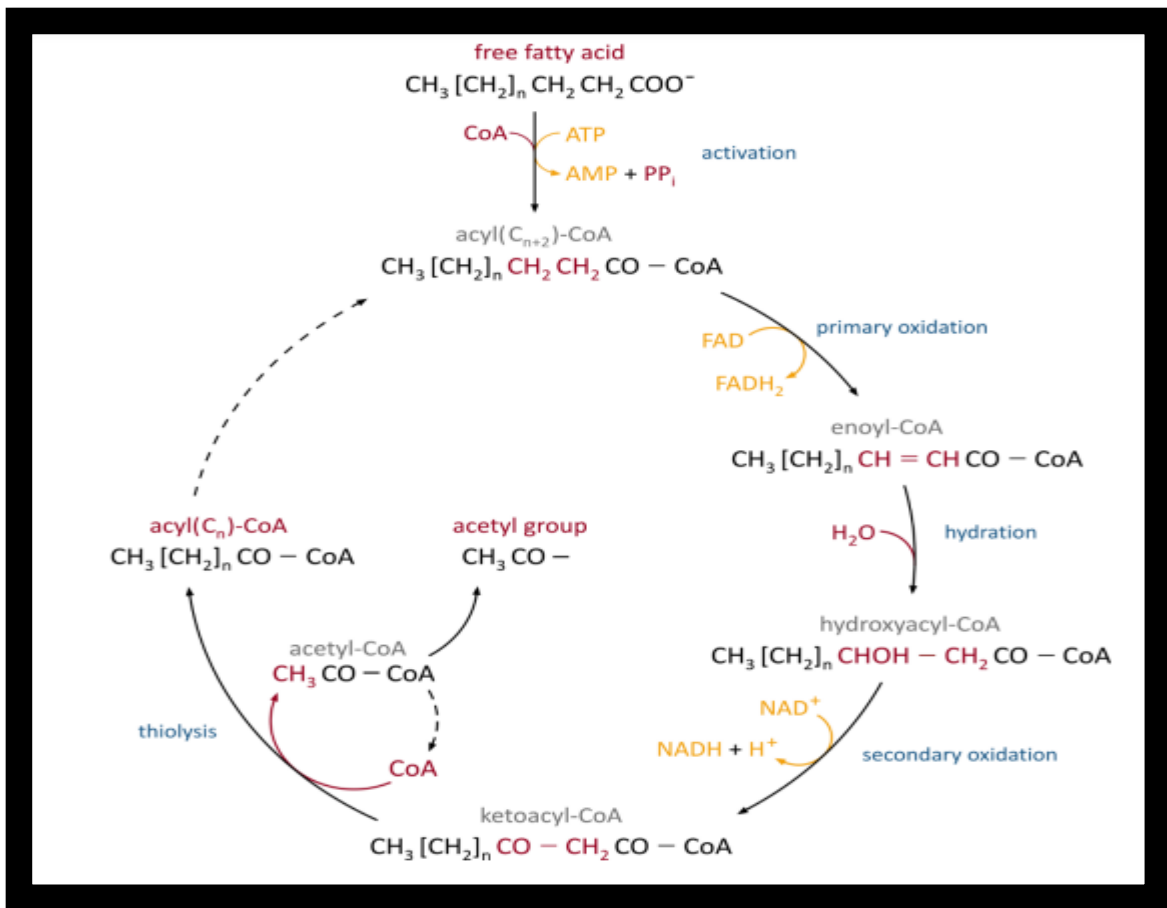


Figure 2.8 Beta Oxidation of Long Chain Fatty Acids, Taken from Weinrich *et al.*, 2021

2.15 Acetogenesis

The third step of Anaerobic Digestion is Acetogenesis. Here, the products of fermentation such as alcohols and organic acids undergo a process in the conversion to carbon dioxide, hydrogen and acetic acid. In order to produce acetic acid and oxygen, carbon is needed for acetogenic bacteria. Oxygen bound or that solved in solution is used to aid this process. This allows the bacteria which produce acid to create an environment free from oxygen. This is an essential step to facilitate the methane producing microorganisms in the fourth step of anaerobic digestion: Methanogenesis (Weinrich *et al.*, 2021).

2.16 Methanogenesis

Methanogenesis is the final stage of Bio Gas formation. Here, obligate anaerobic bacteria create methane, carbon dioxide and water through the conversion of acetic acid, carbon dioxide and hydrogen. There are a number of possible formation pathways: via carbon dioxide reduction with formate, disproportionation using methanol or methylamines (Chynoweth *et al.*, 1996). However, commercially the predominant mode of formation is via acetoclastic and

hydrogenotrophic methanogenesis. 70% of which is formed via degradation of acetic acid and the remaining 30% through hydrogen reduction of Carbon dioxide (Smith, 1966).

2.17 Supply of Nutrients

In order for the above process to take place, an adequate supply of nutrients is necessary to feed both the aerobic and anaerobic microorganisms in the conversion of biomass to biogas. A reduced supply of nutrients will have a detrimental effect on output resulting in decreased microbial growth, high levels of acid concentration and ultimately an unstable growth environment (Demirel *et al.*, 2011). Figure 2.9 illustrates nutrients deemed essential for the process. A diverse range of nutrients has been noted of importance due to the lack of diversity observed from feedstock derived from energy crops such as cereals or maize (Pobeheim *et al.*, 2010). Therefore, a substrate source containing a diverse range of nutrients and micronutrients is deemed favourable to allow constant and stable processing conditions.

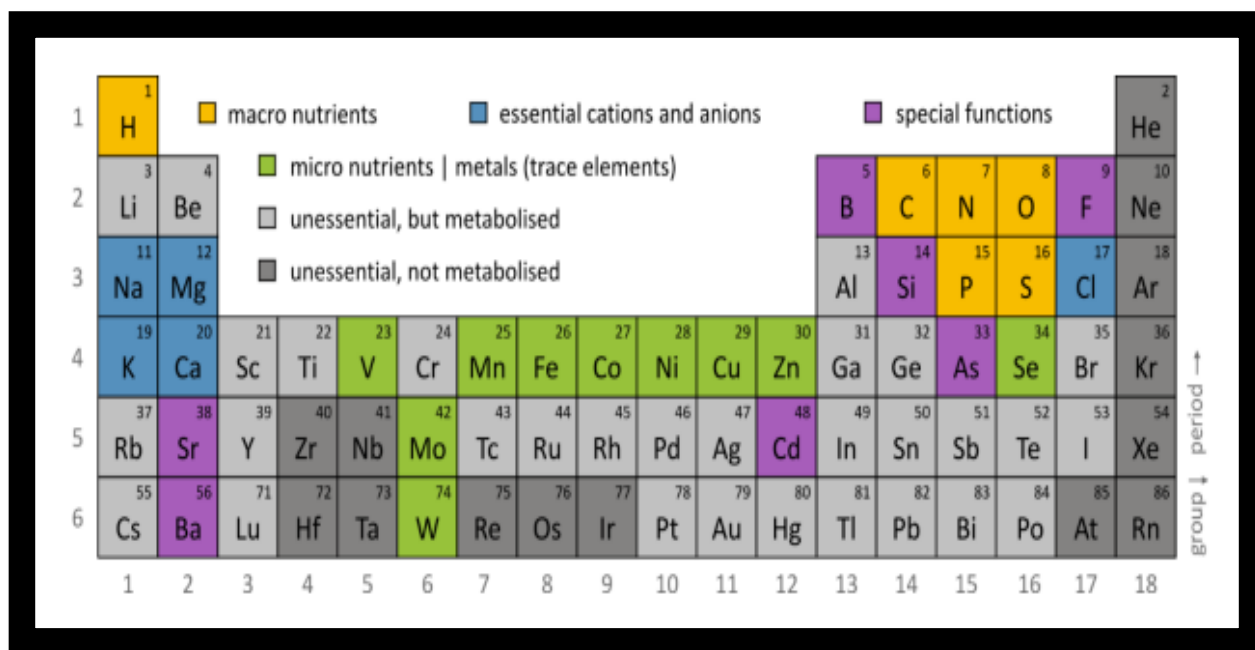


Figure 2.9 Essential Nutrients for Biogas Production, taken from Weinrich *et al.*, 2021.

2.18 Macronutrients

Macronutrients are defined as those required in large amounts for ongoing stable processing to feed the microorganisms. Macronutrients are those directly involved in the synthesis of ATP and NADP described above in the formation of critical cell material. Table 2.1 summarises the most important Macronutrients and their role in Bio Gas Formation.

Table 2.1 Essential Macronutrients, taken from Weinrich *et al.*, 2021

| Macronutrients | |
|----------------|--|
| C | <ul style="list-style-type: none">• Essential component of cell material ^{a,b,c}• Main energy source of microorganisms ^{b,c} |
| N | <ul style="list-style-type: none">• Component of many proteins, nucleic acids and enzymes ^{b,c,d} |
| P | <ul style="list-style-type: none">• Synthesis of energy carriers ATP and NADP ^{c,d}• Component of many nucleic acids, phospholipids and enzymes ^{a,b,c} |
| S | <ul style="list-style-type: none">• Component of the amino acids cysteine and methionine ^{a,d}• Cofactor and component of many enzymes ^{a,b,c} |

2.19 Cations and Anions

Essential cations and Anions are summarised below in Table 2.2.

Table 2.2 Role of essential Cations and Anions, Taken from Weinrich *et al.*, 2021

| Cations and Anions | |
|--------------------|---|
| K | <ul style="list-style-type: none">• Supports nutrient transport and energy balance ^{b,c}• Important inorganic cation ^{a,b,c} |
| Ca | <ul style="list-style-type: none">• Component of exoenzymes (amylases and proteases) ^a |
| Mg | <ul style="list-style-type: none">• Cofactor and activator of many enzymes ^{a,c}• Component of ribosomes, membranes and cell walls ^a |
| Na | <ul style="list-style-type: none">• Formation of ATP (sodium-potassium pump) ^{c,d}• Nutrient transport within the cell ^{a,c} |
| Cl | <ul style="list-style-type: none">• Important inorganic anion ^a |

2.20 Trace Elements

There are a wide variety of micro nutrients which play a key role in co factors associated in the production of Biogas. Metals, Iron and Manganese act as an electron acceptor during redox reactions. They also help minimise inhibition of the anaerobic degradation stage through the precipitation of sulphides (Oleszkiewicz *et al.*, 1990). They play a vital role in the metabolism of the microbial microflora even at small quantities, there impact is significant.

Previous studies have shown a great variation in trace elements based on the substrate available (Schattauer *et al.*, 2011). Studies have shown higher nutrient concentrations present during the fermentation process of complex residues such as Dairy slurry (Schattauer *et al.*, 2011). Micronutrients which are often lacking from substrate include: iron, selenium, cobalt, tungsten molybdenum or nickel (Banks, 2012). Where these nutrients could be added to the substrate, production stabilised and output increased significantly. However, conversely, should trace element content be sufficient and additional volumes introduced to the environment, lower growth rates are observed due to reduced microbial activity as illustrated in figure 2.10 (Facchin *et al.*, 2013).

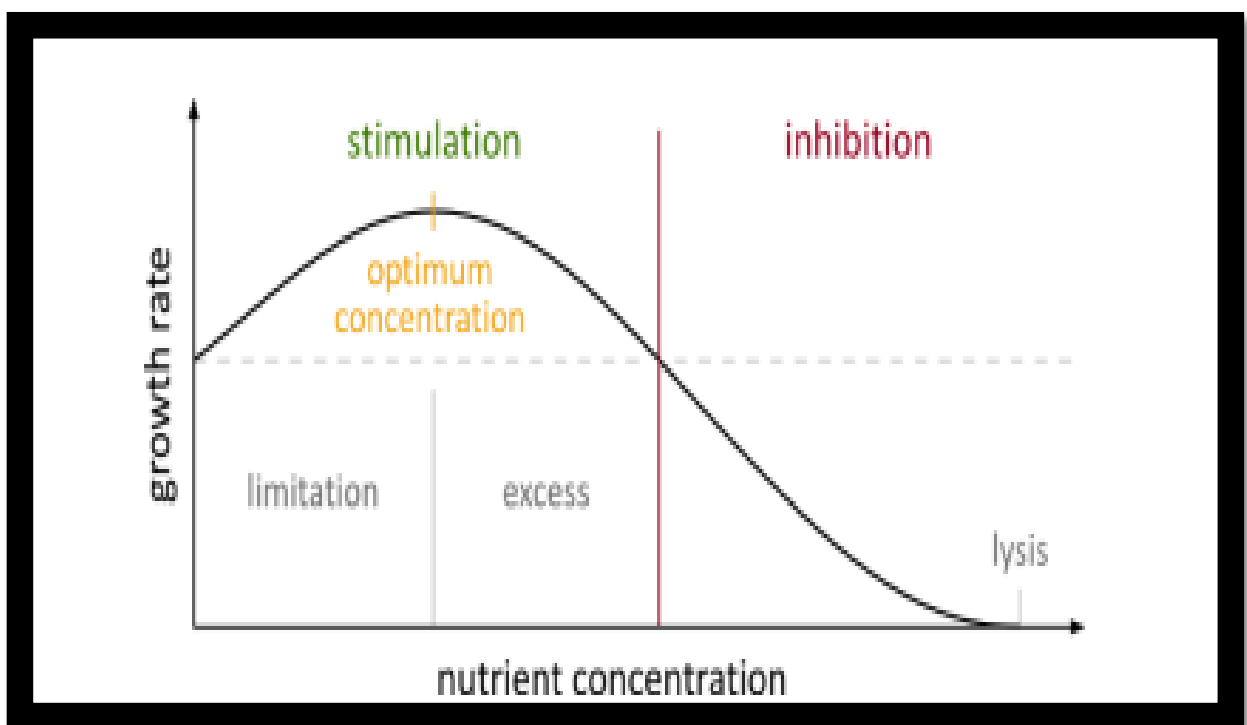


Figure 2.10 Optimum Trace Element Content schematic, taken from Weinrich *et al.*, 2021.

2.21 Irish Agricultural Feedstock

2.22 Slurry and Manure

Ruminants (Dairy animals) produce a large amount of methane daily. This is estimated to be in the region of 250 dm³ of methane daily (Leytem *et al.*, 2011). Studies have highlighted the importance of feed additives in reducing methane in the dairy animal. However, this can be difficult to gain clarity at farm level as results are not visible to the eye. Therefore, the proper management of the by-product of Digestion in the animal i.e. Manure poses a viable option to reduce their impact on the environment (Uddin *et al.*, 2020). Typically, on an Irish Dairy Farm, manure is stored in the form of Mixed Manure with straw or liquid slurry collected in a tank

below a slatted shed. Ireland produce 100 million tonnes of slurry each year of which 40 million tonnes is captured via underground storage (Teagasc,2022)

2.23 Multi Species Swards as Feedstock for Anaerobic Digestion

Multi species swards (MSS) have gained an increased interest in the Agricultural sector due to its additional benefits in its integration to the grazing platform such as increased animal performance and natural anthelmintic properties (Teagasc,2022). They consist of a variety of plant species from a variety of families such as grasses, clover, herbs and brassicas. However, there also poses an important opportunity in the utilisation of MSS for their benefit to the environment. Primarily, the use of MSS boasts the benefit of reduced fertiliser requirement. Specifically, where a MSS consists of 20-50% clover inclusion, chemical fertiliser applications can be reduced by 50% in that field in the Dairy rotation (Teagasc,2022). From an environmental standpoint, GHG emissions are reduced in turn as harmful Ammonia and Methane emissions are produced in the production and subsequent application of the fertiliser (Teagasc,2022). Figure 2.11 outlines the potential fertiliser saving comparing standard perennial ryegrass as the standard grass type used on commercial dairy farms today (KPMG,2021).

| SWARD | NITROGEN APPLICATION (KG N/HA/YR) |
|--------------------|-----------------------------------|
| Perennial ryegrass | 170 |
| Permanent pasture | 135 |
| 6 MSS | 70 |
| 12 MSS | 70 |

Figure 2.11 Difference in Fertiliser applications comparing MSS to standard pasture type, Taken from KPMG 2021.

Furthermore, there lies an opportunity for MSS to be used as a feedstock due to their favourable yields and where surpluses occur in times of additional growth on the farm during the grazing

season. A report by KPMG researched the potential of MSS as feedstock on a commercial farm in Dowth Co Meath. In terms of yield, they found that MSS had the potential to out yield traditional Perennial Rye Grass (PRG) by an average of 2t Dry matter (DM) per hectare (ha). Furthermore, a total chemical nitrogen reduction of 100 kg Nitrogen per ha was achieved. This also holds an economic saving of 80€ per hectare based on current cost of chemical nitrogen as of 23/07/22 (Glanbia,2022). This was attributed due to natural nitrogen fixation contributed by legumes present in the MSS. The use and uptake of MSS on Dairy farms has been encouraged and incentivised through industry in Ireland. For example, Glanbia Co-Op offer farmers an extra .25c per litre produced to sow MSS in conjunction with 6 other sustainable actions as part of their sustainable action plan for Dairy Farming (Glanbia,2022).

2.24 Anaerobic Digestion and The Circular Economy

In line with EU Circular Economy action plan, Anaerobic Digestion and its by products hold potential to create and sustain a circular economy with reduced reliance on a linear based model. The traditional linear economy is disposal in nature where resources are produced, utilised and disposed of. Conversely, a circular economy sets out to utilise resources for as long as possible, taking maximum value from them whilst in use and at the end of each cycle, resources are reused and regenerated where possible (Blades *et al.*,2017). The key principles circular economy involve preserving and enhancing natural capital, optimal yields from resources used and adopt efficiency and effectiveness of system (Blades *et al.*,2017). Figure 2.12 details how Anaerobic Digestion may be adopted in the promotion of a circular economy through optimal use of resources produced.

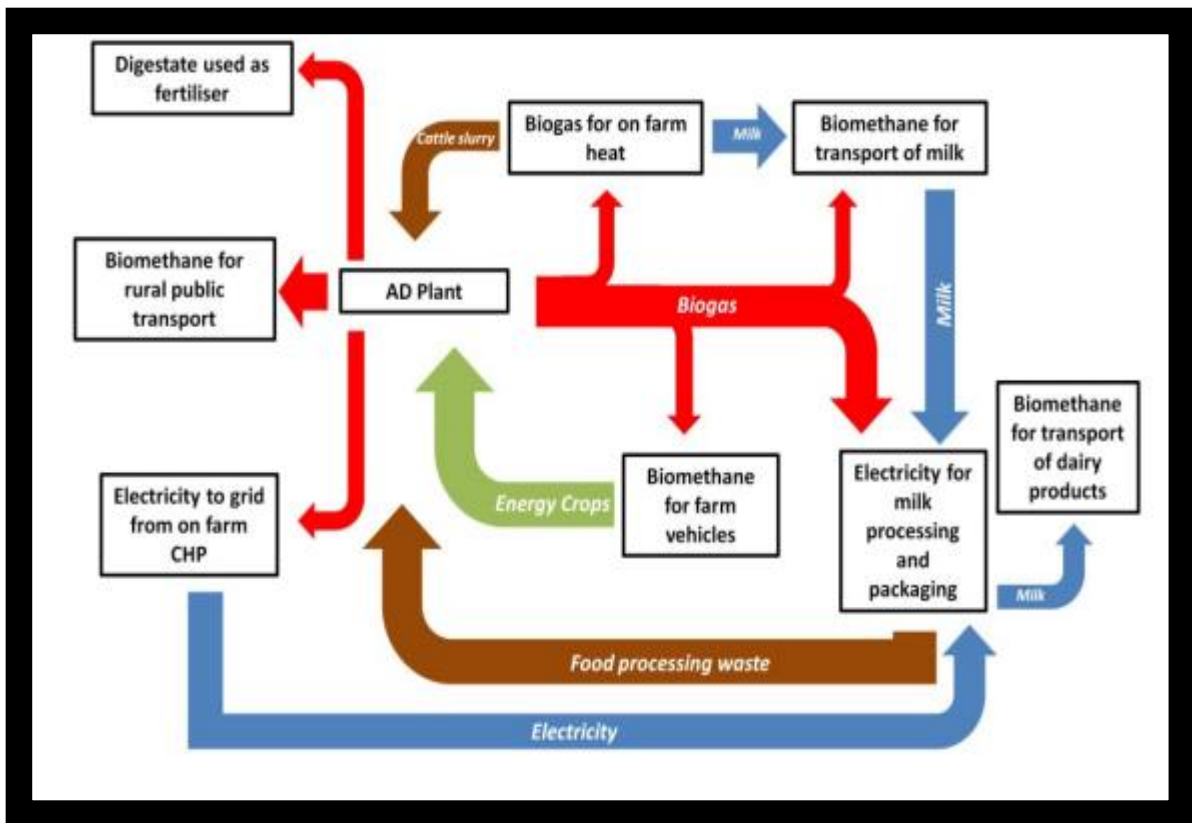


Figure 2.12 Anaerobic Digestion and the Circular Economy, taken from Blades *et al.*, 2017.

Dairy farms supply feedstock through Energy crops and slurry to produce Biomethane and electricity. This energy may thereby be used in the local community through fuelling of farm vehicles and local industry. Furthermore, electricity produced may be reused on farm, local industry and in the home. In addition, Digestate as a by-product of production may be used as a fertiliser in crop production, regenerating the cycle once more (Blades *et al.*, 2017).

2.25 Digestate

Typically, Digestate has been viewed as somewhat of a waste product of the Anaerobic Digestion process with many operators historically paying for its disposal. However, it has become apparent that Digestate poses as a significant material as an organic fertiliser for Irish Grassland management. This aligned with current European Farm to fork legislation whilst reducing costs and emissions produced in the production of chemical fertiliser. Fertiliser value is dependent on feedstock used and its availability.

2.26 Chemical Composition of Digestate

Literature has attributed varying replacement rates of chemical fertiliser with digestate from 15 to 100% (McCabe *et al.*, 2019). Differing processing techniques have shown differences in digestate quality. For example, nutrient quality of availability has been reported to improve

where solid liquid separation processing techniques have been used (European Biogas Association,2014). In processing, Nitrogen (Organic) is released from the feedstock as ammonium and is available for plant nutrient uptake. Livestock slurry has the highest Nitrogen concentration in comparison to raw slurry (Vaneekhaute *et al.*,2017). The Anaerobic digestion process does not have a huge impact on Phosphorus availability versus average animal slurry feedstock. However, the process has been recorded to increase the availability of available Phosphorus to the plant roots.

With repeated land use, studies have shown up to an 80% of chemical fertiliser reduction (KPMG,2021). Unlike chemical fertiliser, response to application is not instant and a period of adaption is required for growth to occur (Vaneekhaute *et al.*,2017). Other nutrients of note including Potassium, Magnesium, sulphur and calcium are not impacted by the Anaerobic Digestion process and therefore their nutrient value is much dependant on the nature of the feedstock supplied.

Digestate exists in 3 differing forms: Liquid, whole and fibre. Whole Digestate mimics the appearance of Dairy cow slurry due to its low dry matter yield. Furthermore, liquid Digestate represents Digestate where solids have been removed and fibrous opposes the characteristics of solid Digestate.

Chapter 3: Biochar: The by Product of Pyrolysis

3.1 Biochar: By Product of Pyrolysis

Biochar is an organic substance similar in appearance to common charcoal. It is a light, black, porous material containing up to 70% carbon. However, it is characterised by methane mitigating characteristics, posing as an additive of great potential for the use in Agriculture. It is the by-product of the burning of organic matter derived from agriculture and forestry such as Wood chip or leafs. This process is called Pyrolysis, a process which ensures the safe storage of carbon and minimises contamination. Through the use of thermochemistry, syngas and bio oil reach temperatures between 350 and 700 degrees Celsius. Organic matter is burned in a container in vastly anaerobic conditions producing very few fumes in the process. As a result, carbon is safely stored in the resultant Biochar which is not lost to the atmosphere through volatilisation (Oni *et al.*, 2019). The production of biochar from Pyrolysis has been attributed with many Environmental benefits and Greenhouse gas mitigation including: sequestration of Carbon (Gupta *et al.*, 2020), removal of heavy metal from the environment (Zhong *et al.*, 2019), mitigation of salt (Guo *et al.*, 2016), the production of bioenergy (McHenry *et al.*, 2009) and effective waste management (Dahal *et al.*, 2018).

3.2 Biochar Properties

Characteristics of biochar have been defined in order to determine its function to facilitate the removal of pollutants amongst other benefits to the environment. Structural analysis aids the prediction of this impact. Many interactions take place in its function: metal interaction is a result of pH 1 whereas its function will differ when pH is 2. Furthermore, contamination with metal will also vary with pH. This has allowed biochar to be an effective means of soil pollutant removal through its absorptive characteristics. The characteristics of biochar are as a result of functional groups, structure and analysis of elements (Brewer *et al.*, 2014). Many characteristic techniques have been developed to report on the function of biochar detailed in figure 3.1 including:

1. Scanning Electron Microscopy (SEM)
2. Fourier Transform Infrared Spectroscopy (FTIR)
3. Thermo Gravimetric analysis (TGA)
4. X-ray Diffraction (XRD)
5. Brunauer Emmett Teller (BET)
6. Nuclear Magnetic Resonance Spectroscopy (NMR)

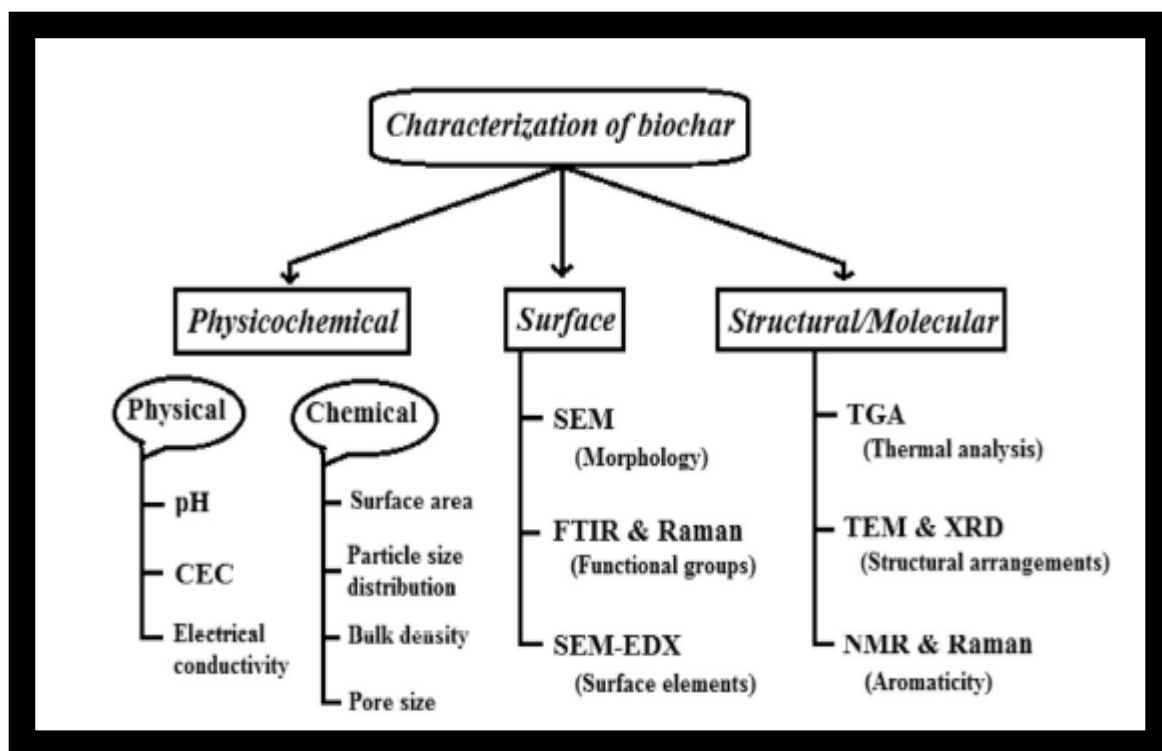


Figure 3.1 Characterisation Techniques of Biochar, taken from Yaashikaa *et al.*, 2020.

3.3 Functional Groups

Surface functional groups which aid the properties of sorption include: amine, lactonic, carboxylic, hydroxyl and amide groups. Major factors of importance which influence these functional groups are temperature and biomass (Li *et al.*, 2017). There may also be an interactive effect which may reduce these functional groups such as porosity, pH and surface area. FTIR is used to characterise the functional groups of biochar. For example, biochar which has been produced at different temperatures display great difference in their functional groups present (Yaashikaa *et al.*, 2020).

3.4 Porosity and Surface Area

By in large, where biochar displays a great surface area and porosity, sorption properties will also be significantly high. This surface area porosity is created during the process of pyrolysis where water loss is high during the dehydration stage. The pores of biochar vary greatly in size from <2 nm (Micro), 2-50nm (Meso) to >50 nm (Macro) (Yaashikaa *et al.*, 2020). Smaller pore size is associated with reduction capacity of sorption. Size of Pores may be attributed by SEM. The size of the surface area is the key characteristic determining the sorption capacity of biochar and temperature in regards to the type of biochar formed. Surface area characteristics is affected by the nature of raw materials, be it treated or untreated. Where carbon process has been activated, more surface area is present. This is generally completed in commercial

scenarios for this reason. In the absence of activation, biochar produced is less porous and displays less surface area versus activated (Li *et al.*, 2017).

3.5 Stability

The overall stability of biochar may be attributed to a number of factors including temperature. Pyrolysis temperature is seen as one of the most important considerations when referencing biochar stability. Three main methods of determining its stability include:

1. Determining Carbon structure, directly and indirectly processing
2. Determination of Carbon stability through chemical or thermal means
3. Place biochar in an incubation environment and measure mineralisation of Carbon

The carbonisation of biochar contains two phases: amorphous and crystalline stage. Stability of biochar is therefore the main functional element in determining its stability. Two traits of importance within carbon structures are its aromaticity and condensation. Where resultant biochar is deemed to have a high degree of aromaticity and aromatic condensation, thermal and chemical challenges are resisted and the biochar product is highly stable. Elements make up of biochar consists of aromaticity. Other properties such as biochar pore size, structure, sorption and pH will also affect its stability (Yaashikaa *et al.*, 2020). Ideal stability is attained via incubation in the soil waiting for complete breakdown and calculate the time taken for break down. This process takes in excess of a hundred years; therefore, exact stability characteristics are difficult to achieve. Many of the techniques are not economically viable and take too long to achieve tangible data, highlighting the need to develop new methods in order to gain accurate results to put into practice of environmental benefit (Yaashikaa *et al.*, 2020).

3.6 Pyrolysis Process Mechanism

The Mechanism of pyrolysis can be defined as the thermal decomposition of materials of organic origin facilitated by an anaerobic setting under high temperatures in the range of 250-900 degrees (Osayi *et al.*, 2014). The resulting process aids both the destruction of waste material and the creation of value add products which can be further utilised such as Biochar, bio oil and syngas. Components derived from lignocellulose such as lignin, hemicellulose and cellulose undergo three processes. Specifically, they enter a reactive process of depolymerisation, fragmentation and cross linking at varying temperatures. Depending on the feedstock and process, the resulting by product may be in liquid, solid or gas stage (Yaashikaa *et al.*, 2020). From the liquid and solid products, components such as bio oil and char are produced, whereas gas produces products such as syngas, hydrogen and carbon monoxide.

Varying reactors are used in the process including bubbling fluidised bed, paddle kiln, wagons and rotating sand kilns.

Yields of Biochar is dependent on the nature of the feedstock used. Efficiency of operation is largely dependent on temperature used (Wei *et al.*, 2019). Under normal operating conditions, it is generally accepted that Biochar yield reduces and syngas production increases where temperature is high during the process of pyrolysis. Figure 3.2 details the basic mechanism of production.

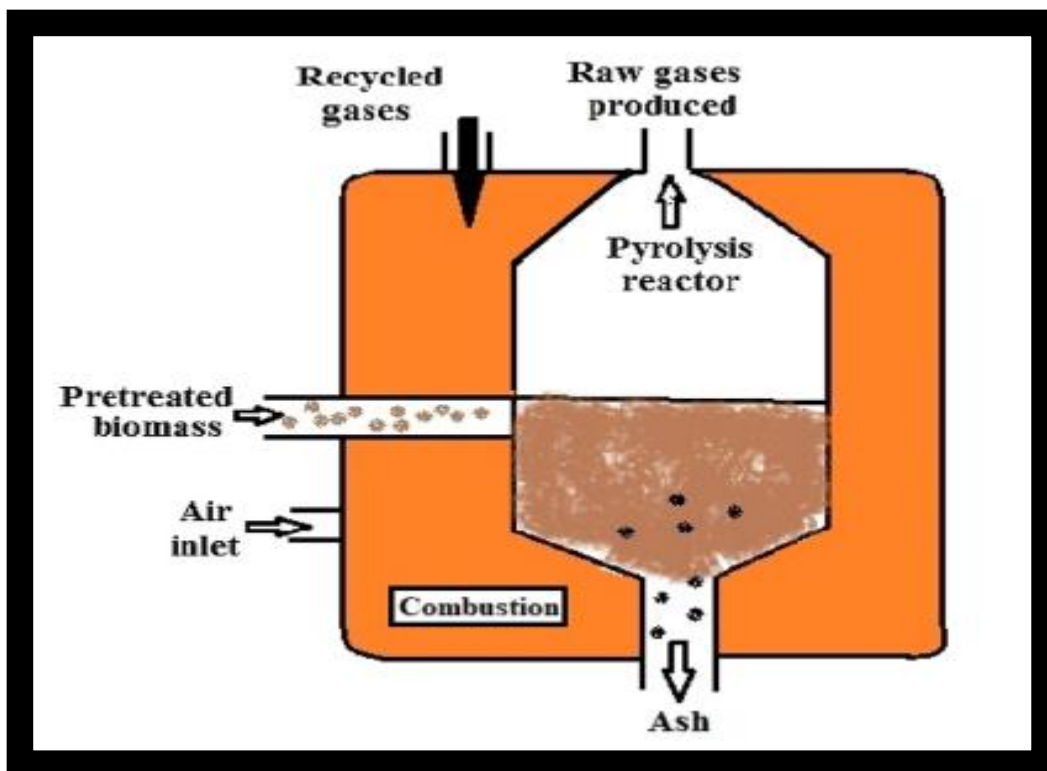


Figure 3.2 Pyrolysis Process, taken from Yaashikaa *et al.*, 2020.

There are two different types of Pyrolysis classified by temperature, rate of heating, time and pressure: Fast and Slow Pyrolysis. Fast pyrolysis is a direct procedure involving the interaction of chemicals and heat in tandem. Solid feedstock is liquefied into bio oil and further used for energy production. Identifying categorists of Fast Pyrolysis include:

1. Rapid warming of Biomass (> 100 degrees per minute)
2. Rapid timing of particles of biomass and fumes of pyrolysis at high temperatures.
3. Moderate temperature ranges 400-600 degrees.
4. Fume residence in hot zone to base (Oil Production)
5. Rapid cooling of fumes (Wang *et al.*, 2014).

Identifying categorists of Slow Pyrolysis include:

1. Less heating to Fast Pyrolysis at 5-7 degrees per minute
2. Greater time under resistance (Greater than 1 hour)
3. Greater Yield of Char
4. Quality Biochar which may be further utilised (Arni *et al.*,2018).

3.7 Breakdown Process of Biomass Components

3.8 Cellulose

The decomposition of cellulose takes places in two reactions, identified by the rate of polymerization.

1. Slow Pyrolysis: decomposition at lower heat range under increased time of resistance
2. Fast Pyrolysis: creation of levoglucosan through quick volatilization at high temperatures. Solid Biochar is produced and levoglucosan is dehydrated to create hydroxymethyl furfural which may be further broken down to liquid and gas to produce syngas or bio oil. Furthermore, the hydroxymethyl furfural can be further processed in a reaction step such as aromaticization, polymerisation or condensation to again produce solid Biochar.

3.9 Hemicellulose

The decomposition process of hemicellulose is similar to that of cellulose. Hemicellulose biomass goes under a depolymerisation process in the formation of oligosaccharides. This occurs in a series of reactions including depolymerisation, decarboxylation, aromatization and rearrangement of intramolecular particles to produce Biochar or further decomposition to syngas and bio oil (Huang *et al.*,2012).

3.10 Lignin

Lignin decomposition is a much more complex process. Beta 0-4 linkage of lignin breaks to produce free radicals. The resultant free radicals surround and capture protons from other species to form decomposing compounds. Free radicals then continue to move around the cell to other molecules resulting in chain propagation (Yaashikaa *et al.*,2020).

3.11 Environmental Benefits of Biochar

It is important to note that there are many functions for Biochar aside from direct removal of Green House Gas emissions from Agriculture as seen in Figure 3.3.

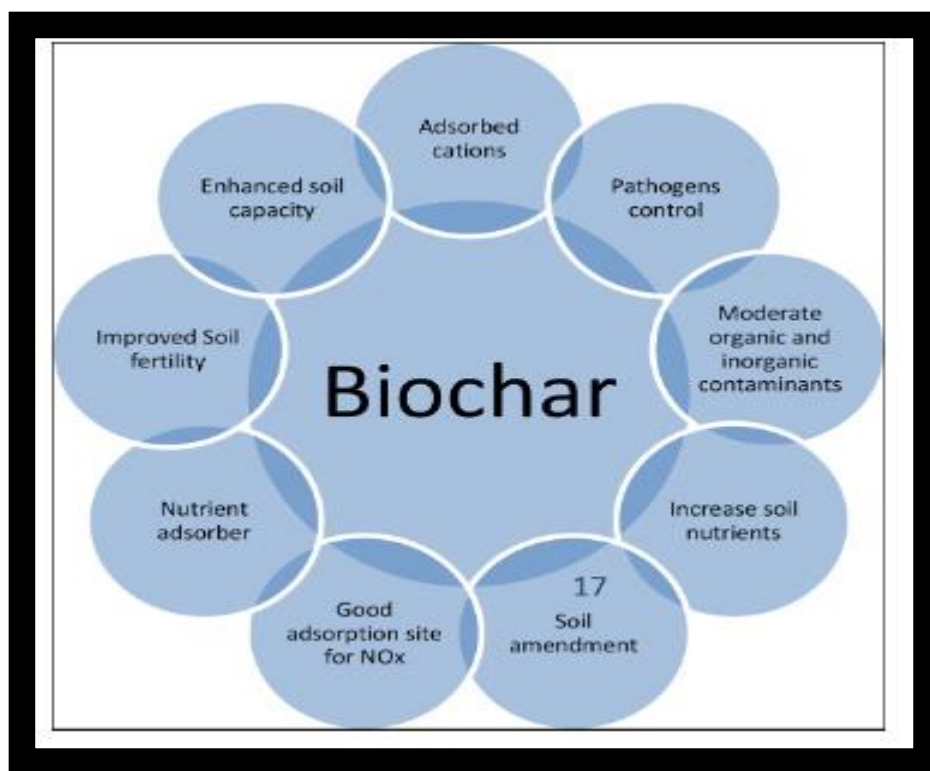


Figure 3.3 Environmental Benefits of Biochar, taken from Oni *et al.*, 2019.

3.12 Biofuel from Biochar

It has been reported that Biochar may also play a significant role in the future through its contribution to the circular economy in the production of biofuel. Biofuel is noted as the replacement of choice for petrol due to its favourable characteristics. Biofuel is nontoxic, biodegradable, renewable and performs similarly. It is created by transesterification of oils such as vegetable or the esterification of free unsaturated fats with alcohol (Yaashikaa *et al.*, 2020). Catalysts of Biochar produce biofuel in this manner and are categorised into two types: Solid acid catalysts and Solid alkali catalysts.

3.13 Carbon Sequestration

Carbon dioxide is an important Greenhouse gas with considerable global warming potential. Agricultural soil plays a significant role in ensuring carbon dioxide loss to the environment is minimised through the carbon cycle. Carbon sequestration has been reported as a feasible method of reducing the amount of CO₂ emissions produced by the soil (Mendez *et al.*, 2012). Biochar plays a role due to its physical properties/ aromatic structure which make it difficult for breakdown by microbes. However, its benefit may be due to the soil type present also. Mineralisation of the organic matter was greater in soils of low fertility versus those of higher status. This was also found to be true regarding carbon content where mineralisation of carbon

was higher in soils of higher carbon content versus lower status. Therefore, the carbon content of Biochar is classified as either liable or recalcitrant carbon (Yaashikaa *et al.*, 2020). Biochar defined as liable and is utilised by soil microbes where Biochar is applied to the soil. As a result, at initial application, mineralisation of carbon is increased. Conversely, Biochar defined as recalcitrant remains in the soil for a much longer period of time (Puga *et al.*, 2015). Hence, carbon fixation as a result of Biochar application is enhanced due to liable carbon mineralisation. However ongoing work is required to determine the exact cause of action in relation to biomass used and conditions of pyrolysis.

3.14 Removal of Organic Pollutants

Biochar has been utilised as a source of pollutant removal from water and soils. Where Biochar is applied to the soil, it absorbs pollutants present. Such organic pollutants or Agricultural chemicals which are removed include: pesticides, herbicides, fungicides and insecticides such as carbofuran etc. (Yaashikaa *et al.*, 2020). Studies have shown that where Biochar was incorporated into the soil, the absorption capacity of pollutants was increased (Mondal *et al.*, 2016). Pesticide residue was also reduced through the usage of Biochar in the soil with a reduction in harmful carbofuran noted (Mondal *et al.*, 2016). This pesticide absorption and degradation characteristic may be attributed to the presence and quality of phenolic and carboxylic functional groups present on the surface of Biochar.

The process of removal is as a result of a direct link between pollutants and Biochar. This is through a process of physio sorption and chemisorption in the presence of functional groups e.g. OH (Yaashikaa *et al.*, 2020). Biomass of choice, temperature, pH and amount of pollutant versus availability of biochar are some of the main factors dictating the effectiveness of pollutant removal (Yaashikaa *et al.*, 2020).

3.15 Removal of Inorganic Pollutants

Biochar also has a role to play in the removal of inorganic pollutants from the environment. These are toxic metals which are non-degradable in high concentrations posing a threat to life and the greater environment. examples include zinc, lead and mercury (Yaashikaa *et al.*, 2020). Conversely to organic pollutants, Biochar produced at low temperature pyrolysis is suitable for the sorbing of contaminants from inorganic sources. Biochar produced in this manner contain many functional groups are highly porous and contain a large amount of carbon.

The mechanism for removal is ion exchange and is particularly aimed at heavy metals. Properties of immobilisation demonstrated by biochar aid the modification of metals on functional groups, pH and its capacity of cation exchange (Yaashikaa *et al.*, 2020). Feedstock

utilised in the production of this type of biochar is of Agricultural origin, including animal waste and energy crops. The sorbent capacity of biochar has also been proven to be effective in the removal of inorganic pollutants from water such as Uranium. The rate of biochar application is a determining factor of its success.

3.16 Biochar as a Biocover

Studies conducted now suggest Biochar may have a potential role in direct mitigation of methane and associated greenhouse gas emissions from stored slurry. Liquid slurry is an important source of Methane and Ammonia loss to the environment. A method of choice which is increasingly been utilised is the use of Biochar as a physical shield or cover which floats on the surface of the liquid manure. This is commonly referred to as a Biocover, a material derived from biological sources to create a physical barrier between the slurry and the atmosphere. Increasing interest and research has taken place in this space including Clanton *et al.*, 1999, Guarino *et al.*, 2006, Regmi *et al.*, 2007 and VanderZaag *et al.*, 2008. Several other Biocovers have been utilised from sources such as wood chip, vegetable oil and straw with varying degrees of success (VanderZaag *et al.*, 2008). Although proven to be effective in reducing emissions and odours, their use has not been widespread.

Biochar is seen as a viable choice of biocover due to its physical state of vast range of particle size and highly porous structure. Its resistance to breakdown when placed in this environment allows it to withstand volatile conditions. Moreover, due to this persistence an amount of the carbon which is stored in the Biochar may be considered that which has been sequestered from the environment when it is returned to the soil as fertiliser (Lehmann, 2007). The resulting fertiliser may therefore improve soil health and production characteristics, most notably in low performing soils (Lehmann, 2007).

3.17 Biochar as a replacement for Chemical Fertiliser

3.18 Methane Emissions Saved

The benefit of Biochar in relation to Methane emissions may be two fold. The chemical fertiliser industry is a key source of Ammonia emissions which is a potent GHG and every tonne of chemical displaced by an organic source such as Biochar is of benefit to the environment. However, a recent study by Zhou *et al.*, 2019 suggest there may also be a direct saving in Methane emissions by making the switch from a chemical source of fertiliser. By in large, estimations of Green House Gas emissions from the Chemical fertiliser industry have focused on upstream processes (Production) and midstream processes such as storage and transportation. However, an analysis of the downstream emissions in the surrounding areas

surrounding fertiliser production facilities show high amounts of methane are being produced industrially. Zhou, in their study used a Google Street view vehicle which was equipped with a high tech series of sensors to determine methane emissions on the roads downstream from chemical fertiliser plants. They surveyed 6 plants over the course of a year during normal production times and found methane emission losses to the environment to be 29 Gig grams per year. This was a significant increase on the self-reported 0.2 Gig grams of Methane from each facility, an increase of over 100 fold (Zhou *et al.*, 2019).

3.19 Biochar Benefit to Soil Health

Chemical fertiliser, in its usage is much more available to the crop in comparison to organic forms and therefore its usage is much higher and efficient than its organic counterpart (Han *et al.*, 2016). They outperform the initial mineralisation of Nitrogen however this has also been reported at the expense of compaction of soil and acidification (Liu *et al.*, 2010). Symbiotic relationships between costs and efficacy have been observed where both chemical and organic fertiliser types can be incorporated into the farms fertiliser plan (Fageria *et al.*, 2005). They reported enhanced soil productivity and fertility where both fertiliser types are used in tandem on the farm. Biochar, as an organic fertiliser, contains plant nutrients and acts as a source of organic matter unlike chemical depending on the feedstock source which is selected. This organic matter also aids aggregation of soil, porosity of soil particles, nutrient holding capacity and an enhanced ability to hold water during drought periods (Kumar *et al.*, 2017). When applied to a crop of wheat, a crop frequently grown on Irish farms, the crop seen beneficial attributes over and above that of chemical fertiliser. Specifically, regarding Nitrogen concentration which is the most important macro nutrient for crop growth. Protein content was recorded a desired 20%, nitrogen content in the leaves at 24%, straw 24%, stem 20% and most importantly 56% from the grain which the farmer is ultimately paid to grow (Ali *et al.*, 2015). From an environmental and nutrient holding standpoint, Biochar holds great capacity to absorb ammonia and nitrate in water and soil particles. Hence ammonium storage is enhanced where Biochar is incorporated into the ground and less losses are reported to the environment (Taghizadeh-Toosi *et al.*, 2012). As a result, increase Nitrogen uptake is observed in the plant, including above and below ground parts. El- Nagggar *et al.*, 2019, reported of the role Biochar plays in sustainable Agricultural practices due its role in soil rehabilitation from chemical fertiliser damage (Acidification) whilst maintaining if not improving growth of the plant in question.

3.20 Pyrolysis in Ireland

The opportunities associated with Biochar as a result of Pyrolysis have great potential for both the environment and the circular economy. Ireland is set on a journey to begin utilising these opportunities with the announcement of the planned construction of the World's Largest Pyrolysis Plant in County Offaly constructed by Tsk (TSK,2021). The project which is valued at 65 million euro will process 75,000 tonnes of waste each year from Bord na Mona, a semi state Irish company.

It represents a significant step by Ireland in recognition of the importance of the Circular economy and the environment, avoiding the loss of processed waste to landfills and instead reusing it to create syngas. The state of the art plant will include a cleaning system where harmful tars and oils are removed and avoid contamination.

The plant will have a total capacity of 10MW, not only making the system self-sufficient in terms of energy usage but also providing excess back to the Irish grid for usage by private homes and Industry. This sets out to be the first project of its kind in Ireland with a second phase construction planned for a separation line for waste valorisation and increased capacity. It is reported that the plant will be fully functional and receiving biomass by 2030 over a total construction period of 20 months (TSK,2021).

Chapter 4: Methods

4.1 Design of Study

From this section, methods used to demonstrate how Renewable Energy can reduce Methane Emissions from the Irish Dairy Herd to Safeguard Future Production is outlined. Desk research of peer reviewed publications along with supplementary data from commercial and government sources was used to answer the research question.

4.2 Thesis Outline

Research has indicated that methane is a highly potent and dangerous GHG of which the Dairy sector in Ireland is a key contributor. Therefore, means to mitigate its risk for continued production is necessary and presents the thesis question: “How can Renewable Energy Reduce Methane Emissions from the Irish Dairy Herd to Safeguard Future Production?”

Chapter 1 reviewed the background to methane and its relevance to the Irish Dairy sector in light of Green House Gas emissions targets set out by the European Union and Government. An overview was also given to the importance of the Irish Dairy sector to the economy in light of its expansion post milk quota abolition.

Chapter 2 outlines anaerobic digestion as a renewable means of reducing methane from the Dairy herd whilst creating a usable energy source.

Within Chapter 3 the potential of Biochar as a by-product of pyrolysis is observed. It is explored as a slurry additive to reduce methane escape from manure and as an organic fertiliser to displace the use of Chemical Fertiliser. Potential symbiotic characteristics outside of Methane mitigation was also discussed including soil health and pollution removal.

Chapter 4 will define materials and methods used surrounding the research question whilst Chapter 5 outlined the results of relevant literature and studies to reinforce and help further understand the significance of the research question factors.

Chapter 6 reviewed and provided discussion on the results found in chapter 5 to determine the accuracy of the research question and will bring forth a synopsis on key outcomes and comment on future work direction.

Finally, Chapter 7 concluded on the research question and offered guidance on future work carried out.

4.3 Research Scope

The scope of the research question focuses on Renewable energy sources and its by-products as a means to reduce methane emissions from the by-product of digestion, centred on efficacy,

legislation, cost and feasibility. The scope will include Renewable energy processes: Anaerobic Digestion and Pyrolysis which will symbiotically benefit the primary producer and the country as a whole in reaching climate action targets. These conditions have been chosen due to its significance in meeting Green House Gas emission targets set out by the European Union and relevance to primary producer uptake at farm level.

4.4 Data Inclusion

Data utilised was taken from studies carried out both in vitro and in vivo primarily from systems which are similar to the Irish temperate climate for relevance of feasibility. To obtain the most relevant data, recent studies within the last 5 years have been used where new data has been discovered. However, where no new advancements have been made or where definitions have not changed, older studies were used.

4.5 Data Exclusions

For the purpose of Data driven discussion, all research which has not been peer reviewed has been excluded from this thesis.

4.6 Feedstock Selection

In line with Feedstock availability in Ireland and relevance to reducing methane producing practices from Dairy farms, research data was selected based upon Animal Manure and Energy Crops which can be grown and utilised in Ireland. Multi species swards are also included as a relevant feedstock with potential in Irish Dairy grazing systems.

4.7 Scale Range

In order to gain an appropriate feasibility assessment of Data in an Irish system, only data relevant to the average Irish Dairy herd was utilised. Both indoor and outdoor systems of grassland management are studied.

4.8 Legislation Concerns

In order to gain a picture of feasibility to Renewable energy in Ireland, only legislation of European concern derived from the European Union was taken into consideration along with any indigenous policy derived from the government of Ireland. Similarly, only GHG emission targets relevant to Ireland were considered for this study.

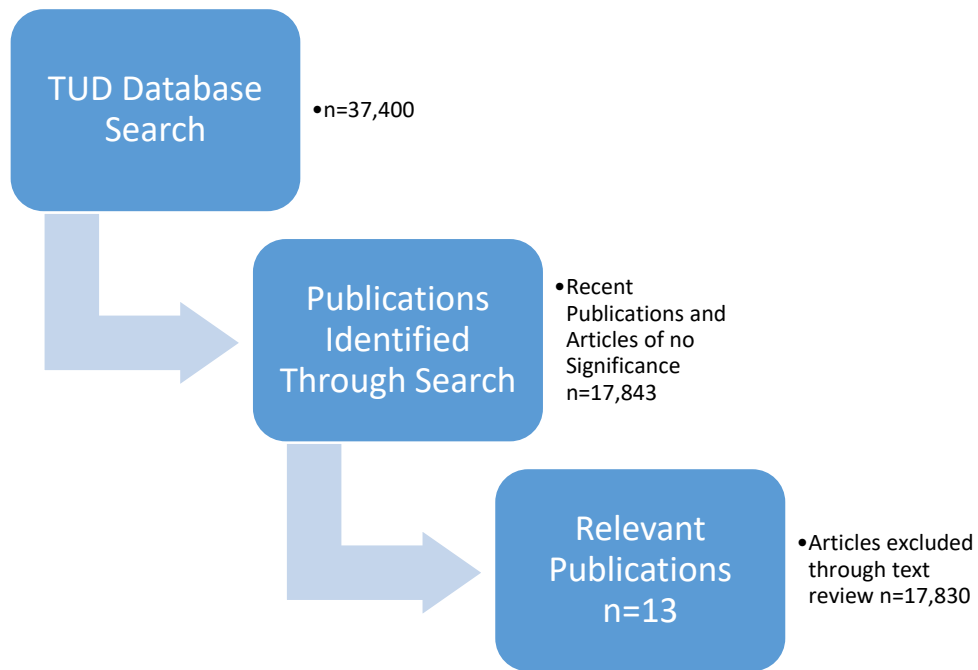


Figure 4.1 Schematic detailing process of Information collection

Chapter 5: Results

5.1 Farmer Attitude and perception towards sustainable farming

A key driver to success to help mitigate methane emissions from the Irish Dairy herd is understanding the psyche of the Irish Dairy Farmer as ultimately, the responsibility lays with the primary producer to implement the necessary measures. Therefore, its vitally important have clarity and understanding amongst this cohort to ensure sustainable farm practices from the ground up. From these results, the Industry can then aid in developing programmes and strategies to allow sustainable farming practices to become norm and something which the farmer can appreciate is making a positive impact both on their farm and to the wider community (Shorthall,2022).

It is well documented that the Irish grass based system of producing milk is one of the most environmentally friendly means of production. However, it is important to consider just how is this grass produced. Not all grass is grown sustainably, there are significant concerns surround the leaching of nutrients from the increased usage of chemical fertilisers and high stocking rates in intensive systems to name a few (Van den Pol-van Dasselaar *et al.*, 2020).

Orla Kathleen Shortall *et al* therefore set out a means to quantify farmer perception of sustainable Dairy farming practices by extracting data from a Quantitative from a sample representative of the island of Ireland. Three main areas of study were assessed from the qualitative interviews carried out

1. How does the Primary producer define a “good farmer” with regards to grass based milk production?
2. Define how the idea of intensive and extensive farming systems align with the definition of a “good farmer” in the grass based system.
3. Is there scope for multi species swards to be incorporated into the “good farmer” category? (Shortall *et al.*, 2020).

For reference, the industry and advisory agencies set about a number of criteria which in theory defines a “good farmer” and this sets out the standard for which this study was gauged against. This is broadly set around the best use of grazed grass and the usage of advisory tools and methods set out by the industry of benefit to promote efficient and sustainable grazing which in turn will help reduce methane output. These tools will be covered in detail in a later chapter but for reference include: usage of grass measurement, rotational grazing, grass allocation/ budgeting, adhering to the spring rotational planner as set out by Teagasc and the usage of Multi species swards (Burton *et al.*, 2021).

5.2 Intensive and Extensive Farming

The Primary producer's definition of intensive and extensive farming will also be described and assessed. Again, for reference, the industry accepts a "intensive" farm as those who require more inputs to grow grass required whereas extensive are the opposite. This is a very broad definition.

The focus of this study was therefore not to draw general assumptions on a large cohort of people but to focus in detail, reasoning behind certain behaviours and determine outcomes and conclusions based on specific responses (Bryan 2001). The sampling type used was purposive in order to obtain a wide range of information from a wide geography from differing areas of the Island of Ireland (Maykut *et al.*, 1994). Interviews were then carried in the period from December of 2019 and January of 2020. From an original panel of 396, 20 specific farmers were interviewed in depth from a range of geographies including: two participants from the midland, four participants from the Northeast and fourteen participants from the southwest (Table 5.1) The largest amount of participants was chosen from the southwest as this is representative of the milk pool in Ireland where the largest amount of Dairy farmers resides (Gilsenan,2019).

Table 5.1 Geographical spread of farmers interviewed (Adapted from Shortall *et al.*, 2020).

| Farmer Pseudonym | Location | Cow Numbers | Amount of Concentrate Fed per Cow |
|------------------|-----------|-------------|---|
| F1 | Northeast | 460 | 1500 kg/year |
| F2 | Northeast | 200 | 1000 kg/year |
| F3 | Midlands | 180 | 7 kg/day in winter, 2–5 kg/day in spring/summer |
| F4 | Midlands | 130 | 500 kg/year |
| F5 | Northeast | 400 | 600–700 kg/year |
| F6 | Northeast | 260 | 1200 kg/year |
| F7 | Southwest | 200 | 800 kg/year |
| F8 | Southwest | 80 | No data |
| F9 | Southwest | 170 | 650–700 kg/year |
| F10 | Southwest | 200 | 800 kg/year |
| F11 | Southwest | 250 | 2000 kg/year |
| F12 | Southwest | 50 | 6 kg/day |
| F13 | Southwest | 110 | 700 kg/year |
| F14 | Southwest | 100 | 250–300 kg/year |
| F15 | Southwest | 80 | 1700 kg/year |
| F16 | Southwest | 80 | >1500 kg/year |
| F17 | Southwest | 75 | 700 kg/year |
| F18 | Southwest | 180 | 3 kg/year in summer |
| F19 | Southwest | 130 | 500 kg/year |
| F20 | Southwest | 75 | 700 kg/year |

Farmers were asked to express how much concentrates were fed to give an indication of how intensive their system is in line with the Industry recommendations set out by Teagasc which champion the use of a low input system that maximises the use of grazed grass as a pose to a high concentrate based system (Table 1.1).

5.3 Findings of Interviews

Results from the interviews are described under the 3 key areas of discussion outlined above.

5.4 Definition of a “Good Farmer”

Those interviewed outlined the qualities, knowhow and facilities necessary to produce good quality grazed grass. Farmer No 7 expressed views on reasoning behind the high input system. They detailed that the requirement for a high input system may be down to poor management and the unwillingness to educate themselves around how grass grows and how to best manage the growth cycle. As a result, these high input farmers are happy to graze low quality excess covers of grass and feed a high level of concentrate to produce the same amount of milk as a farmer who is managing grass correctly, in the interviews opinion. They believe that in order to use a low input system then a high level of knowledge is required and put to practice. This practice is not only unsustainable but also unprofitable, according to farmer no 7 (Shorthall,2022).

Grazed grass was accepted by the interviewees as a low cost feed and therefore linked to farm profitability. This practice has changed over the years with research and more progressive farmers were observed to uptake these technologies from countries such as New Zealand according to the panel. Farmer No 2 made reference to how he has adapted to changes in technologies with regard to grass management and what F2 regards as good practice. F2 spoke of grassland measurement and how it was never previously practiced on their farm before. They believe that all young farmers now measure grass, highlighting a generational shift towards todays best practice. By utilising this tool, they found that they can now plan and manage the grass ahead of them which in turn reduces their need to feed high cost concentrates (Shorthall,2022).

Farmer number 4 highlighted the fact that there are many farms only recently adapting grass measurement, highlighting the fact that many Irish farmers are late adopters to technology in their opinion.

Conversely, these farmers identified as utilising a high input system believed that they were not replacing grass with concentrates but simply supplementing it. Farmer number 11, a high

input farmer outlined that the need to feed a high level of concentrate was to look after the cow and insure she produces a high yield as this was the type of cow which is on the farm. F11 outlined that the desire was not to replace grass with concentrates but to find the correct balance between yield and profitability (Shorthall,2022).

Farmer number 1 outlined a social dynamic behind the definition of a low input farmer. F1 believes that there is an element of “Ego” attached to being a low input farmer, highlighting that some farmers want to be the first to have the cows out to grass in the spring and last to house in the winter feeding little or no concentrate in his opinion.

5.5 Alignment of Intensive and Extensive Farming with a “Good Farmer”

According to Food Harvest 2020, Irelands national document on Agriculture defines Irelands extensive and low input system of grass based production as the basis of our green image worldwide (DAFM, 2020). Therefore, those farming intensively are not working in tandem with the policy ideals. The survey set about finding farmer opinion on why this was a necessary production type in Ireland.

Farmer 8 demonstrated how growing as much grass as possible was linked to being a good farmer and this becomes somewhat of a competition amongst farmers to the point where profitability or indeed sustainability takes a back seat. Displaying how much grass you can grow over and above your neighbours is seen as a symbol of status he details.

Furthermore, when asked what the group believed what then is a “good farmer” in their eyes, the results yielded interesting results. Farmer no 10, indicated a good farmer is one which hits production targets within certain norms such as in excessive fertiliser usage and good management practices. Whilst at the same time farmer no 8 believed that low input farming to be underutilising the resources available to the farm and therefore deemed a waste (Shorthall,2022).

Therefore, farmer’s opinion of a good farmer and those linked with government strategy to reduce emissions and methane are in somewhat of a conflict in the eyes of today’s farmer as a good farmer is seen as one who utilises resources should as harmful chemical nitrogen to drive grass growth. In terms of farmer opinion, the more grass grown is linked with a better farmer, this is largely in contrast to where the industry needs to be in regards to reduced chemical nitrogen usage as more chemical nitrogen usage is directly linked to grass grown (Shorthall,2022).

5.6 Multi species swards and a “Good Farmer”

As discussed earlier, multi species swards with clover are seen as a means to help increase biodiversity and sustainability which in turn helps reduce methane yields through decreased usage of chemical nitrogen. The same group of farmers were asked their opinion as to the potential of such a crop in Ireland and would they be open to utilise such a crop. The vast majority of respondents reacted positively to the development and some had already tried the crop whilst others questioned the harm associated with spreading chemical nitrogen in respect to grass grown.

Farmer 19 praised the incorporation of clover into grazing swards into commercial grass mixes and could appreciate the science behind nitrogen fixation and how this may bring about a reduction in the reliance on chemical nitrogen. Farmer 11 admitted there was a need to practice reseedling with clover more frequently, hailing the benefits of not only reduced chemical nitrogen cost but also the environmental benefit as well whilst maintaining if not improving cow performance (Shorthall,2022).

Where clover inclusion received a resoundingly positive response, multispecies swards received somewhat of a reserved reaction with farmers doubting their knowledge in regards to its management in terms of persistence, weed control and its ability to cause bloat in animals. However, in light of this, there is very much a heightened awareness towards its potential, particularly in the last 12 months according to farmer 8.

The conversation surrounding clover and multi species swards changed the direction of the interviews and farmers became open to the uptake of new technologies and practices, particularly where Chemical nitrogen could be reduced. Farmer number 8, in their response highlighted that too much of any nutrient cannot be good for the soil, directing this comment towards the overuse of chemical nitrogen and comparing it to excessive sugar in a human’s diet manipulating and upsetting the insulin system causing Diabetes. Furthermore, Farmer 8 creates a link between the usage of clover and multispecies swards with the practices of a good farmer who is engaged in the improvement of faring practices.

5.7 Digesters needed to Meet Targets

The above data was then compiled and used to calculate how many Anaerobic Digesters would be required under each of the three scenarios as seen in figure 5.1

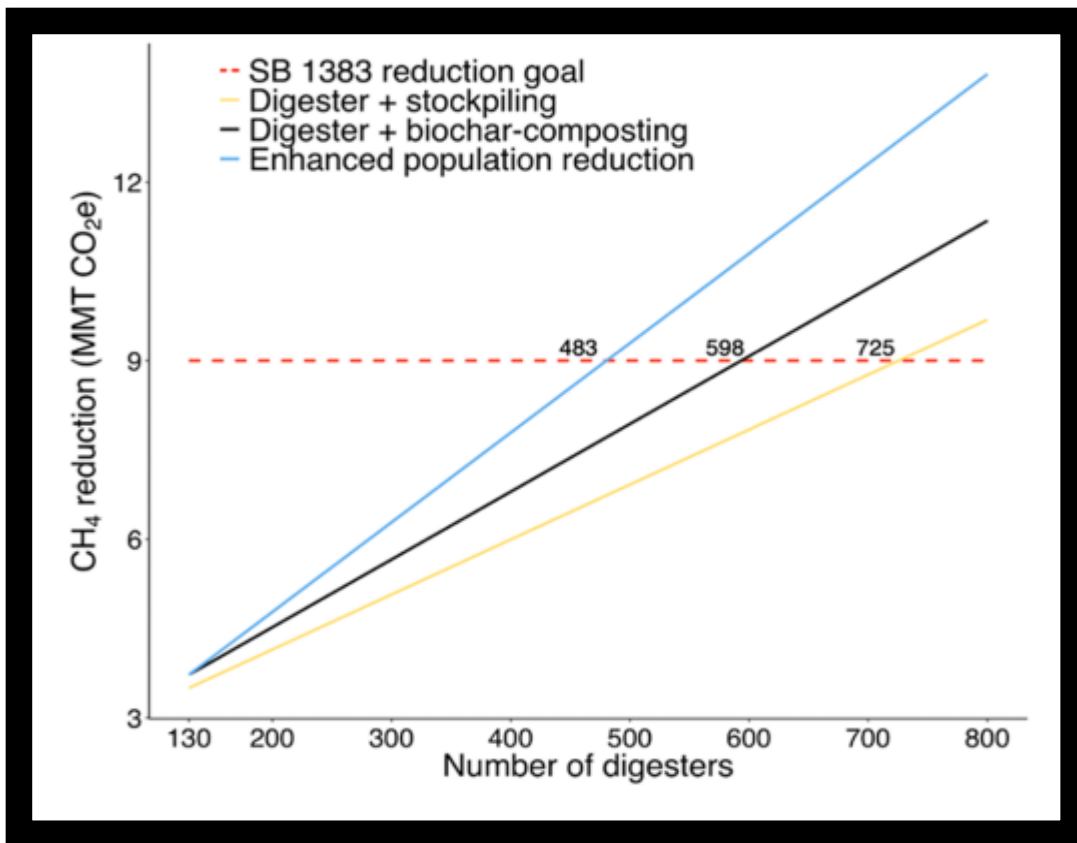


Figure 5.1 Digesters required to reach targets, taken from Maldaner *et al.*, 2018.

5.8 Methane saved from storage as Digestate

Previous studies by Owen and Silver, 2015, indicate the importance and significance of GHG emissions resulting from liquid manure from dairy cow systems. They identified clear opportunities for reduction in conventional systems whilst highlighting the need for further research into the topic.

In this system, the liquid manure is transported from the farm and placed in a biodigester where it is subjected to a stable range of pH, temperature and supply of feedstock (Gomez, 2013). Typically, for on farm Anaerobic Digestion facilities, a singular phase system is adopted within the mesophilic range of 32-42 degrees. Fermentation of wet material takes place where dry matter content is less than 20% in a feeding system of constant supply (Gomez, 2013). Additional organic matter (Degradable) gains additional supply with the addition of extra substrate feedstock often comprising of waste products from the food sector. The process comes to an end where biogas is produced to supply additional heat or electricity, replacing fossil fuel alternatives in the process. The resultant digestate is moved to a storage facility tank through a pump after the separation of liquid and solids has taken place. This by product may then be used as an organic source of fertiliser thereafter. This system of manure storage has

been proven to be of environmental benefit versus conventional storage systems (Gomez,2013).

Amon *et al.*, 2013, in their study first suggested that specifically methane emissions from storage of Digestate in this manner are comprehensively lower than that of a commercial Dairy farm storage facility. They suggested that this trend to be the result of volatile solids consumed during storage in the biodigester and an additional reduction in volatile solids after the separation process versus conventional systems. There have been additional factors identified by Clemens *et al.*, 2006, Sommer *et al.*, 2007 and Gromke *et al.*, 2015 that suggest the controlled temperature environment results in lower methane emissions from storage.

Specifically, temperature of substrate and digestate were identified. In their study, Liebetrau *et al.*, (2013) found the storage tank for digestate as a major source of significance regarding methane specifically. This was shown from slips in Methane from data determining the utilisation of gas from 10 facilities in Germany. This was further proven by Gromke (2015), who identified the emission residual production greater than 10% from 10 plants in the studied 12 within the range of 4-23%.

Augmented Gas resulting from Digestate alone was found to represent 12% of all methane produced from the digester (Balde *et al.*, 2016). This highlighted the importance of the storage facility in utilising the maximum energy potential in recovering additional methane for Biogas production.

Studies surrounding the actual avoidance of methane emissions from Anaerobic Digestion are scarce. Comparative studies have been carried out by Amon *et al.*,2006, Clemens *et al.*, 2006 and Rodhe *et al.*, 2015. The concluding results shown potential of Anaerobic Digestion to reduce GHG emissions. However, studies of a pilot scale have shown results of great variance, highlighting the need for further investigation. For example, in their study, Amon *et al.*, 2006 found methane reductions from storage phase of Anaerobic digestion through the lower temperature of digestate at this stage versus conventional storage over an 80-day period. However, in contrast, Rodhe *et al.*, 2015 found methane emissions each day over a 3-month period yielded higher than that of untreated manure. In response to these varied findings, Hrad *et al.*, 2015, shown the significance of a long term approach to predict and determine variance in supply and conditions throughout the year. This was further emphasised by Liebetrau who found a variance in methane losses from digestate from differing stages of storage. They found losses from two, one week periods and determined losses to be 50% higher during the summer

than the winter where energy crops and manure were used as feedstock. This was mirrored by Rodhe, signifying minimal emission losses from digestate as methane during the winter period.

A need for a constant measurement throughout the year was thereby deemed necessary to gain a true reflection of methane emissions from digestate over a 12-month period vs traditional storage. This was explored by Balde using sensors with a backward Lagrangian Stochastic (bLS) method of measurement to determine methane emitted from Digestate. The bLS and micrometeorological mass balance (MMB) are two models implemented for year round analysis. However, MMB may be more suitable as it is a highly adaptive measure accounting for a vast range of wind direction (VanderZaag *et al.*, 2011).

5.9 Case Study Digestate vs Untreated Year Round Study

There remained a need to quantify a year round response of methane emissions from digestate versus traditional storage. With this in mind, Maldaner *et al.*, 2018, explored methane saved as a result of liquid manure storage as Digestate in the production of Biogas. Here, emissions from a traditional commercial dairy farm manure storage facility (Open Storage) were surveyed and measured with the MMB system over the course of the year. This data was then compared to data from a similar study by Kariyapperuma *et al.*, 2017 to gain a rounded perspective of data. This study gained further clarity on previous work carried out by drawing comparison of methane emissions from a solitary dairy farm before and after the install of an Anaerobic Digestion facility. This allowed variables in relation to manure production to be identified and studied. Results set out were to determine:

1. Emissions of Methane throughout the year from Digestate.
2. Determine correlations between emissions and their influences.
3. Draw comparison from untreated manure and resulting digestate from the one farm.

5.10 Study Design

The study carried out by Maldaner took place on a commercial Robotic Dairy Farm in Canada comprising of 140 cows predominately of Holstein genetics, similar to that of an Irish Dairy Farm. Feeding regime was also somewhat similar to an Irish system consisting of Silage (Corn)(Alfalfa), hay and straw. Waste water from dairy washings entered a separate tank to that of liquid manure and was not incorporated into the Anaerobic Digestion process. The main manure source from underground storage was held in tanks of 3000 m³ capacity before pumped to the biodigester. Farm layout referencing proximity of buildings to the Anaerobic Digestion facility is outlined in Figure 5.2 below.

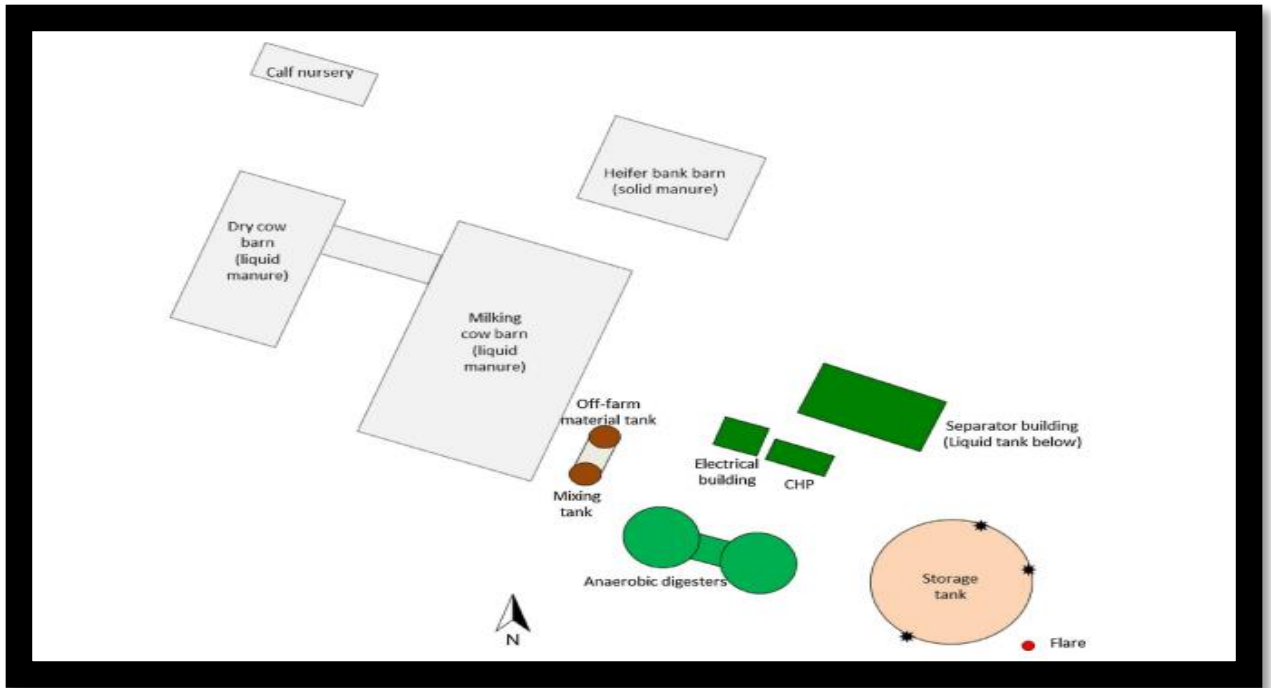


Figure 5.2 Site Layout, taken from Maldaner *et al.*, 2018.

5.11 Methane Flux and Influences

Over the course of the year, many cycles took place both loading and emptying as seen in Figure 4.2. during the first half of the year, the recorded temperature was low (<10 degrees). As a result, the flux in methane temperatures was also low ($< 50 \mu\text{g m}^{-2} \text{s}^{-1}$) (Figure 5.3). during the winter period, the only fluxes recorded were in response to an increase in air temperature. Into the summer months, fluxes increased further. For example, in June where the tank was loaded from empty, average fluxes of Methane was $178 \mu\text{g m}^{-2} \text{s}^{-1}$, an eight-fold increase on recorded fluxes the month previous in May at $21 \mu\text{g m}^{-2} \text{s}^{-1}$ (Figure 5.4).

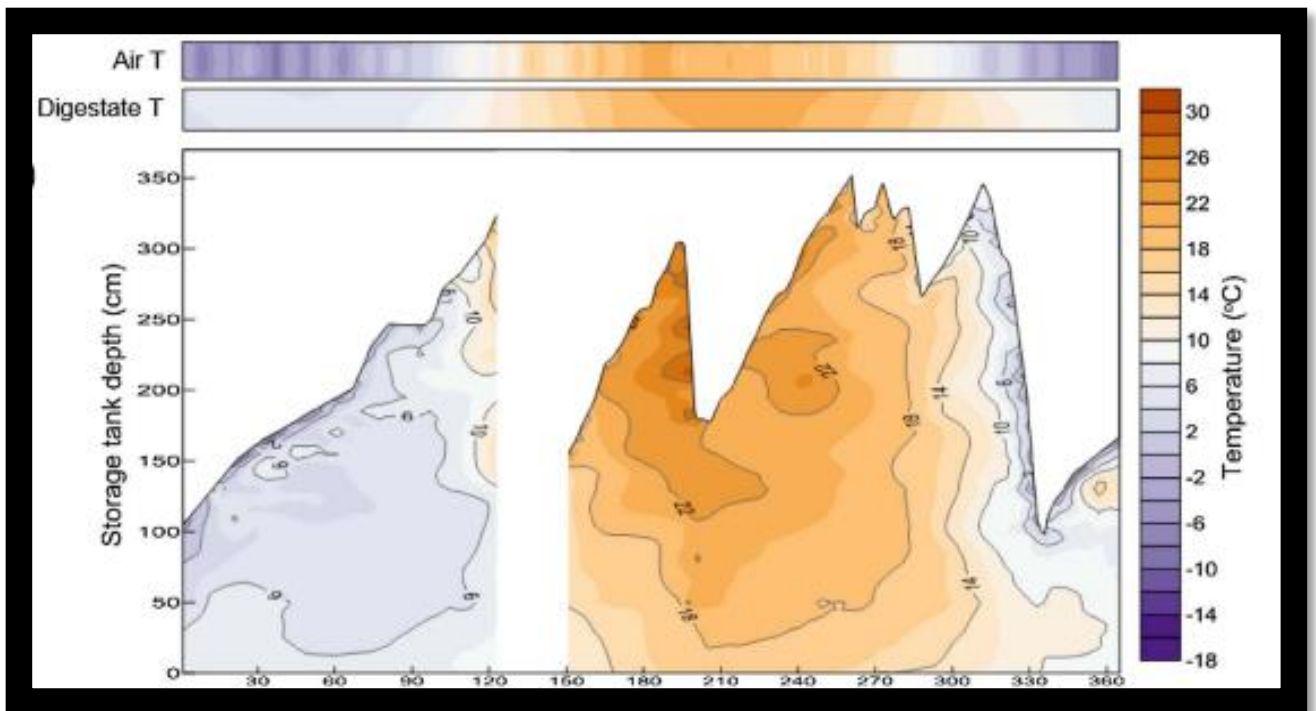


Figure 5.3 Temperature and Depth of Digestate throughout the year, taken from Maldaner *et al.*, 2018.

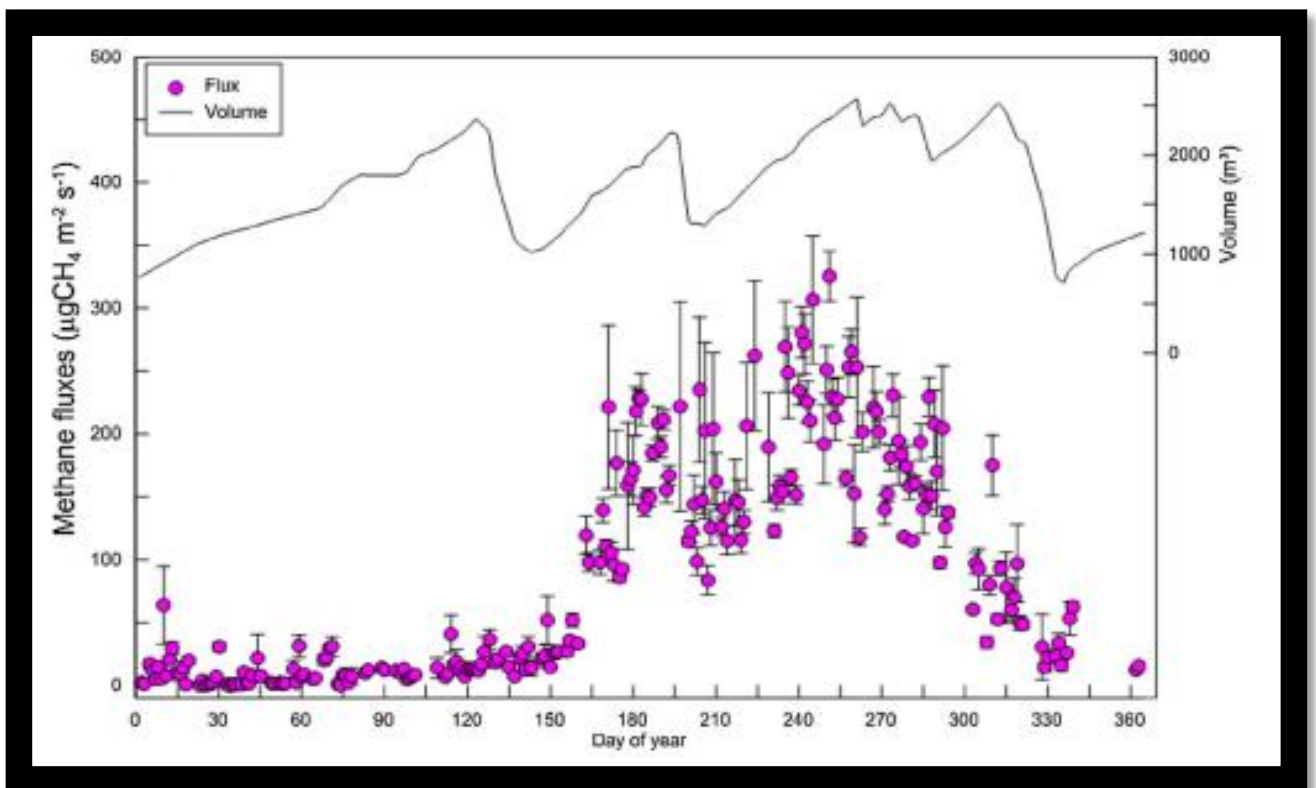


Figure 5.4 Flux in Methane emissions recorded over the year, taken from Maldaner *et al.*, 2018.

Figure 5.5 detailed correlations between Methane fluxes and temperature, both air temperature and Digestate temperature on a monthly basis. a strong positive correlation was observed between Methane flux and temperature, most significant at 2 meters deep. The same correlation was not recorded between Volatile Solids concentration and Methane from Digestate fluxes.

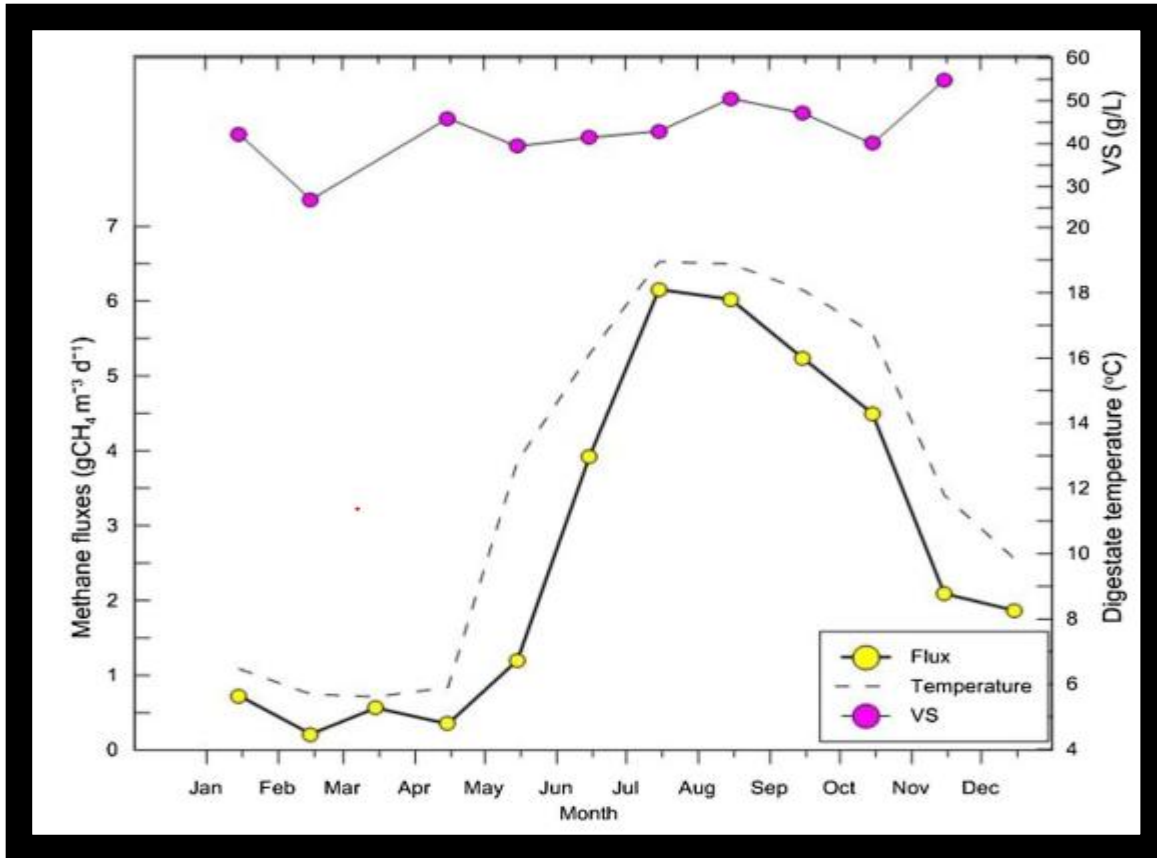


Figure 5.5 Average Methane fluxes, Digestate Temperature and Volatile solids concentration. Taken from Maldaner *et al.*, 2018.

5.12 Comparison of Methane from Digestate versus Untreated Slurry

Figure 5.6 outlined the monthly average Methane Fluxes derived from both Digestate and untreated slurry whilst also accounting for Volatile Solids concentrations. A 32% reduction in Volatile solids was recorded on average in Digestate vs Untreated manure. Total production of methane from the year was recorded as 1.0kg m⁻³ y⁻¹ from Digestate. In comparison to untreated manure which yielded 6.6 kg m⁻³ y⁻¹, an 85% reduction in Methane per volume was observed (Figure 5.6).

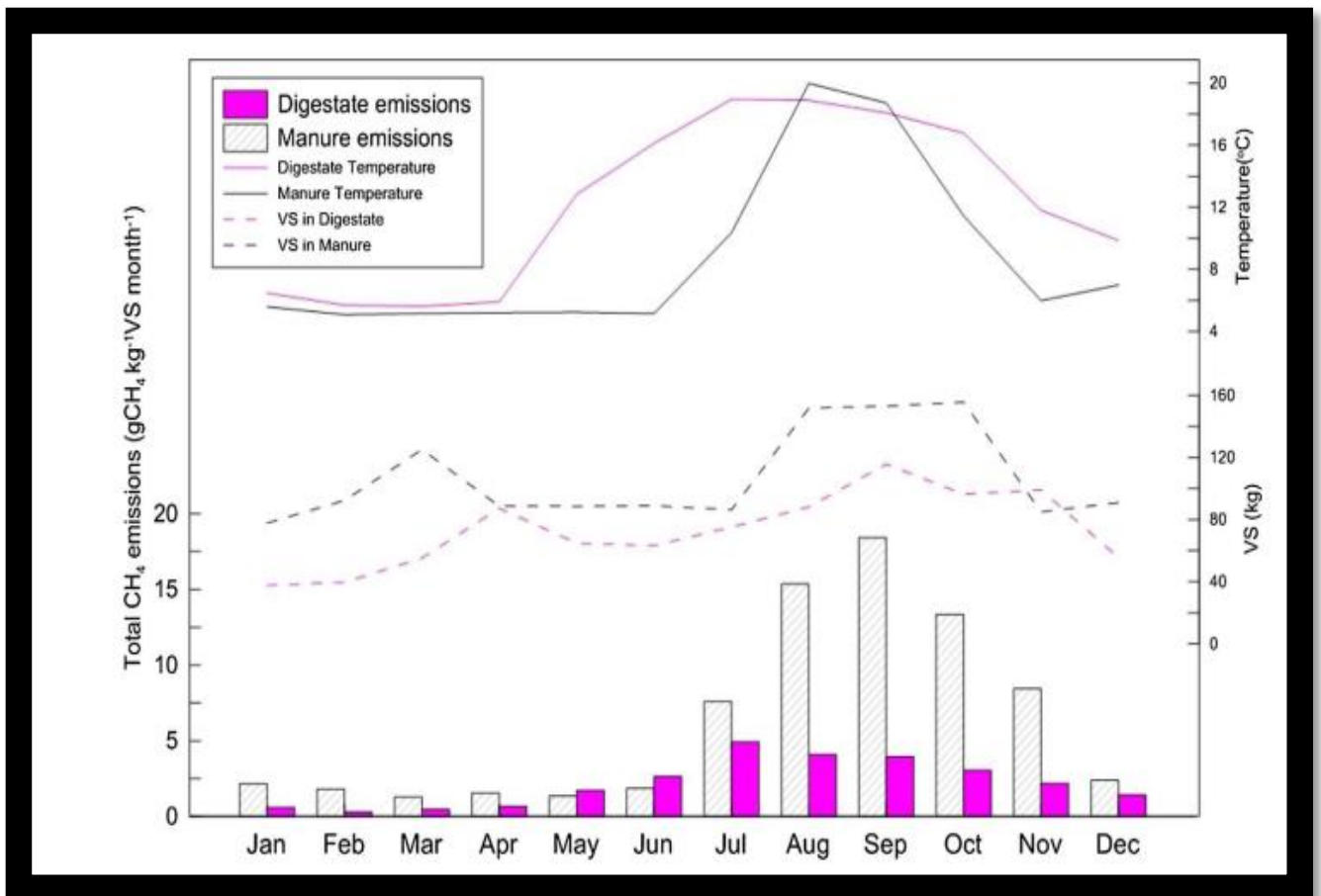


Figure 5.6 Monthly average Methane from Digestate Vs Untreated Slurry, taken from Maldaner *et al.*, 2018.

5.13 Case Study: Feasibility of Anaerobic Digestion to an Irish Dairy system

Sean O'Connor *et al.*, 2020, comprised a case study to determine the feasibility of small scale Anaerobic Digestion for Irish Dairy Farms. Despite the outlined benefits of Anaerobic Digestion such as energy production, Greenhouse gas reduction and the creation of a fertiliser by product, uptake of the technology in an Irish system has not reached the potential outlined. In fact, in Europe Ireland has one of the lowest uptake rates recorded at 20th in penetration rate from a total of 28 countries (Stambasky *et al.*, 2016). One of the main reasons detailed to the lack of uptake nationally has been in comparison to systems such as Germany and other European countries where plants are particularly large scale and the concern for an Irish system is whether there is ample feedstock available to feed the system (O'Connor *et al.*, 2018). Studies have indicated that for medium and large scale plants to be operational on Agricultural feedstock alone, there would not be enough feedstock to satisfy operations based on the average dairy herd of 90 cows (De Paor, 2018).

Therefore, the switch of attention has moved to small-scale anaerobic digestion (SSAD) as a means to overcome both economic and technical obstacles relating to smaller quantities of biomass available. Such plants have the capacity for 15-100kWe of electrical output (O'Connor *et al.*, 2018). SSAD is seen as a more viable option given the large amount of livestock (1.4 million dairy animals). As a result, energy demand prediction and potential feedstock availability are easily calculated, presenting a promising opportunity to achieve its benefits outlined in Chapter 2. Therefore, this case study set out to:

1. Assess the commercial viability of SSAD on Irish dairy farms
2. Determine technical needs in the operation of a SSAD plant.
3. Conduct an economic viability test on the technology

5.14 Feedstock Availability

The study in line with the Irish Dairy farm system assumed the co digestion feedstock products as cow manure and grass silage from small and medium sized farms. Grass silage was chosen due to its use and availability in Ireland, given 80% of all land is dedicated to pasture (Government of Ireland, 2018). 5 dairy farms of differing sizes were used to represent 5 differing scenarios. Specifically, Scenario 1 (50 cows), Scenario 2 (100 cows), Scenario 3 (150 cows), Scenario 4 (200 cows) and Scenario 5 (250 cows). Cow type represented consisted of Holstein-Friesian cows typical of a commercial dairy farm in Ireland (Wickham,2007). Manure was collected from cattle housing and milking parlour (Ryan,2006). Table 5.2 details the typical amount of manure collected over a 16-week winter period where cows are housed, it was difficult to find exact data on manure typically produced during the grazing season as manure produced is collected in the milking parlour twice per day, 20% collection rate was assumed (Teagasc, 2016).

Table 5.2 Manure Characteristics of Dairy Animals, taken from O'Connor *et al.*, 2020.

| Livestock | Livestock Weight Target | Total Manure Production (FW day ⁻¹) |
|---------------------------|-------------------------|---|
| Adult cows (<24 months) | 550 kg | 52.2 kg |
| Heifers (12 to 24 months) | 406 kg | 37.2 kg |
| Calves (>12 months) | 175 kg | 18.6 kg |

The model assumed Dairy farming to be the primary source of income on the farm and that only surplus crops were used as feedstock for biogas production. Available farmland to grow this extra feedstock was calculated by taking the average farm size from land necessary to sustain the dairy herd. The corresponding farm size to cow numbers indicated were as follows: Scenario 1 (43.51 hectares), Scenario 2 (68.74 hectares), Scenario 3 (93.96 hectares), Scenario 4 (119.19 hectares) and Scenario 5 (144.41 hectares). Recommended stocking rate was placed at 2.8 cows per hectare with a 20% margin of safety applied for variation in season and land which is unsuitable (Teagasc,2016). Typical yields of silage in Ireland range from 11 to 15 tonnes of dry solids per hectare with higher yields evident in the southwest and less in the northeast (Teagasc,2018). An average yield of 13 tonnes of dry solids was therefore applied to the model in this case study.

A point of interest from this case study indicated that as more land became available for the production of biogas, an increase of just 35.4% was noted between Scenario 1 (smallest) and Scenario 5(Largest). This indicates that perhaps a larger amount of land is available for biogas production in smaller farms than bigger farms once cow demand has been accounted for (Fig 4.13). Similarly, feedstock as grass silage represented a larger proportion in Scenario 1 (Smallest 51%) versus Scenario 5 (Largest 23%).

5.15 On Farm Activities Prior Digestion

The case study determined both direct and indirect costs of co digestion products associated with the energy produced detailed in Table 5.3 and 5.4. Cultivation calculations were based on cultivation of land every 7 years on average as per Teagasc guidelines. Cow manure feedstock accounted for energy inputted in the process of collecting, loading and movement of animals from housing to the milking parlour and finally to the digester site. Based on a previous study by Berglund *et al.*, 2006, the figure associated with the energy input involved in the transport and loading of manure is 2.5 Mj t⁻¹ km⁻¹. Digestate produced was assumed to be spread on the farmers own land.

Table 5.3 Energy consumed from raw material, taken from O'Connor *et al.*, 2020.

| Operation | Average Diesel Fuel Consumption (l ha ⁻¹ y ⁻¹) |
|---------------------------------------|---|
| Crop production | |
| Soil ploughing and crumbling | 4.67 |
| Sowing and maintenance | 6.9 |
| Weed control | 0.24 |
| Transport and spreading of fertiliser | 18 |
| Crop collection and transport | |
| Harvest | 47.20 |
| Harvest transport | 25.49 |
| Silo compaction | 8.80 |
| Digester feeding (grass) | 23.57 |

Table 5.4 Consumed energy and emission from production of raw materials, taken from O'Connor *et al.*, 2020.

| | Application Rate (kg ha ⁻¹ yr ⁻¹) | Energy Consumed (MJ kg ⁻¹) | CO ₂ Emitted (kg CO ₂ kg ⁻¹) |
|----------------------------|---|---|---|
| Mineral fertiliser | | | |
| Nitrogen | 82 | 70 ± 34 | 2.5 ± 0.1 |
| Phosphorus pentoxide | 11 | 12 ± 4 | 1.1 ± 0.4 |
| Potassium oxide | 29 | 7.5 ± 2.5 | 0.67 ± 0.19 |
| Other raw materials | | | |
| Diesel | N/A | 56.3 ± 5.6 | 3.64 ± 3.6 |
| Weed control | 0.11 | 200 ± 20 | 15.45 ± 1.5 |

All 5 farms generated enough energy to create a surplus of supply for external use as seen in Figure 5.7 Interestingly, energy demand for the farm itself represented a small proportion of overall energy created with range of 3.08% to 4.66% (Fig 4.14). The vast majority of energy created was for export off site, totalling between 73.04% to 79.13% of all energy produced.

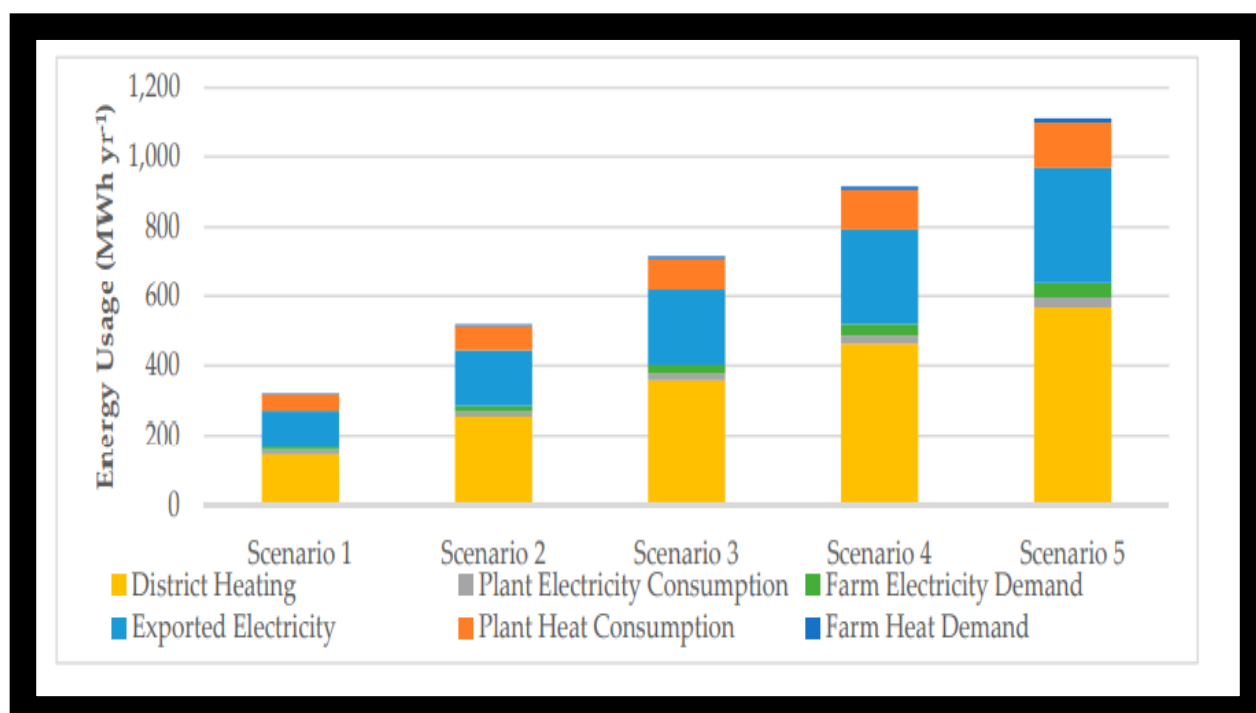


Figure 5.7 Energy usage on farms, taken from O'Connor *et al.*, 2020.

5.16 Biogas Plant operation and output

Biogas produced is much dependent on the portion of VS in feedstock supplied. Greater amounts of VS correlate to an increase in biogas produced (Manchala *et al.*, 2017). The physical and chemical properties of the feedstock were determined using the Boyle Buswell stoichiometric relationship for flowrates of biogas per kg of VS and detailed in Figure 4.12 (Boyle, 1977). Methane emitted from this process accounted for. The resultant methane yield was 0.6376 m³ CH₄ kg⁻¹ for manure and VS 0.822 m³ CH₄ kg⁻¹ VS for grass silage respectively. Predicted output is tabulated in Table 5.5 below.

Table 5.5 Properties of dairy cow slurry and grass silage both Physical and Chemical, taken from O'Connor *et al.*, 2020.

| Physical Properties | Dairy Cow Manure | Grass Silage |
|--|------------------|--------------|
| DS (g kg ⁻¹) ^a | 87.5 ± 2.1 | 292.7 ± 3.4 |
| VS (g kg ⁻¹) ^b | 66.9 ± 1.8 | 87.5 ± 2.1 |
| VS DS ⁻¹ (%) ^{a b} | 76.5 | 91.7 |
| Carbon (%) | 58.62 | 46.43 |
| Hydrogen (%) | 7.69 | 6.43 |
| Oxygen (%) | 30.50 | 44.72 |
| Nitrogen (%) | 2.92 | 2.36 |
| Sulphur (%) | 0.27 | 0.06 |

^a DS is dry solids; ^b VS is volatile solids.

Table 5.6 Determined characteristics of study, taken from O'Connor *et al.*,2020.

| | Scenario 1 | Scenario 2 | Scenario 3 | Scenario 4 | Scenario 5 |
|---|---------------|---------------|---------------|---------------|---------------|
| Herd Characteristics | | | | | |
| Herd size (adult cows) | 50 | 100 | 150 | 200 | 250 |
| Cow manure yield (t FW yr ⁻¹) | 505 | 1010 | 1515 | 2020 | 2,525 |
| Crop Characteristics | | | | | |
| Land available for energy crops (ha) | 21.19 | 24.10 | 27.00 | 29.90 | 32.81 |
| Grass silage yield (t FW yr ⁻¹) | 941 | 1070 | 1,199 | 1,328 | 1,457 |
| CHP Specifications | | | | | |
| CHP engine power (kW _e) | 17 | 26 | 39 | 46 | 55 |
| Methane Yield | | | | | |
| Methane yield ^a (m ³ yr ⁻¹) | 42,316 | 66,718 | 91,120 | 115,521 | 139,923 |
| Energy Consumption of AD Plant | | | | | |
| Electricity consumption (kWh yr ⁻¹) | 10,414 | 14,979 | 19,544 | 24,109 | 28,674 |
| Heat consumption (kWh yr ⁻¹) | 48,225 | 69,212 | 90,173 | 111,117 | 132,048 |
| Farm Energy Demand | | | | | |
| Electricity demand (kWh yr ⁻¹) | 8125 | 16,250 | 24,375 | 32,500 | 40,625 |

Availability of Dairy cow manure increased in line with an increase in cow numbers (Table 5.6). Plant type for the Case study consisted of a continuously stirred mesophilic tank reactor (CSTR). Biogas produced was used in a combined power and heat unit (CHP) as described in Chapter 2. The plant was in operation for 91% of the time or 8000 hours to allow for ongoing maintenance. 25 days was allowed for hydraulic retention (Bioenergy Training centre, 2020). The required CHP unit size was determined through the equation outlined in Figure 5.8.

$$CHP\ capacity\ (kW_e) = \frac{Biogas\ production\ (m^3) \times [Calorific\ value\ of\ biogas\ (\frac{MJ}{Nm^3}/3.6)}{Operational\ full\ load\ (\frac{h}{yr})} \times Electrical\ efficiency\ (\%),$$

Figure 5.8 CHP Capacity calculation, taken from O'Connor *et al.*,2020.

Typical of similar sized systems, CHP unit was attributed with thermal efficiency of 55% and efficiency of electricity of 30% (Enerblu,2019). The main source of power was required by the

stirring and subsequent pumping of feedstock at 7.2 kWh t⁻¹ in line with previous studies by Berglund.

5.17 End use of Energy Produced

Electricity produced by the system was first used to cover the demand of the farm and any surplus sold back to the National Grid. Specifically, 4 main demands were identified as:

1. AD plant operation.
2. Farm Demand to produce milk
3. Surplus electricity supplied to the National Grid.
4. Surplus exported to thermal energy.

Average energy demand for the farm was determined by calculating the energy required per litre of milk produced (Humphrey *et al.*, 2013), where yield averaged was assumed as 5000 litres per cow. Energy displaced by the CHP unit was assumed to be kerosene as the main fuel source used on Irish Dairy Farms (Humphreys *et al.*, 2013). Excess heat produced by the plant also had a number of potential uses including:

1. Drying of woodchips
2. Horticultural usage
3. Local Industry
4. District Heating Scheme

5.18 Cost of Construction and Operation

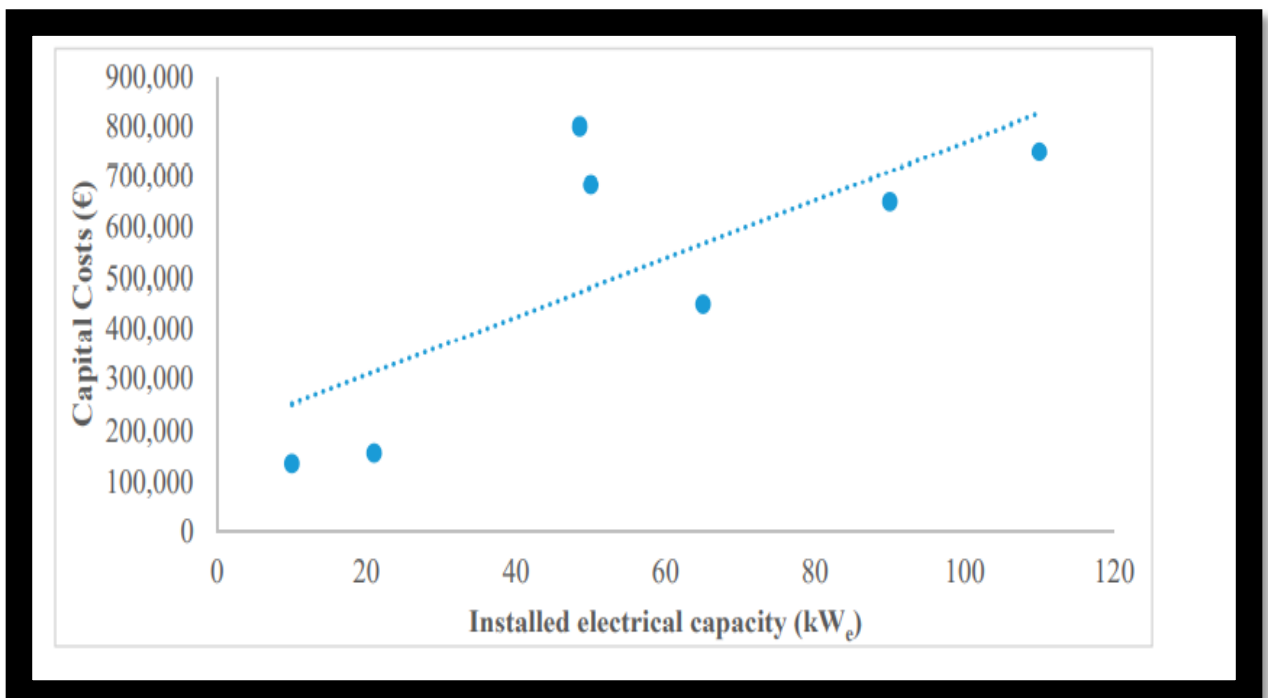


Figure 5.9 Costs of AD plants of differing electrical capacity, taken from O'Connor *et al.*, 2020.

Figure 5.9 details the costs associated with the construction and establishment of an AD plant of Differing electrical capacities. Capital costs were determined through combining the capital costs with the CHP capacity to produce electricity from previous studies from Redman 2016 and Samir. Capital costs reduced as the capacity of the plant increased. Other costs associated with the running of the plant include a maintenance cost of 2.5% of capital cost and insurance fee 1% of capital costs (O'Connor *et al.*, 2020). Staffing costs associated with the daily operation of 8.5 per kWe were determined to be €15 per hour in line with standard pay scale in Ireland for such a position. It was not possible to calculate the cost of tax due to an unknown surrounding total profit or loss. Similarly, interest could not be calculated due to the nature of fluctuation on the financial market.

5.19 Revenue Potential

Exported electricity to the National Grid is sold through the Renewable Energy Feed in Tariff (REFIT) introduced by the Irish Government in May 2010 (Department of Communications Energy and Natural and Resources, 2013). Tariffs were available for a 15-year period through indexation to a rate of 15.8c€ kWh⁻¹ for AD electricity exported with CHP of up to capacity of 500kW. Current REFIT schemes have ceased as of December 2015 with an expectation for it to reopen again with support period of 20 years. Revenue was therefore calculated from the point electricity is sold to the National grid and didn't include losses after this point such as distribution or transmission.

Demand for electricity on site at the farm was determined through an average electrical rate of 6 months in 2017. Two rates of usage were used: consumption less than 0.02 GWh yr⁻¹ (19.9c€h⁻¹ purchase rate) and consumption at 0.02 to 0.5 GWh yr. ⁻¹ (15.1c€ kWh⁻¹ purchase rate). At the time of study, the rate of displacement between kerosene with CHP was outlined as a fuel cost of 8 c€ l⁻¹ (SEAI, 2018). Plants in the case study were also subject to the Support Scheme for Renewable Energy of 2019 allowing a tariff of 2.95 c€ kWh⁻¹ for 15 years on plants producing up to 300 MWh yr⁻¹ (SEAI, 2018). Outside of infrastructure cost, thermal energy sales through a heating system (district) was predicted at €0.03 kWh⁻¹.

Financial indicators were also applied to the study to determine the economic performance of the plants. Four main parameters were assessed including: Net Present Value (NPV), Internal

rate of return (IRR), discounted payback period and simple payback period. NPV was used to determine project profitability accounting for cash flow during set periods of time. IRR represented a discount rate making NPV of all cash flows inclusive to zero. Discount rate was used to show investor risk when choosing to invest. Larger risk is associated with a greater discounted rate as compensation. This case study set the discount factor at 5% over a 20-year plan lifecycle in line with previous studies by Redican (2018). Payback period shows how long it took to create revenue to break even on the investment.

Government grant aid in previous studies accounted for a significant portion of establishment costs such as those employed in France and England which have accounted for up to half of expenses incurred (Lukehurst,2015). On this basis, a grant aid of 50% was applied to the case study.

The above data was incorporated over the 20-year lifespan of the plant under the 5 scenarios of differing cow and land numbers and detailed in table 5.7 below. Results indicated suggest commercial SSAD plants to be feasible from an economic standpoint for farms with greater than 100 cow (Scenario 2-5). Significantly, payback periods of farms between 100 and 200 cows were considerably long (Scenario 2-4). this figure may be subject to change given the potential to sell to the National grid and energy sold thermal power as they generated the largest amount of revenues. Due to economies of scale, capital expenditure that was required as plant capacity increased.

Government Capital infrastructure grant of 50% shows a significant impact on feasibility and potential to use this figure to utilise a political pathway to SSAD uptake in Ireland as seen in countries such as France (Lukehurst,2015). As portrayed in Figure 5.10 and 5.11, the grant aid significantly reduced payback periods where all 5 scenarios are paid back with 17 years or most significantly under 8 years in a 100 cow scenario.

Table 5.7 Project Revenue Prediction under scenarios, taken from O'Connor *et al.*, 2020.

| | Scenario 1 | Scenario 2 | Scenario 3 | Scenario 4 | Scenario 5 |
|---|------------|------------|------------|------------|------------|
| Herd size (adult cows) | 50 | 100 | 150 | 200 | 250 |
| Project Revenues (€) | | | | | |
| On-site electricity savings | €32,338 | €64,675 | €73,613 | €98,150 | €122,688 |
| On-site heating savings | €3,932 | €7,864 | €11,796 | €15,728 | €19,660 |
| Sale of exported electricity | €323,727 | €504,099 | €684,472 | €864,844 | €1,045,216 |
| Sale of exported heat to district heating | €88,916 | €151,751 | €214,600 | €277,461 | €340,329 |
| Support Scheme for Renewable Heat | €66,663 | €114,091 | €161,530 | €208,977 | €256,430 |
| Total Revenues | €515,576 | €842,480 | €1,146,000 | €1,465,159 | €1,784,322 |
| Project Expenditures (€) | | | | | |
| | | | | | |

Table 5.8 Investment costs less Financial Indicators, Taken from O'Connor *et al.*, 2020.

| | | | | | |
|---|-----------|----------|----------|----------|------------|
| Investment Costs | | | | | |
| Capital Costs Inc. CHP | €290,099 | €345,479 | €400,860 | €456,241 | €511,622 |
| Operating Costs | | | | | |
| Maintenance and Repair Costs incl. CHP | €145,049 | €172,740 | €200,430 | €228,121 | €255,811 |
| Insurance | €87,030 | €103,644 | €120,258 | €136,872 | €153,487 |
| Labour | €42,625 | €67,204 | €91,784 | €116,363 | €140,943 |
| Total Operating Costs | €274,704 | €343,588 | €412,472 | €481,356 | €550,241 |
| Financial Indicators | | | | | |
| Profit before tax (€) | €240,872 | €498,892 | €733,538 | €983,803 | €1,234,082 |
| NPV at 5% (€) | -€135,418 | -€26,758 | €67,339 | €171,168 | €275,006 |
| IRR (%) | -2% | 4% | 7% | 9% | 11% |
| Payback period (Years) | 25.65 | 12.87 | 10.18 | 8.66 | 7.75 |
| Discounted payback period (Years) | N/A | 24.02 | 14.56 | 11.64 | 10.05 |
| Payback period Incl. capital grant (Years) | 11.03 | 6.43 | 5.09 | 4.33 | 3.88 |
| Discounted payback period Incl. capital grant (Years) | 16.34 | 7.96 | 6.02 | 5.00 | 4.42 |

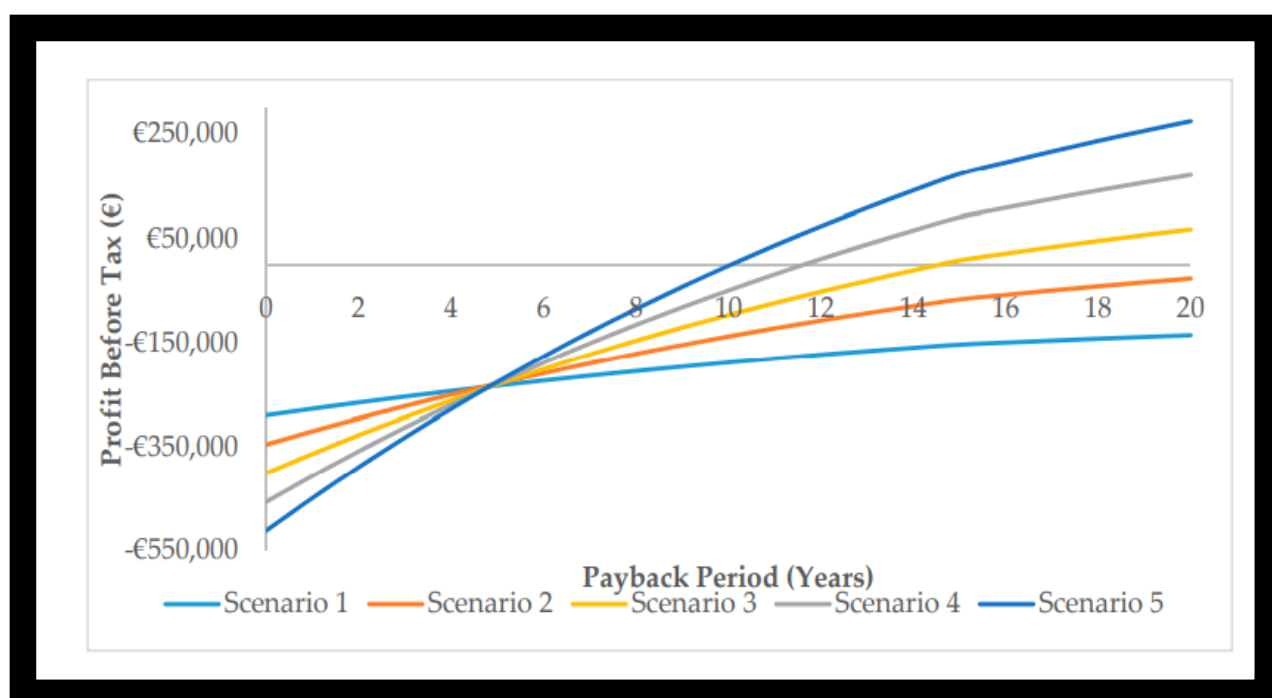


Figure 5.10 Payback period excluding 50% Grant aid, Taken from O'Connor *et al.*, 2020.

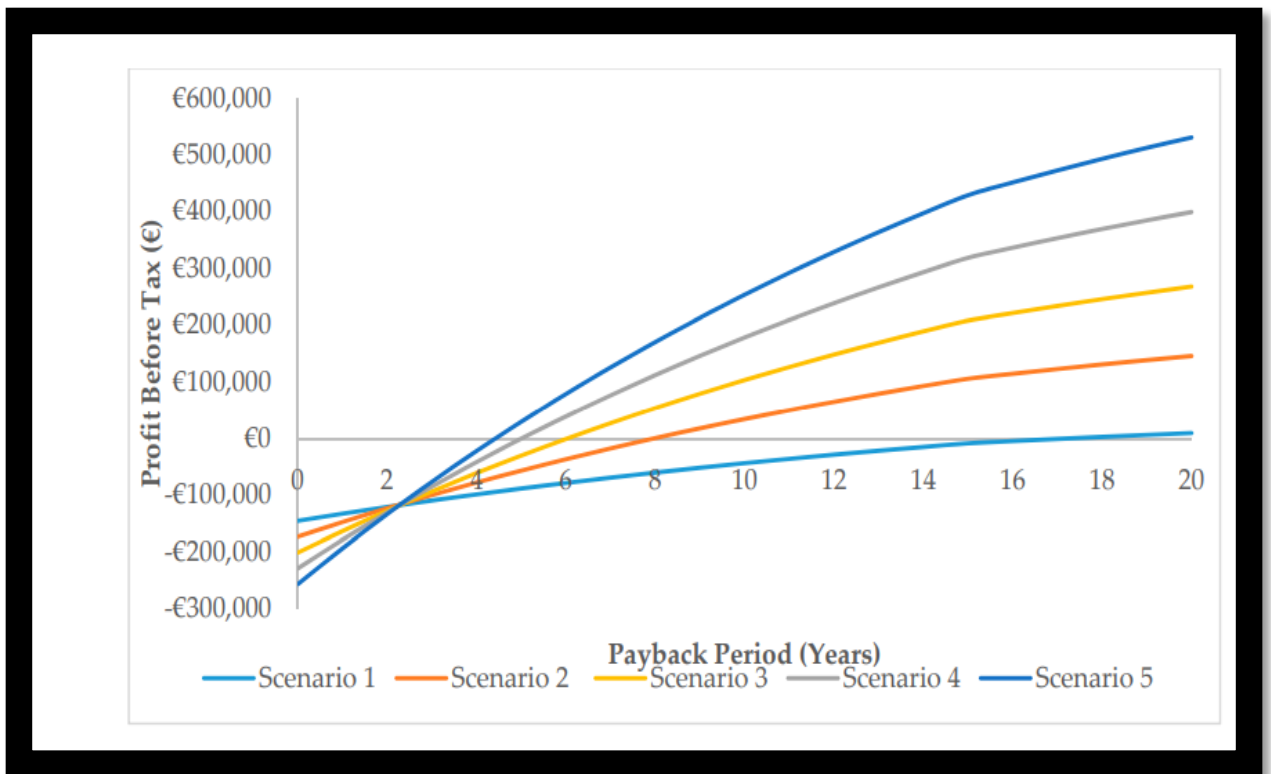


Figure 5.11 Payback period including 50% Grant Aid, Taken from O'Connor *et al.*, 2020

5.20 Renewable Energy Directive Considerations

As outlined in Chapter 1, RED II requires for all biomass fuels in the creation of electricity, heating or cooling to satisfy a 70% reduction in GHG, rising to 80% by 2026. This presents a challenge to the Agricultural Industry to consider feedstock availability to reach these targets. KPMG, SEAI, Teagasc and Ricardo Energy & Environment 2021, drafted a study to determine Ireland's ability to reach outlined targets through 3 differing scenarios of feedstock inclusion type.

Scenario 1 (Figure 5.12) examined the ability of Standard Ryegrass and slurry inclusion to satisfy eligibility criteria. Scenario 2 (Figure 5.13) examined MSS inclusion with slurry and Scenario 3 (Figure 5.14) represented a hybrid model consisting of Rye/ Clover and Slurry inclusion. The SEAI RED compliance model was utilised to detail their findings in Fig 5.12, 5.13 and 5.14

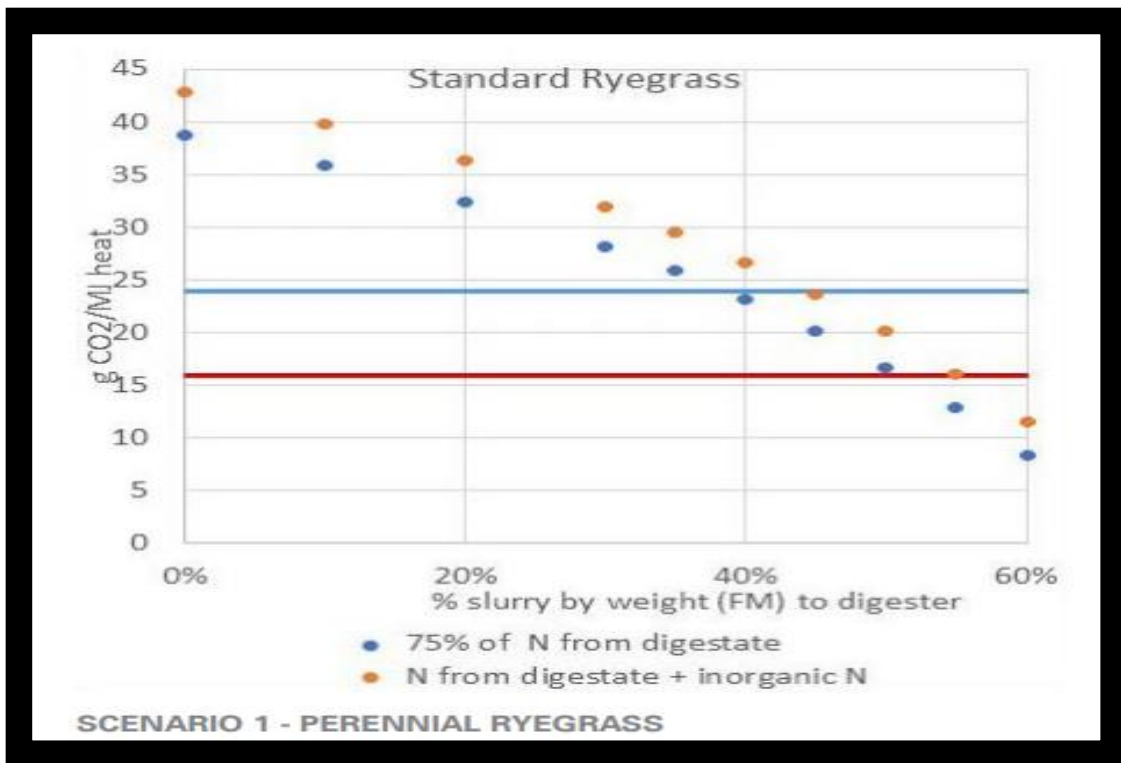


Figure 5.12 Scenario 1 Perennial Ryegrass inclusion, taken from KPMG,2021

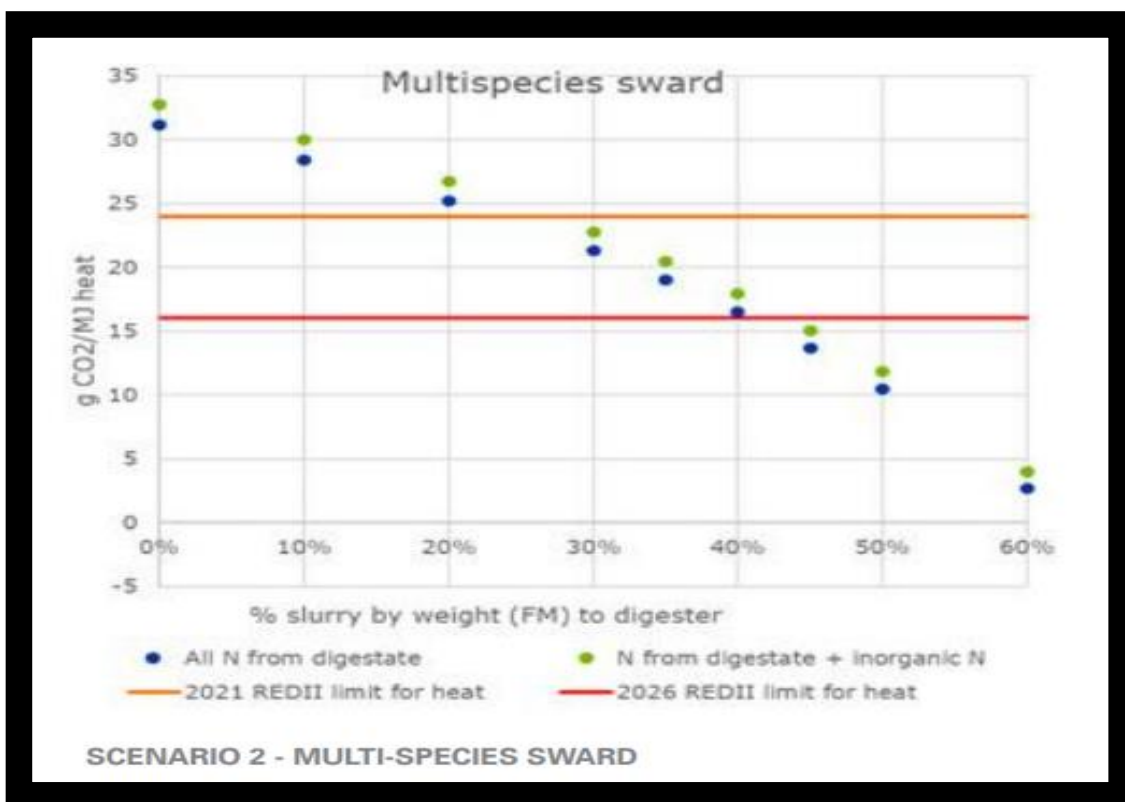


Figure 5.13 Scenario 2 Multi-Species Sward Inclusion, taken from KPMG, 2021.

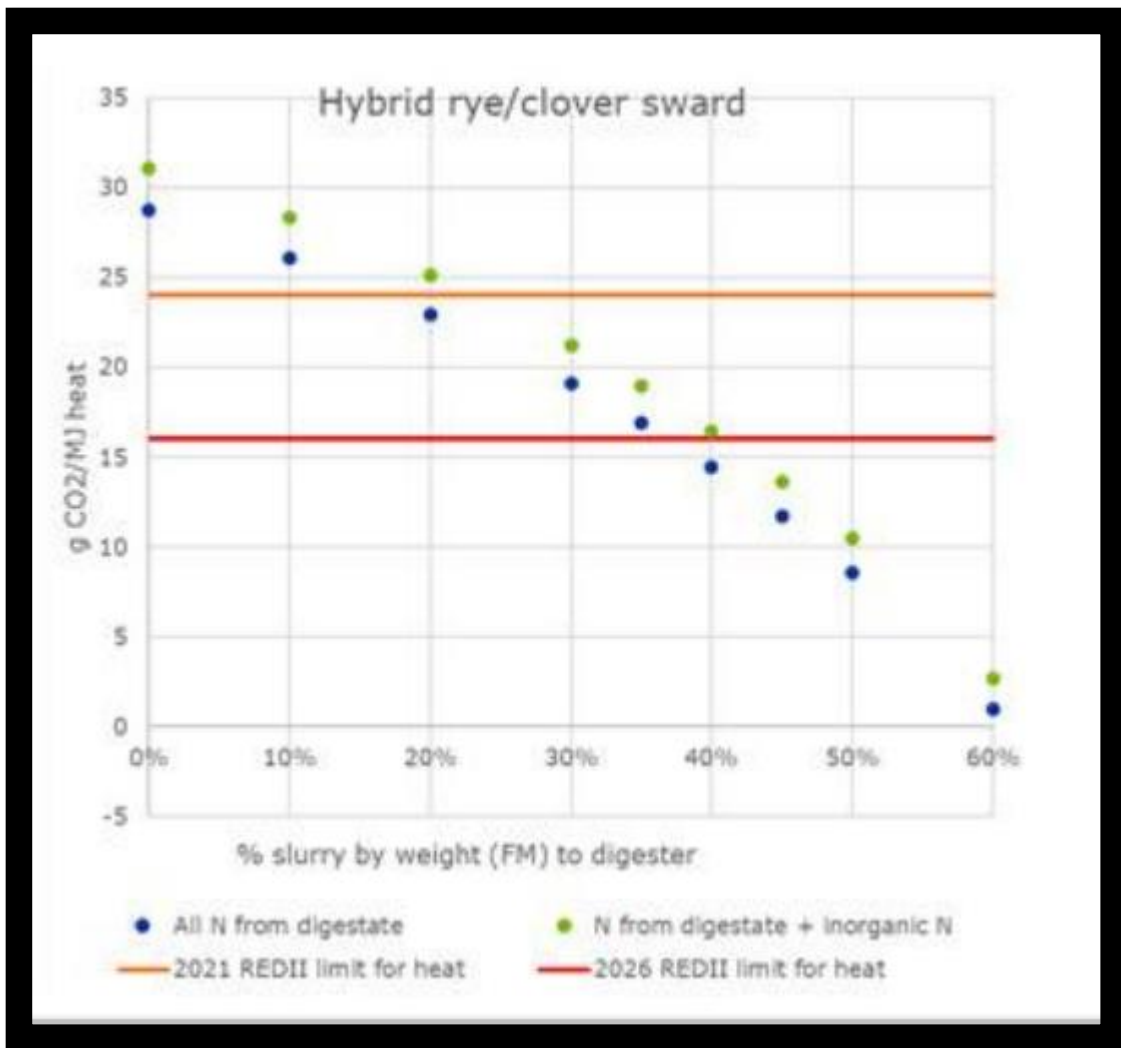


Figure 5.14 Scenario 3, Hybrid Inclusion, Taken from KPMG, 2021.

As a benchmark of the typical grazing variety used on Irish Dairy Farms, Perennial Ryegrass requires between 55-60% inclusion of chemical fertiliser or digestate in order to meet RED II criteria. Furthermore, if 75% of fertiliser requirement was met by Digestate then slurry incorporation can be reduced to 50-55%. Predictive model results suggest both S2 MSS and S3 Hybrid model would not satisfy RED II protocol based on Forage alone. For S2 MSS to reach the initial reduction target of 70%, a 29% inclusion of slurry is required (KPMG,2021). This is mirrored in S3 Hybrid model with a 21% inclusion of slurry required. Furthermore, to reach the 80% target by 2026, S2 will require a 43% inclusion of slurry along with MSS. Similarly, S3 Hybrid model will require a 41% inclusion of slurry along with the Hybrid grass/ clover mix.

5.21 Anaerobic Digestion and the Environment

All of the energy required for the operation of the plant are facilitated internally through the CHP engine, producing no CO₂ emissions. Any excess heat was utilised on site as a replacement for conventional kerosene. A previous study by Upton (2019), attributes 36.4Mj 1-1 output energy cost to kerosene and associated CO₂ emissions of 0.25 tCO₂ MWh⁻¹. Electricity produced beyond the needs of the AD plant or farm are exported to the National grid for profit. This represented a CO₂ saving of 0.367 t CO₂ MWh⁻¹ at the time of study (Commission for Regulation of Utilities. Fuel mix disclosure 2020).

The release of CO₂ from combustion of biogas was set at a rate of 83.6kg GJ⁻¹ (Nielson *et al.*,2014). A “do nothing” approach was also incorporated to show GH savings if no AD plant was constructed to include emissions from the release of emissions from manure and land application subsequently. These calculations followed OECD guidelines which detail emission release during storage based upon 20% of biogas potential production from a 2-month timeframe. Land application emissions were predicted based on 10% biogas potential remaining, emission factor for biogas was predicted to the equivalent of 11.9kg CO₂s from GWP of methane at 28 (Myhre *et al.*,2013).

Table 5.9 outlines the resultant CO₂ balance accounting for both CO₂ inputs and outputs for each scenario.

Table 5.9 CO₂ balance under each Scenario, taken from O'Connor *et al.*, 2020.

| | Scenario 1 | Scenario 2 | Scenario 3 | Scenario 4 | Scenario 5 |
|--|------------|------------|------------|------------|------------|
| Herd size (adult cows) | 50 | 100 | 150 | 200 | 250 |
| CO₂ Produced (kg CO₂-eq. yr⁻¹) | | | | | |
| Crop Production | | | | | |
| Soil ploughing and crumbling | 264 | 300 | 336 | 372 | 408 |
| Sowing and maintenance | 300 | 341 | 382 | 423 | 464 |
| Sowing | 90 | 102 | 114 | 126 | 139 |
| Weed control (fuel) | 13 | 15 | 17 | 19 | 21 |
| Weed control (mineral production) | 36 | 41 | 46 | 51 | 56 |
| Fertiliser spreading (fuel) | 381 | 434 | 486 | 538 | 591 |
| Fertiliser (mineral production) | 5013 | 5699 | 6386 | 7073 | 7760 |
| Feedstock Collection and Transport | | | | | |
| Harvest | 2665 | 3030 | 3395 | 3760 | 4125 |
| Harvest transport | 1439 | 1636 | 1,833 | 2030 | 2227 |
| Silo compaction | 497 | 565 | 633 | 701 | 769 |
| Digester feeding (Crops) | 1331 | 1513 | 1695 | 1878 | 2060 |
| Collection and digester feeding (Manure) | 92 | 185 | 277 | 370 | 462 |
| Biogas Production Process | | | | | |
| CO ₂ Content | 133,652 | 210,722 | 287,722 | 364,863 | 441,933 |
| Digestate Disposal | | | | | |

Each scenario under investigation represented a CO₂ reduction from 2,059 to 173,237 kg CO₂ eq yr⁻¹. This represented a significant reduction under each scenario. Significantly, even the smallest plant in Scenario 1 represented a CO₂ saving of 41,180kg CO₂ eq or the emissions of 87 cars. The biogas production process itself exhibited the largest amount of CO₂ emissions. In this process, CO₂ is released in the combustion of biogas. This represented 90-95% of CO₂ emissions each year over the 5 Scenarios.

5.22 Environmental Impact of Digestate

Replacing the use of untreated dairy cow slurry with Digestate has the potential to displace a significant amount of GHG emissions to the tune of c.54 kgCO₂ e/ tonne slurry (Ruiz *et al.*,2022). However, this figure is largely dependent on the nature of the feedstock supplied, type of animal. Its diet, time of the year and manure management system in place. Typically, slurry storage is via open tanks in which methane is released to the air and the organic matter left behind spread on the land through a tanker system. Utilising this slurry and diverting it towards Biomethane production not only creates a renewable energy source but also reduces methane and associated GHG emissions whilst creating a usable bioorganic fertiliser.

Nitrous oxide and methane are the two main GHGs associated with stored slurry. Research by Nolan *et al.*,2020 indicated that stored slurry produces twice as much nitrous oxide than Digestate in the process and spreading of the material. Odour emissions are reduced, however an increase in ammonia may occur due to an increase in pH as a result of ammonia nitrogen availability. However, this may be mitigated with technologies proven to reduce its occurrence such as reduction of slurry pH on arrival, increased storage infrastructure or covers on storage areas (Nolan *et al.*,2020).

From a chemical fertiliser standpoint, Digestate has the potential to offset its use from 15-100% depending on the nature of the feedstock supplied and associated conditions (McCabe *et al.*, 2019). The Anaerobic Digestion and Bio resources association have reported that for every 1 tonne of chemical nitrogen replaced with Digestate, a tonne of oil, 108 tonnes of water supplied and 7 tonnes of CO₂ emissions are saved.

5.23 Biochar as a Natural Methane Mitigation additive

This thesis has outlined biochar as a potential additive to reduce methane from stored slurry both stockpiled and liquid storage which further compliments Anaerobic digestion. The resultant digestate created in the process may be used as feedstock in the production of syngas via pyrolysis where biochar is created as a by-product. This link requires further assessment to determine is biochar a feasible addition to the manure storage on Irish Dairy Farms today.

5.24 2022 Californian Study

The uptake of Biochar as a manure additive is very much in its infancy. However, there are a number of studies which suggest significant reductions in methane yield can be made. For example, di Pertha *et al.*, 2020 in her study found a 33% reduction in methane in vitro when comparing against the control slurry which had no biochar present. This was due to the formation of a thick crust which was less permeable to volatilisation compared to the control.

Harrison *et al.*, 2022, recently conducted a study to identify the impact dairy manure treated with biochar had on stockpiled manure to allow Methane targets set about by the American Government to be reached. Recent legislation such as the short lived climate pollutant reduction law – SB 1383 and Global methane pledge call for significant reduction in methane outputs from Agriculture by 2030. Specifically, SB 1383, introduced in 2016 requires methane emitted from the Californian dairy herd to be reduced to 40% below levels recorded in 2014 by 2030 (Lara *et al.*, 2016). More recently, the conference of the parties 26 or COP26 saw the introduction of the Global Methane pledge. This pledge signed by 110 countries sets about a 30% reduction in Methane levels from Agriculture on 2020 levels by 2030 (Global Methane Pledge 2021). The primary action which California plan to utilise is in the form of Anaerobic Digesters to reduce methane output. However, this target is not currently being reached due to financial and legislative barriers hindering the progress of uptake and construction (Satchwell *et al.*, 2018). Furthermore, Anaerobic digestion in California is not suitable for stockpiled manure and here presents an opportunity to mitigate methane from this stock which represents a significant proportion of total waste (Harrison *et al.*, 2022). Therefore, the successful uptake and efficacy of biochar to the Californian study may not only help reach emission targets but also reduce the need to construct extra costly Digesters.

Data of significance for an Irish system entails the treatment of the Ruminant Dairy slurry and how biochar of similar nature can be utilised nationally in Ireland. This study was of great significance as within the Californian system, intensive dairy systems and the associated manure management may account for up to half of methane emissions with average of 25% (Harrison *et al.*, 2022). Therefore the Dairy feedlots present a significant challenge to the output of methane emissions due to their high stock density, manure output and the spatial decouplement from livestock and the production of feed (Owen *et al.*, 2015). Studies by Steiner (2015) and Wang (2013) have shown that when biochar is added to a stockpile to create a compost, lower greenhouse gas emission output are recorded through gas absorption, improved aeration and stimulating anti methanogenic microorganisms. This study set about detailing potential methane reductions from stockpiled manure through co composting with biochar material, the by-product of pyrolysis.

5.25 Experimental Design

This study hypothesised that methane can be reduced from biochar amended stockpiles via improved aeration (Harrison *et al.*, 2022). A field based study was carried out testing this hypothesis with and without biochar present in the trial sites. Greenhouse gas results from the trial sites were then worked into a life cycle assessment (LCA) of a typical management system of solid manure. These results are then incorporated into a model to estimate how effective biochar composting is in meeting California's methane goals (Harrison *et al.*, 2022). The trial took place for two months between August and September 2021. The biochar used was derived from approximately 85% Douglas Fir, Ponderosa pine and remaining waste material sourced from Oregon Biochar Solutions from pyrolysis at 900 degrees Celsius. Full composition of biochar used is detailed in Table 5.10.

Table 5.10 Composition of Biochar used, taken from Harrison *et al.*, 2022.

| | |
|---|----------------------------|
| Total C (g kg ⁻¹) | 790 |
| Total N (g kg ⁻¹) | 1.92 |
| H:C (molar ratio) | 0.102 |
| O:C (molar ratio) | 0.068 |
| Particle size range (mm) | 1-4 mm |
| pH | 9.2 |
| EC (dS m ⁻¹) | 1.21 |
| Bulk density (g cm ⁻³) | 0.08 |
| Moisture content (fresh wt. %) | 8.97 |
| Volatile matter (dry wt. %) | 55.61 |
| Ash content (dry wt. %) | 4.43 |
| Fixed carbon content (dry wt. %) | 39.96 |
| NH ₄ ⁺ -N (mg kg ⁻¹ dry) | Below instrument detection |
| NO ₃ ⁻ -N (mg kg ⁻¹ dry) | 3.51 |
| BET surface area (m ² g ⁻¹) | 437.17 |
| Total pore volume (cm ³ g ⁻¹) | 0.2549 |
| Sorption average pore size (diameter in nm) | 2.3 |
| Cumulative surface area of pores between 0.3-1.34 nm hydraulic radius (m ² g ⁻¹) | 619.15 |
| Cumulative pore volume of pores between 0.3-1.34 nm hydraulic radius (cm ³ g ⁻¹) | 0.245 |

Each pile consisted of a trapezoidal shape, 30 meters long, 3 meters in width and 1 meter of height approximately. The control pile, containing only manure contained 15.34 tonnes of solid manure fresh and 1.32 tonnes of residue from orchard clippings. The experimental pile

containing the biochar contained 15.35 tonnes of solid manure fresh, 1.32 tonnes of orchard residue and 1 tonne of biochar (Fig 4.1). During the 35-day trial period, both piles were turned on days 8,15,22 and 29. The three main Greenhouse gases measured were CH₄, N₂O and CO₂ each day over the 35-day trial period via a spectrometer linked to a closed system static chamber from nine different locations on each pile. Fluxes were discovered via the Picarro Soil Flux Processor program (Hutchinson *et al.*,1981). To determine physiochemical properties, new samples were taken each week once the piles were turned and moisture content determined.

5.26 Life Cycle Assessment

Part 2 of the study involved the incorporation of a life cycle assessment (LCA) into the equation to estimate the potential impact linked to each stage of biochar composting, composting and final stockpiling (Vergara *et al.*, 2019). The first consideration on this system begins with the transportation of raw feedstock and final application of compost to the soil as fertiliser. 20 and 10-year global warming potential (GWP) were accounted for each experiment. The 20 year GWP was used as methane possess a significant GWP over a 12-year period lifecycle. This was also most relevant to SB 1383 and Global Methane Pledge as America seeks a transition period away from fossil fuel (Isaksson *et al.*, 2020). Fossil fuel emissions avoided as a result of the process of pyrolysis was calculated using a net energy value of 4043 MJ/ feedstock and biochar yield of 28.8%. Default factors of emissions from IPCC were also used assuming a mix of 50/50 (IPCC, 2006). In this scenario, biochar was also said to reduce GHG from the burning of biomass such as crop and forestry residues, assuming up to 10% of the feedstock in biochar and compost production would have been burned. This was based upon the percentage of corn and wheat burned per annum in America (FAO,2019). The feedstock and compost was also transported by diesel lorries weighing 36 tonnes and delivered with 40 kilometres which was also accounted for in the calculations. From an economic standpoint, an estimation was also calculated regarding extra Anaerobic digesters required to meet the 40% reduction target set. Calculations were based on Digesters required without Biochar composting, with Biochar composting and Biochar composting along with a 1% reduction in herd numbers.

5.27 Methane Produced

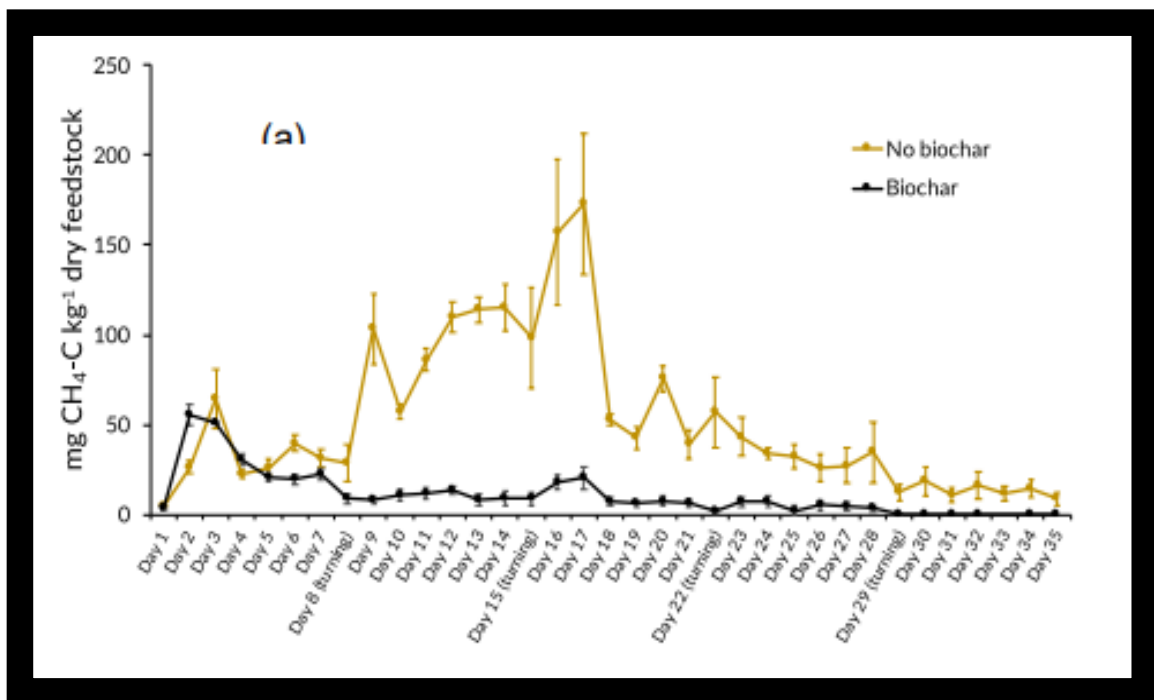


Figure 5.15 Daily CH₄ output with and without Biochar, taken from Harrison *et al.*, 2022.

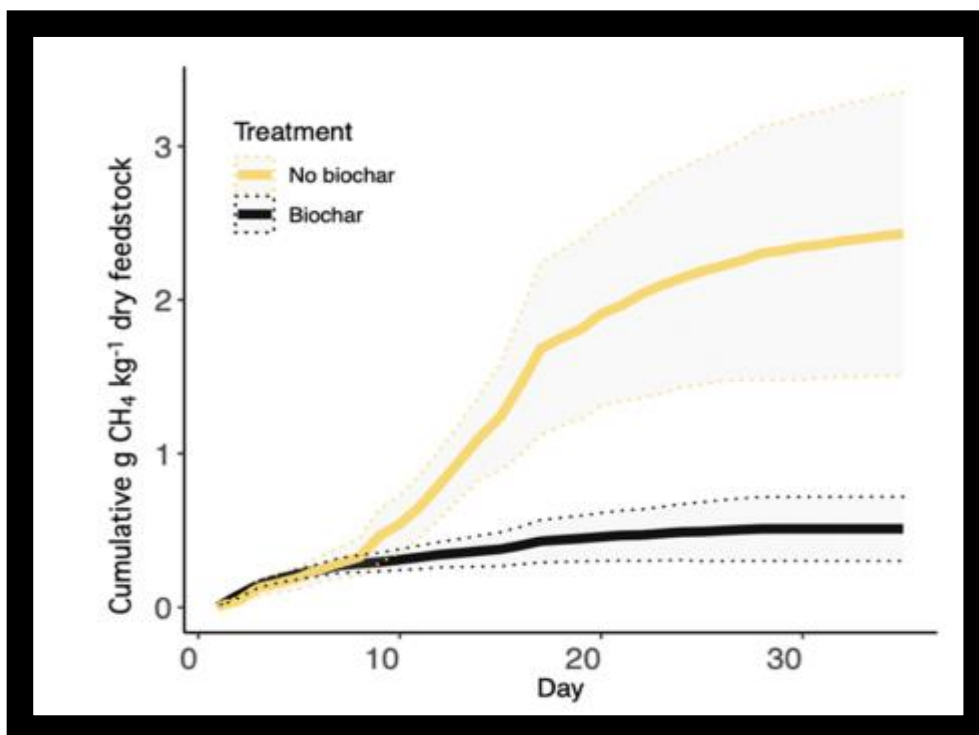


Figure 5.16 Cumulative CH₄ production with and without biochar, taken from Harrison *et al.*, 2022

As seen from fig 5.16, over the 35-day trial period, the pile containing manure only released 2.43g CH₄ kg of dry feedstock per day. 218g CO₂ kg dry feedstock and 0.029mg of N₂O per kg of dry feedstock was also emitted. Conversely, emissions from the biochar stockpile resulted in accumulative CH₄ kg of dry feedstock of 0.51g. CO₂ and N₂O were not statistically significant at 177g and 0.075mg respectively. This result in CH₄ reduction indicated a 79% reduction to that of the manure only stockpile with majority of emissions taken place in the first 3 weeks of the trial. The mode of action was said to be consistent with previous studies which indicated the increase in O₂ from the addition of the biochar reduced methane production by methanogens and increased uptake or consumption by methanotrophs which reduced the flux of CH₄.

5.28 Emissions saved by association (LCA)

The findings from the Gas measurement experiment were incorporated into the LCA model to detail the significance of this reduction in meeting their GHG targets. The results indicated a vast reduction in GWP. This was based on functional unit comprising of a metric ton of solid manure from a dairy animal managed by composting of biochar in line with a reference system where solid manure separated is stockpiled as seen in Figure 5.17.

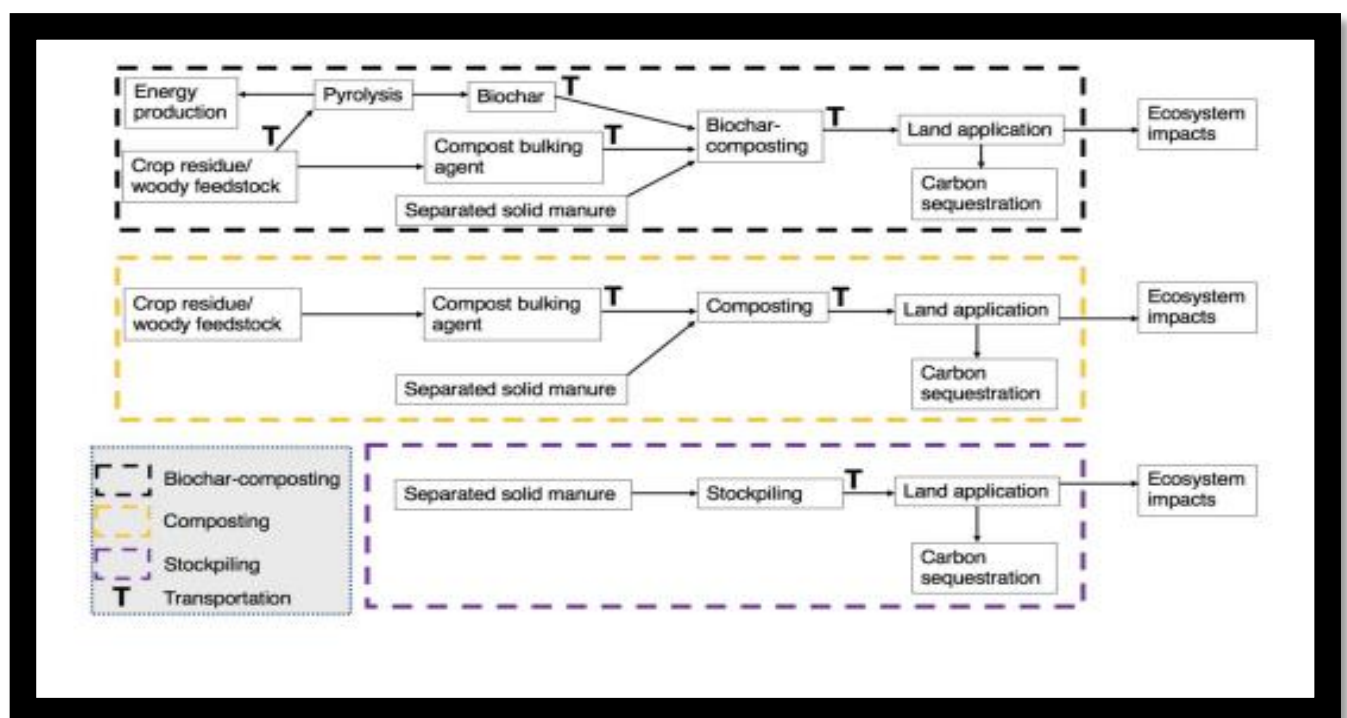


Figure 5.17 Schematic detailing boundaries for each of the three management approaches, taken from *Harrison et al.*, 2022.

Results from the 100 year GWP, the impact of composting, biochar composting and stockpiling were $-535 \text{ kg CO}_2\text{e}$, $-194 \text{ kg CO}_2\text{e}$, and $102 \text{ kg CO}_2\text{e}$ simultaneously as seen in Figure 5.18.

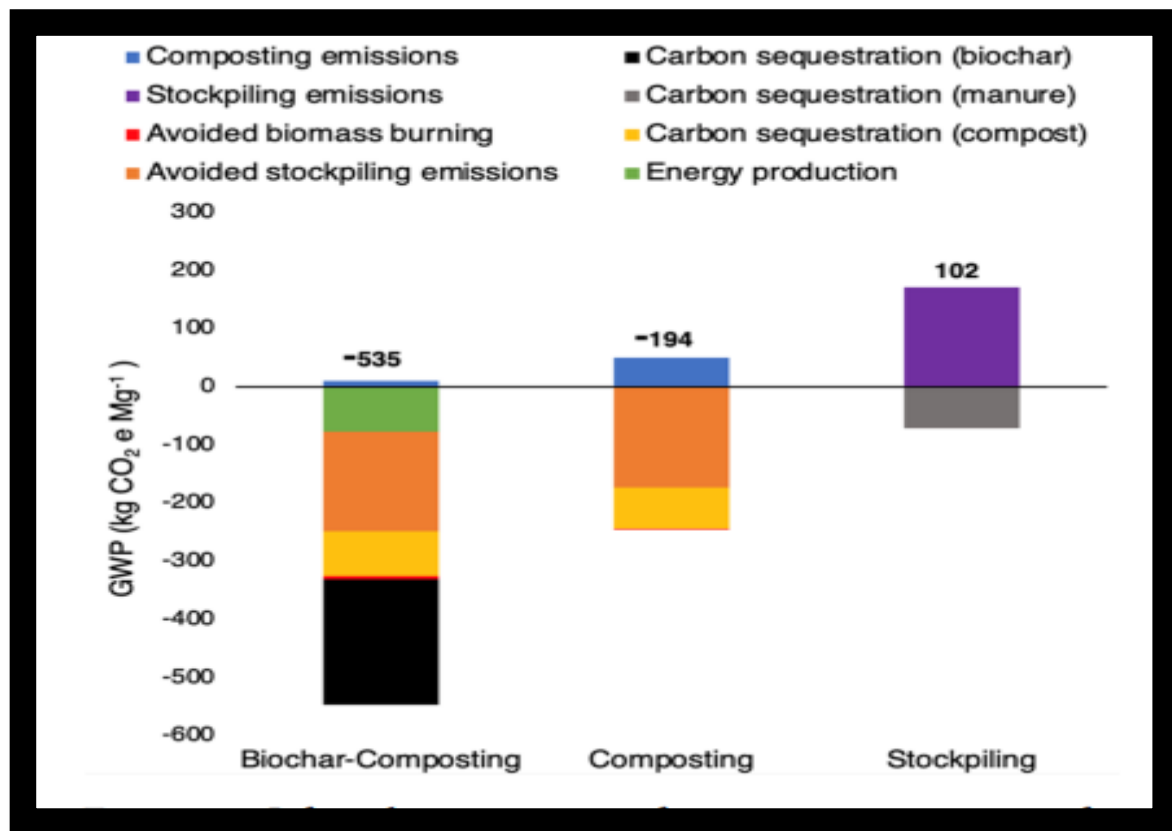


Figure 5.18 LCA strategies under 100 year GWP. Number indicates net GWP in kg, Taken from Harrison *et al.*, 2022.

The results of the 20 year GWP model are seen in Figure 4.7 below. Impact is detailed as $-870 \text{ kg CO}_2\text{e}$, $-441 \text{ kg CO}_2\text{e}$, and $446 \text{ kg CO}_2\text{e}$ for biochar composting, composting and stockpiling individually (Figure 5.19).

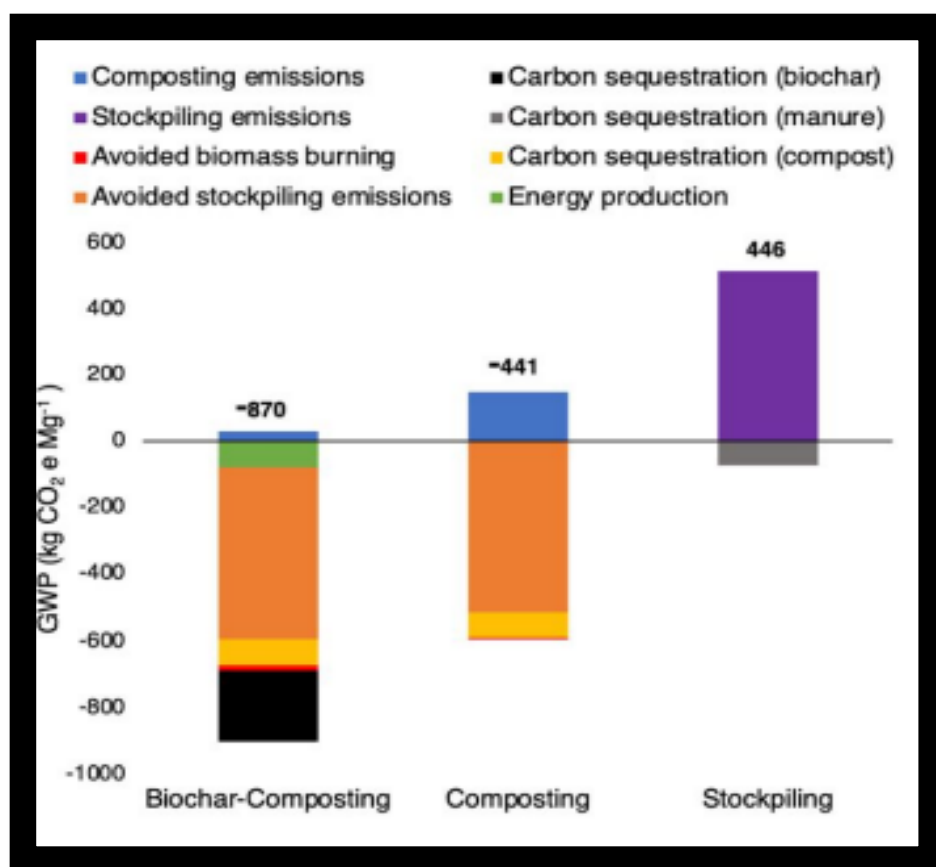


Figure 5.19 Results of 20 Year GWP Model, Taken from Harrison *et al.*, 2022.

5.29 Avoided Fossil Fuel

Avoided fossil fuel was detailed in figure 4.7 above. this was a s a result of the biochar produced and the energy/ electricity created as a result. A reduction of 76CO₂e was observed.

5.30 Biochar as a Biocover

Dougherty *et al.*, 2020 in their study explored the potential of biochar as a potential Biocover based on previous work which suggest it may be beneficial in reducing emissions lost to the environment during slurry storage. Over an 8-week period, emissions of Ammonia and Hydrogen Sulphide were measured from a lagoon protected with biochar versus a control without. Manure stored was typical of that of a commercial Dairy farm consisting of dairy washings and manure from an underground collection tank.

The biochar covers used were created and sourced through Bio-Logical a company based in Philomath. Four different treatments were applied to the slurry as follows:

1. Douglas Fir biochar produced through gasification at 650 degrees (FC650)
2. Douglas Fir Biochar produced through slow pyrolysis at 600 degrees (HF600)
3. Straw derived from Wheat

4. No Cover (Control)

Covers applied reached a depth of 5cm. The treatments were repeated three times in terms of emissions in comparison to a control without any cover. Gas emissions were measured via a sampling port to the side of the lagoon through Colorimetric analysis of gas. Samples were taken on the first day and subsequent days 14, 28, 42 and 56 to gauge the change in headspace concentration over the trial period and detailed in Figure 5.20 below.

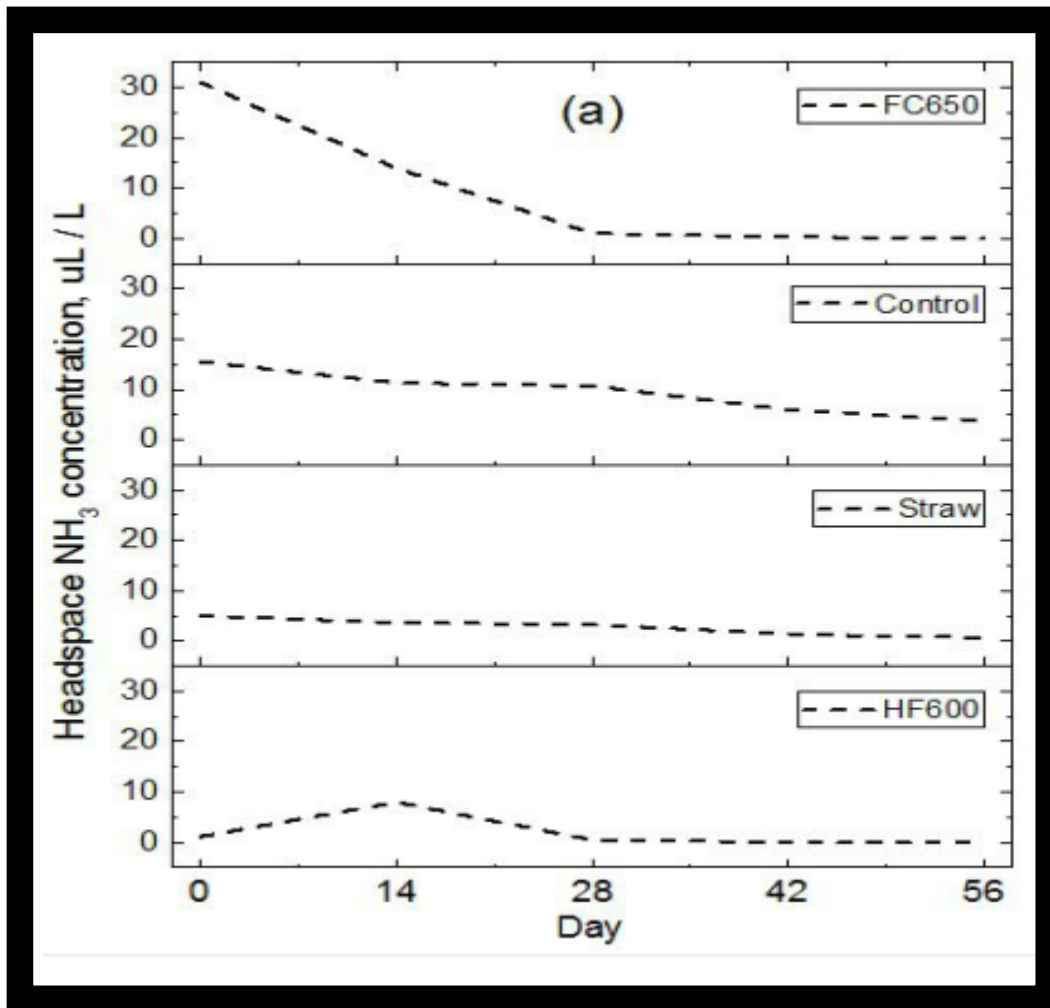


Figure 5.20 Ammonia concentration during trial period for 4 treatments for two manure types used, taken from Dougherty *et al.*, 2020.

Concentrations of Hydrogen Sulphide were below levels of measurement and therefore were deemed irrelevant for this study. As seen in figure 5.20, concentrations of Ammonia declined with the straw, control and FC650 treatments over time. HF600 covers displayed an increase in Ammonia emission on Day 14 unexpectedly. To compare concentration of Ammonia in the headspace two sample t tests (Unpaired) were conducted. Significant reductions ($p < 0.05$) was

observed with straw and HF600 covers. In comparison to the control, a reduction in ammonia emissions was also observed in FC650 covers. However, this was deemed statistically insignificant ($p < 0.05$) displayed in figure 5.21 (Dougherty *et al.*, 2020).

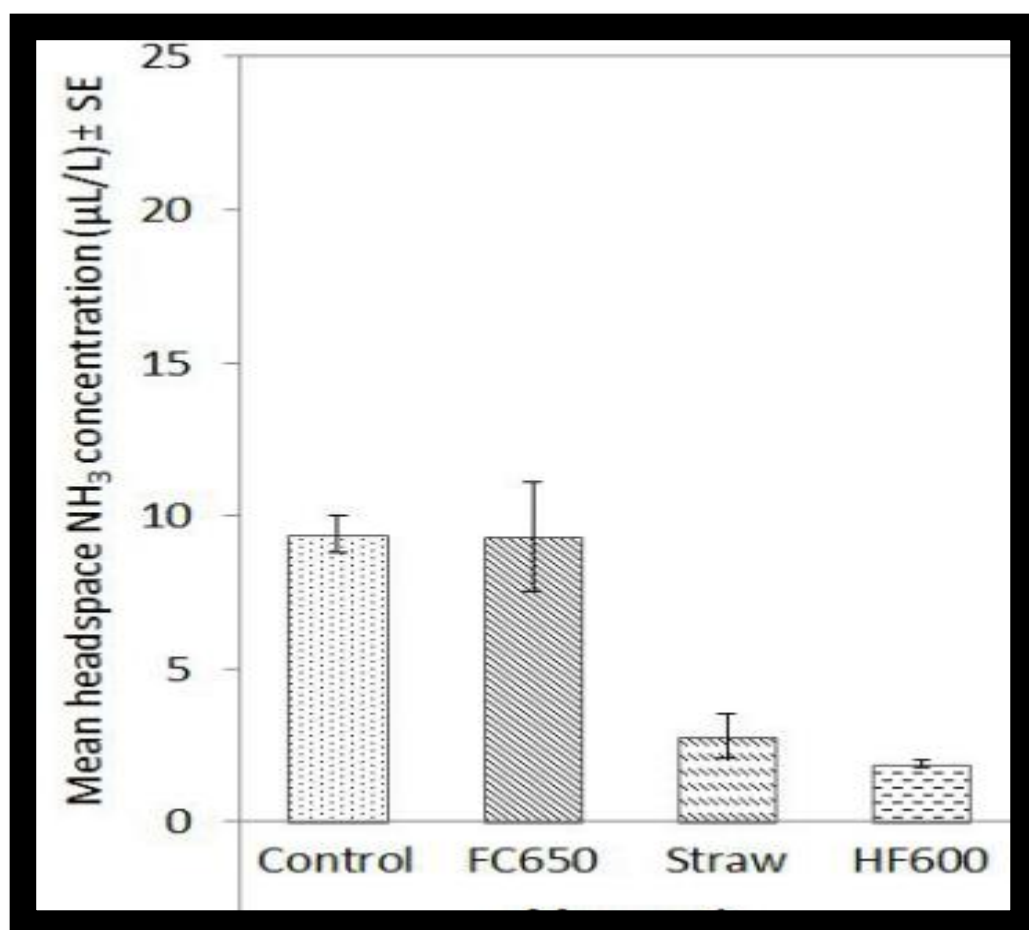


Figure 5.21 Headspace Ammonia concentration comparison, taken from Dougherty *et al.*, 2020.

5.31 Biochar as an Organic Fertiliser

The use of biochar as an organic fertiliser has been discussed as a potential replacement for chemical fertiliser or as an aid to offset its use which produces harmful GHG emissions in its creation. Based on quotations from local trade in Ireland, there may also be a heavy financial incentive for its usage with quoted prices of chemical nitrogen ranging from 800-850€ per tonne, a fourfold increase in 2018 quoted prices (Teagasc, 2022). On Irish dairy farms, chemical nitrogen is one of the most widely used fertilisers to grow grass and crops to feed their animals. Khan *et al.*, 2022, in their study investigated the potential role biochar may have with improving the availability of Nitrogen from the soil when applying other sources of organic nitrogen, reducing reliance on chemical sources in the production of wheat. Availability of

nitrogen from Urea was also conducted to observe its effect on chemical sources over a 2-year period.

5.32 Study Design

The study set out to find the influence Biochar has on the availability of Nitrogen from organic sources and a chemical source when applied at 0, 10, 20 and 30 tonnes per hectare. Organic sources used were farm yard manure and poultry manure, both of which are available to an Irish system. Granular Urea represented chemical source of nitrogen used. Manure was applied at a rate of 0, 90, 120 and 150 kilogrammes per hectare. A total of 120 plots of wheat were cultivated and assessed for accuracy of data.

Pirsabak wheat seed was sown at a rate of 120 kilogrammes per hectare in rows of 30 cm apart. Poultry manure and farm yard manure were applied one-month prior sowing whilst, biochar was applied at sowing and Urea administered in a split dose. In the second year, half rate of organic sources was applied to allow appropriate decomposition time. Response to Grain yield, straw yield, nitrogen yield and uptake were recorded.

5.33 Grain Yield

A significant difference in Grain Yield was apparent over the control for each treatment as seen in figure 5.22. Over the 2-year period, grain yield increased significantly. It was observed that where biochar was present in soil, yields were higher than the control without. Peak grain yield was observed as 13.26% over the control at 20 tonnes of biochar per hectare and the lowest yield recorded at the control (No Biochar). In terms of Nitrogen interaction, Grain yield was increased significantly by 49.73% in comparison to the control at 150 kilograms of nitrogen per hectare as poultry manure. This yield was slightly lower at 46.4% extra over the control for Urea. Lowest yields were created in control plots (Khan *et al.*, 2022).

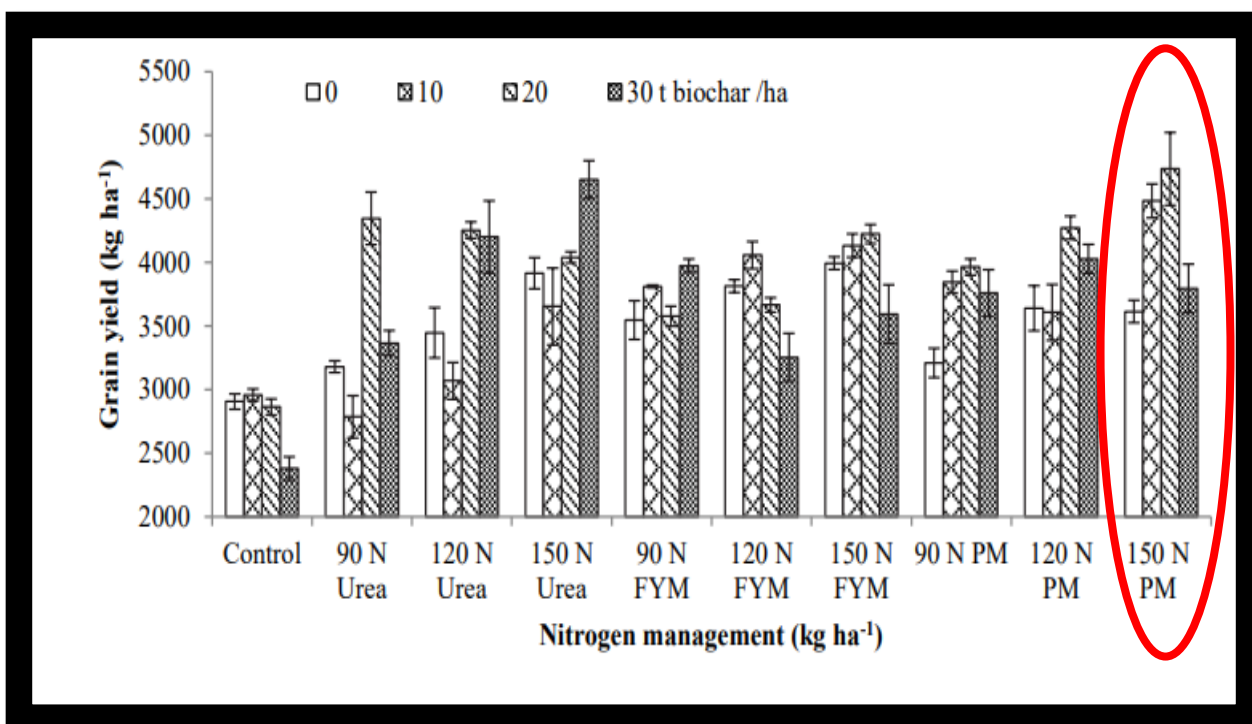


Figure 5.22 Effect of interaction between Biochar and Nitrogen with Urea (Chemical), Farm Yard Manure (Organic) and Poultry Manure (Organic) on Grain yield, adapted from Khan *et al.*, 2022.

5.34 Straw Yield

Variations were observed between biochar, Nitrogen interaction and their yield of straw given as detailed in figure 5.23. Similarly, to Grain yield, significant increases of yield were recorded in the second year of trial work. Maximum yield of straw was recorded where biochar was applied at 20 tonnes per hectare at 15.56% over the control of no biochar. Increases were also observed at 30 and 10 tonnes per hectare yielding an increase of 10.29% and 8.85% accordingly. In terms of Nitrogen management, maximum yield of straw was observed at 7.36% over the control at 120 kilogrammes of Nitrogen per hectare applied as Farm Yard Manure. Interactive effect of biochar and Nitrogen found greatest yield of straw where 20 tonnes of biochar per hectare was applied along with 120 kilogrammes per hectare of Nitrogen as Farm Yard Manure (Figure 5.23) (Khan *et al.*, 2022).

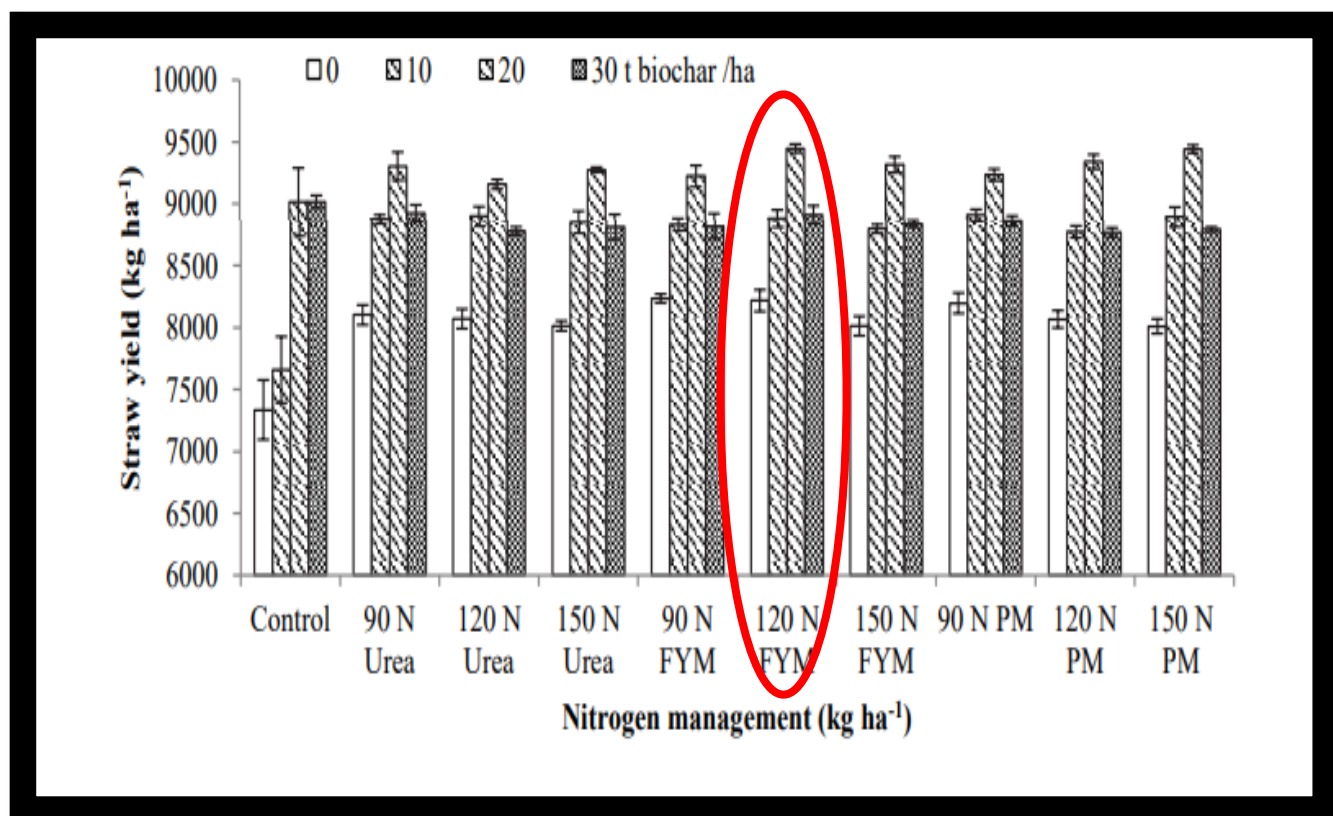


Figure 5.23 Effect of interaction between Biochar and Nitrogen on Yield of Straw when treated with Urea, Farm Yard Manure and Poultry Manure, Adapted from Khan *et al.*, 2022.

Chapter 6: Discussion

6.1 Encouragement of Active Engagement

The willingness of the primary producer is central to the implementation of studied remedies to help mitigate methane emissions from the Dairy herd to help safeguard future production. Overall, results from the survey indicate that farmers are very much willing to engage with practices which help reduce farming's impact on Global warming. However, there was admittedly a knowledge gap evident in these practices and farmers were also somewhat unwilling to engage should this have an adverse financial impact on their enterprise. Therefore, a range of development and financial packages have become available to help incentivise the uptake of methane reducing practices at farm level.

6.2 Glanbia Co-Op Sustainability Action Plan Payment



Figure 6.1 Glanbia Sustainably action plan Payment plan, Taken from Glanbia,2022.

Results from Shorthall *et al* suggest farmers are willing to uptake sustainable practices, thereby facilitating a reduction in associated Methane producing practices. However, it was also commented that the uptake of such practices must may financial sense for the primary producer. The industry in Ireland has begun to answer this call with symbiotic incentives which secure financial viability for the farmer whist securing supply of product for the Industry. Glanbia Ireland is Ireland's largest processor of milk, processing over 8 billion litres of milk globally, producing liquid milk products, cheese products and performance nutrition ingredients.

Glanbia as a company and processor are very much aware of the challenges facing the industry and strive to become market leaders in sustainable practices pledging to become Carbon neutral in the Dairy supply chain. Specifically, the processor has targeted a thirty percent reduction in Green House Gas emissions from each litre of milk produced by 2030. A part of this journey includes the management of raw milk and ensuring it is produced in the most environmentally friendly way. With this in mind, they have introduced a support scheme to help incentivise farmers in sustainable practices by making an 18-million-euro support fund available over 3 years for their 5,000milk suppliers in Ireland. The aim of the project is to reduce the carbon footprint of milk produced, improve water and air quality on farm and ensuring best practices from the ground up incorporating each process from soil to milk (Glanbia,2022).

The 18-million-euro fund translates into the equivalent 0.5 cent per litre produced including value added tax once in compliance with the sustainable actions. On average, each Glanbia dairy supplier will receive a payment of three thousand euro each year or 54 million euro across the duration of the plan.

6.3 Requirements

Glanbia have set a number criterion to meet in order to become eligible for the payment detailed below:

1. Commit to the reduction of carbon emissions through the utilisation of clover and multi species swards, grass measurement practices, breeding to reduce emissions, the use of milk recording or the uptake of renewable energy on farm.
2. Enhance and improve the quality of air by implementing the usage of Protected Urea and slurry spreading technology to reduce emissions lost as volatilisation to the atmosphere.
3. Promote biodiversity through hedgerow growth and native trees.
4. Aid and support healthy soil and water by implementing nutrient management.
5. Improve animal health to ensure efficient operations through disease screening and partaking in the Beef Twenty-Twenty club to ensure a closed loop of sustainably produced Dairy-Beef animals to the consumer.

In total there are 17 measures to choose from in which a farmer must meet a minimum of 6 in order to be eligible to the support payment. This shows an example of how the industry is leading the way in ensuring Milk produced in Ireland is produced sustainably with reduced Green House Gas emissions (Glanbia,2022).

6.4 Multi Species Sward Scheme

This thesis outlined the potential of Multi species swards as a Feedstock for Anaerobic Digestion due to its favourable growth potential and its positive impact on biodiversity. Farmer based surveys also indicate that the uptake in usage of Multi Species sward is linked with that of a “Good Farmer” and there is a willingness to adapt such practices. However, this potential to adapt was met with a financial dilemma in that although MSS was deemed the “right thing to do”, it must also make financial sense to do so. On Friday the 25th of March, the Department of Agriculture in Ireland announced the roll out of the multi species sward scheme for Irish farmers to incentivise the uptake in its growth. The scheme was launched in an effort to reduce the country's dependence on chemical nitrogen whilst also gaining the advantages of the crop without compromising production potential. Farmers eligible received a payment the equivalent of fifty euros per acre towards a twelve-kilogram bag of the seed. The scheme has aided in the establishment of 12,000 hectares of multi species swards, incorporating varieties of white clover, red clover, timothy, chicory, plantain and perennial ryegrass into Irish grassland (DAFM, 2022). This incentive has thereby paved the way for its uptake and creates another potential feedstock for Anaerobic Digestion and one step closer to facilitating feedstock requirements set out by RED II.

6.5 Anaerobic Digestion: Potential to reduce Methane

This thesis has highlighted the potential multi-functional use of Anaerobic Digestion to reduce methane from the Dairy herd for sustained production. Maldaner *et al* in their study concluded significant findings to suggest the storage of untreated slurry as Digestate greatly reduces methane emissions emitted from storage by 85% on average (Figure 5.5). The impact of Volatile solids was also highlighted versus untreated manure. For the month of April where Volatile solids mass percentage was similar for Digestate vs untreated manure, methane emissions per volatile solid were 2.3 times lower in Digestate. This signifies the potential of Volatile solids as an emission precursor in untreated manure and the impact the Anaerobic Digestion process has on Volatile solids and its potential to produce methane. The exact mechanics of this result was not defined and may require future work from various feedstock types to verify.

A strong positive relationship between Methane flux and temperature (Air and Digestate) show that Anaerobic Digestion holds great potential in colder climates with regard to methane emissions. However, this study has also highlighted the need for Irish specific data regarding Methane emissions. This study has set the basis for potential and one could hypothesise a

somewhat steady rate of methane emissions throughout the year given Ireland's temperate climate. However, further work in an Irish system with differing feedstock types is needed to verify this claim.

6.6 Anaerobic Digestion: Significance of Financial Data

As highlighted by Shorthall *et al.*, the uptake of remedial practices must also be financially feasible for the primary producer to partake. The 5 scenarios outlined in the Irish feasibility scenario indicate that SSAD is feasible economically for herds greater than 100 cows (Scenario 2-5). However, it is worth noting that some important financial metrics were not considered in this study such as connection fee to the national grid, civil construction and legal fees. Such metrics would need to be considered to get a true picture of financial feasibility.

This data has outlined the significance of Government funding and support to bridge the gap created through length of payback on investment which may discourage investors from committing to such a project. Such financial incentives presently include the REFIT scheme, which reduces the payback period significantly where applicable. Payments available are based on two payments: 15.8c€/kWh-1 for plants of CHP capacity up to 500kW and 13.7 c€/kWh-1 for plants in excess of this (Department of Communications Energy and Natural Resources, 2013). As a result, smaller plants are left somewhat disadvantaged with higher costs due to lack of economies of scale. As outlined in Chapter 2, Germany leads the way with regards AD uptake with subsequent policy amendments to suit. By way of comparison, Germany offers a tariff rate of 23.73 c€/kWh-1 for plants with capacity not in excess of 75 kWe in an effort to encourage SSAD. Similarly, in the UK a tariff of 4.50£/kWh-1 is provided for plants with capacity which does not exceed 250 kW. Renewed legislation in Ireland through the Support Scheme for Renewable heat has not addressed this problem with current tariff based on 2.95 c€/kWh-1 to all plants which do not exceed 1000 MWh yr.-(Department of Communications Climate Action & Environment, 2018). Although tariffs are welcome, in order to encourage the uptake of SSAD in Ireland, government funding must reflect and support extra costs associated with SSAD in comparison to large production sites.

Based upon findings from the case study and similar to others such as Kampman, 2017, one of the main barriers to SSAD is the cost of finance associated with the construction of a plant. Related issues also included lack of expertise surrounding the technology from investors and financial agencies in assessing feasibility. The government capital grant subvention has been seen as a successful legislation in countries such as France where up to 50% grant funding has been secured (Lukehurst *et al.*, 2015). Figure 5.11 shows the potential impact such a measure

would have in an Irish Scenario, reducing the payback period 3.88 years to 14.62 years. Here lays food for thought for the Government of Ireland in the reduction of Methane and associated GHG from the Dairy herd through the support of AD adoption in Ireland.

Future predictions estimate the overall cost of running such plants will reduce in the coming years as technology and processes improve efficiency of operations. The increased emphasis on smaller plants may lead to cost reductions as modular systems are developed further. There are many companies are in the testing phase and or commercial operations in Europe representing this technology, with many more in development (QUBE Renewables,2019).

6.7 Environmental Impact of Anaerobic Digestion

The SSAD feasibility case study highlighted reductions of CO₂ in each scenario in the range of 2 to 173 tonnes CO₂ eq per annum (Table 5.9). Should SSAD be developed in Ireland on a commercial basis, a CO₂ reduction in excess of 211,349 tonnes is achievable. This is achieved where 20% of all farms with greater than 250 cows (61 farms) implemented SSAD (CSO,2016). With Ireland under pressure to meet its GHG commitment targets of 40% reduction by 2030, creation of a renewed policy which supports SSAD presents itself as a lucrative strategy of improvement.

6.8 Comparative to similar Case Studies

Results indicated in this study are not found in isolation with similar findings reported in various other studies from De Dobbelaere, Walker and Wilkinson where similar livestock and production type are similar. The overwhelming result was the financial feasibility should be assessed individually and is often closely related to conditions locally, energy cost, feedstock availability and Government Intervention. This highlights the need for careful planning to take place on a case by case basis.

SSAD has been subject to extensive research in recent years with topic such as: The optimisation of plant operations and design (Nguyen,2015), pre-treatments of feedstock (Ehimen,2009), trace compound impact (Pauperello,2018) and cleaning technologies of biogas (Kupeckia,2018). Into the future, further developments in these fields may see further integration and improvements to SSAD in Ireland.

6.9 SSAD and Ireland: Future Outlook

With the abolition of the European Milk Quota, Irelands National herd has seen a dramatic increase in cow numbers. This growth in herd size may provide a potential path to implement

SSAD without the reduction of cow numbers as economies of scale may be incorporated into the business model as seen in Table 5.7.

Teagasc is predicting the National herd to grow even further, 19% above figures seen in 2018 by 2025. This would mean the national herd average would thereby exceed 100 cows by 2025. This further reinforces the argument for economies of scale in the resultant larger herds along with significant capacity to mitigate GHG emissions including methane to safeguard future production.

6.10 Legislative Concerns

Legislative challenges must also be considered in order to assess the feasibility of Anaerobic Digestion in Ireland to reduce methane from the Dairy Herd. Planning permission for an AD facility is first and foremost the primary legislative challenge facing the viability of Anaerobic digestion to mitigate methane emissions from the Dairy herd. There is requirement to gain permission from the local council to begin construction and subsequent use of the site. It is important to consider the Potential environmental impact of the plants construction and use. This requires the completion of an Environmental Impact Assessment application. As there are a number of Irish Ad plants in operation, issues arising from applications have been identified. The Sustainable Energy Authority of Ireland has published a guide outlining potential issues from the planning process and summarised below.

6.11 Specialised Environmental Permit

Furthermore, to planning permission for construction, each operation within the plant requires prior consent to carry out its activities from the local authority or in the form of a license from Environmental Protection Agency. This legislation from the EPA is in accordance with publication No.821 2008 under Waste Management. Specifically obtaining permit and registration process. The need for such a permit is determined by the size/capacity of the plant. Small plants with intake of less than 10,000 tonnes per year must apply for a permit and this can be obtained through the local authority. However, if a plant exceeds 10,000 tonnes intake, a licence is required from the EPA. Summarised in Fig 6.2 below.

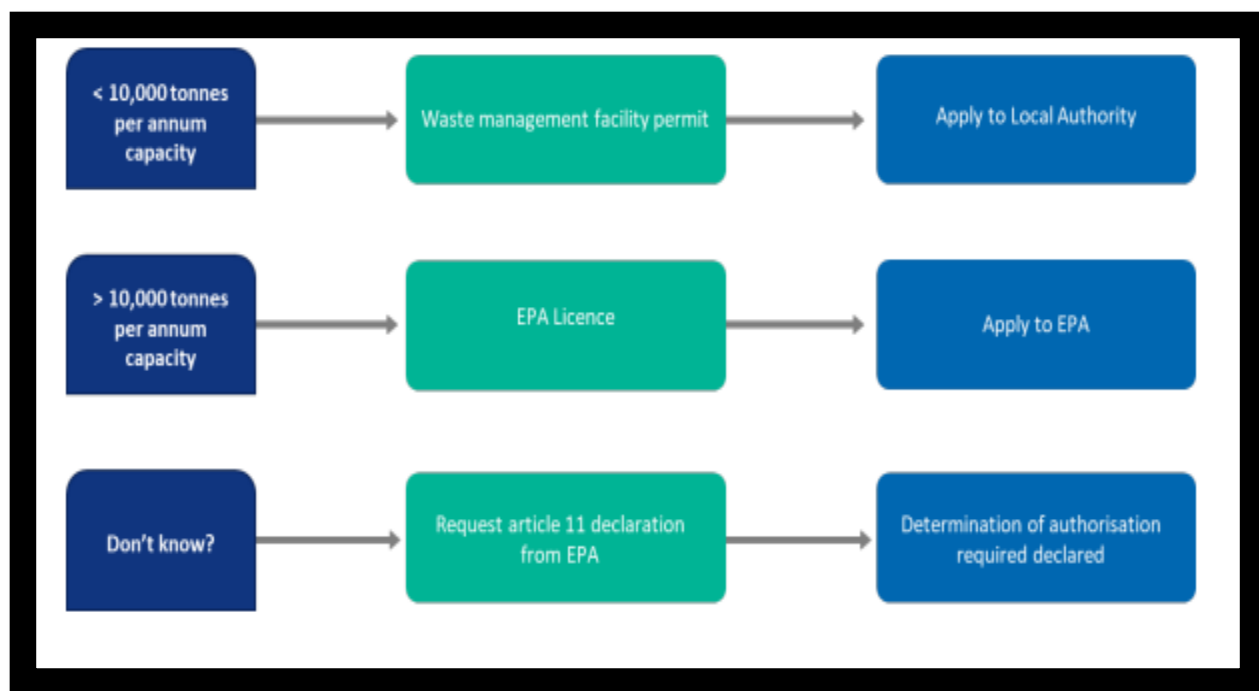


Figure 6.2 Environmental Legislation process, taken from SEAI, 2020

6.12 Legislation on the Handling of Animal by products

For the purpose of this thesis, it is assumed that any such facility constructed will involve the processing of animal by products i.e. Slurry and Manure. Legislation 1069/2009 sets out the requirement to ensure any such facility involved in the processing of animal by products handles them correctly, to ensure risk of disease contamination through the subsequent Digestate is mitigated and controlled. Regulation No 187 2014 enforces this requirement and requires plants to carry out heat pasteurisation. The risk associated with individual animal by products are categorised as such with Category 1 representing the highest risk and 3 the least.

Certification where applicable is obtained from The Department of Agriculture. Certification needed is determined by the facility type and inputs it processes. Slurry and manure are present in Category 2. However, this risk may be downgraded where the facility processes manure only and where the subsequent Digestate is used on the host farm summarised in Figure 6.1 below.

Table 6.1 Category types based on feedstock, taken from SEAI 2020.

| Animal by-product facility type | Processing applied | Main feedstock | Digestate outlets |
|---------------------------------|--|--|--|
| 1 | ≤12 mm particle size. Heated at ≥70°C for ≥1 hour | Category 2 manures and Category 3 catering waste | Land in Ireland and within EU |
| 2 | No heat treatment applied | Only manures from the farm and non-animal by- product feedstocks also from the farm | Land in Ireland only |
| 3 | No heat treatment applied | Category 3 catering waste | Cannot be used on land and must be incinerated or landfilled |

Irrespective of the intended feedstock used to supply the plant, it is considered good practice to design a plant as if it is Categorised as 1 (Figure 5.1). This thereby allows diversification of feedstock and the processing of animal by products into the future should the opportunity or need arise into the future. This would also remove the need for retrofitting pasteurisation units into the future.

6.13 Environmental impact of Digestate

Results indicate a varied environmental saving between 15-100% displacement of chemical fertiliser depending on the nature of feedstock and conditions of processing (McCabe *et al.*, 2019). This varied response is further mirrored through associated ammonia loss due to increased pH of processing versus conventional untreated slurry. This uncertainty is due to infrastructure differences which may improve losses such as appropriate storage facilities, covers and treatment of feedstock on arrival to reduce overall pH. An increased clarity is needed to truly understand the impact the use of Digestate has in the mitigation of methane and associated GHG emissions from the dairy herd both from an environmental and economic standpoint. Such infrastructure to mitigate ammonia losses from processing need to be installed with an economic weight attached to them to reflect the results of the feasibility of SSAD study to truly understand its impact.

6.14 Policy Implications

6.15 Nitrates Directive

Under the Nitrates Directive farmers are required to limit their Nitrogen usage to 170 kg N/ha per annum and 250 kg for those farmers granted a derogation for intensive farming purposes. This policy and particularly that of derogation has been subjected to extensive scrutiny and its implementation beyond 2025 is somewhat in doubt. Anaerobic Digestion presents an opportunity for Dairy farmers to offset a portion of their organic nitrogen created as feedstock in the creation of Biogas. It will also work beneficially into the nutrient management requirement set out by the CAP and related policies. Through the use of slurry as a co feedstock, nutrient management of Nitrogen, Phosphorus and Potassium can be more exact through the digestive process. This therefore improves the amount and quality of nutrients available to the land over and above that of untreated slurry whilst offsetting against Nitrates requirements.

6.16 Renewable Energy Directive II

RED II has set out the requirement for a 70 and 80% GHG saving from biofuel used for electricity, cooling and heating initially and by 2026. This presents Dairy farmers with a challenge in regards to feedstock requirement to meet this necessity. Studies from KPMG and Teagasc suggest that it is indeed possible to produce Biomethane from Agriculture and meet this requirement presented by the European Union. All three scenarios echo the one result that agricultural slurry is required in at least co digestion to produce Biomethane in this regard. This is due to GHG saving of methane in harvesting methane from slurry and subsequent saving to the atmosphere as atmospheric methane loss. Overall slurry required ranges from 40-55% in Scenario 2-3. Differences versus Perennial Ryegrass is due to GHG emissions offset as a result of lower chemical fertiliser required for normal growth in S2 and S3. Therefore, its clear slurry incorporation works in tandem with Anaerobic Digestion not only by reducing methane loss to the environment but also in satisfying policy criteria set out by the European Union.

6.17 Anaerobic Digestion to Feed Pyrolysis to Produce Biochar

This thesis outlined the importance of Bio Digestion in utilising methane containing feedstock such as slurry to help reach Green House Gas emission targets. Furthermore, this thesis creates an important link between Anaerobic Digestion, Pyrolysis and its by-products. As outlined above, in the process of anaerobic digestion, biogas is produced through the fermentation of volatile solids present in the feedstock (Slurry or Energy crops). As a result of anaerobic digestion, Digestate sludge is created. This is a mixture of inert solids along with the substrate, ungradable (Biologically) volatile solids and a portion of biomass formed from bacteria whilst utilising the volatile solids fed as feedstock. Typical solids content range from 2-10%. This by

product may then be utilised in the process of pyrolysis, turning biomass into Biochar, gas and liquid thermos chemically in the absence of oxygen.

Solids present in the Digestate from Anaerobic Digestion possess an energy content through its potential for further oxidation. Pyrolysis can thereby utilise this energy source to produce syngas or synthetic gas that can be used as fuel. The by-product of pyrolysis is the Biochar, an organic compound with potential to reduce methane from stored slurry as outlined above. Therefore, by incorporating the processes of Anaerobic Digestion with Pyrolysis, the two systems may work in tandem to create a full circle of renewable energy which by products are of environmental benefit to the Dairy herd in reducing its emission potential. Specifically, from an Irish standpoint, there holds great potential in creating this full circle at farm level.

However, there are a number of variables to be addressed. Namely from a legislative standpoint, the Government of Ireland need to act on the proposed bill to create a universal approach to Renewable energy sources to incentivise the construction of Anaerobic digestion plants to ensure their viability similar to that seen in Germany through the EEG. There lays positive outlook for potential development as seen through KWS in the commissioning the world's largest pyrolysis site in Ireland in the coming years. Such a plant and future plants will need a continuous source of biomass. Creating a viable link between the agricultural industry and the energy industry is the challenge in safeguarding supply for both industries.

6.18 Biochar as a Manure Additive

Work carried out in this thesis has highlighted the importance of Biochar, the by-product of pyrolysis in the mitigation of methane emissions from the Dairy herd to safeguard future production. Harrison *et al.*, 2022, in their study highlighted a potential end use of biochar indicating a knowledge gap in the Industry regarding the treatment of stockpiled manure on Irish Dairy farms. Most Dairy farms in Ireland hold manure in both a solid and liquid state. However, natural additives to treat methane emissions in this space are underutilised and under researched. This study displayed promising findings in its management in a reduction of 79% displayed over the control within the trial period. This promising result gave insight into the mechanism of methane production within stockpiled manure. The biochar utilised reduced the prevalence of methanotrophs in their production of methane through increased O₂ availabilities (Harrison *et al.*, 2022) This study gives rise to further insight into this mechanism and potential production of a commercial additive which may be utilised at scale within the Industry.

6.19 Biochar as a Biocover

Biochar has been highlighted as a potential physical barrier of emissions created by the Dairy herd from manure management. Dougherty *et al* in their study highlighted important findings regarding manure storage and emissions lost to the environment. Interestingly, there is no data or relevance to show the significance of biocovers in reducing methane from stored slurry. In this study, Ammonia losses were reduced in each case in comparison to the control of no cover. Contrary to other treatments, a spike of Ammonia emissions was recorded in the FC650 covers. This may be due to the higher pH associated with this biochar type which may have caused a conversion of ammonium in the manure to Ammonia. This effect was not observed in HF600 covers at biochar pH of 7.28 (versus 9.32) and Ammonia reduction were significantly higher. This highlights the need for further study into the area of biocovers, factors of effectiveness and a study specific to methane emissions to further quantify its place in safeguarding future production from the Dairy herd.

6.20 Biochar as a fertiliser

This thesis has outlined that there is unreported or underreported methane emitted from industry as a result of chemical fertiliser production. Khan *et al.*, 2022, in their study looked at the potential for Biochar to be used as a fertiliser through its interaction with Nitrogen from a chemical or organic source. Fundamentally, the application of biochar to the soil is seen as a key component in increasing crop yield irrespective of the Nitrogen source used. Critically, from an environmental standpoint, greatest yield increases were observed from the interaction of biochar with organic sources. Specifically, from poultry manure at 62.9% Grain (figure 5.22) and 28.7% straw (Figure 5.23). This was also an increase from the previous year of the same treatment highlighting the long term impact and longevity of biochar applications. This study has therefore highlighted a potential beneficial outlet for biochar produced from the newly constructed pyrolysis site for Bord Na Mona. However, further work will be required specific to an Irish system with this specific biochar derivative to evaluate its potential returns and chemical fertiliser replacement quantity as a result to sustain production.

Chapter 7: Conclusions and Further Study

7.1 Conclusion

To conclude, this thesis has highlighted the major challenge facing the Irish Dairy Industry in Meeting its emission targets set out by the Paris Agreement and most recently COP 26 on the impact methane emissions derived from Agriculture plays on its success or failure. It is clear that at present, Ireland will not reach its Methane targets by 2030 set out by COP 26 and therefore remedial action is required in order to avoid a significant cull of cow numbers which will hamper production and also adversely affect the rural and greater economy as a whole. This thesis has outlined two renewable energy sources as a direct and indirect means to reduce methane from the Dairy herd.

Anaerobic Digestion is seen as a realistic strategy to incorporate the safe disposal of Agricultural waste products and its conversion to usable biogas and digestate. This process is observed not only to reduce methane emitted through the storage as Digestate but also an aid to the circular economy as Energy produced can be sold back to the grid or used any the farmer to reduce the overall energy cost on the farm. Ireland must take note of its success in market leaders Germany in their implementation and how it has benefitted their energy requirements. The major drawback to its implementation is the cost associated with setting up and running a plant. The fact that SSAD was observed as feasible under each scenario incorporating 100 cows, Irelands mean herd size, gives reason for the government of Ireland to incentivise its construction as seen with the EEG in Germany. Such a financial incentive will not only reduce the capital cost for primary producers but also encourage investors interest with reduced payback periods. Digestate as a by-product of the Anaerobic Digestion process is also attributed with methane reducing characteristics through reduced chemical usage up to 80 with repeated use (KPMG, 2021). The supply of feedstock has also been quantified and incentivised in the case of MSS growth. Therefore, a renewable full circle of methane mitigating properties can be attributed to Anaerobic Digestion and its by-products.

This Thesis has also created a link between Anaerobic Digestion and Pyrolysis in its role to reduce Methane from the Dairy herd. In light of construction of the world's largest pyrolysis facility in County Offaly, its process poses potential to reduce methane emissions in the Dairy herd through utilisation of its by-product biochar. Its incorporation into stockpiled manure showing a reduction in 79% Methane emissions versus no biochar signify its direct potential whilst also gaining environmental benefits through reduced chemical fertiliser usage in its application. Where applied to wheat crop, readily grown by Irish dairy farmers, a significant increase and straw and grain yield was observed when further incorporated with organic

sources of Nitrogen such as farm yard manure and poultry manure. Finally, in terms of liquid slurry, biochar has potential as an additive by creating a physical barrier between the harmful gaseous gases and the environment. It is clear that the primary producer is willing to adapt to environmental practices in line with what is perceived as being a “Good Farmer”. However, this desire for environmental compliance must also meet with financial feasibility highlighting the importance of incentive scheme such as the MSS payment and Sustainability bonus by Glanbia, Irelands largest milk producer.

7.2 Future Work

This thesis has highlighted the tangible and feasible actions which will bring about a reduction of methane yield from the dairy herd and help safeguard future production. However, there are a number of issues which need to be addressed and further investigated in order to evaluate their true potential.

Anaerobic Digestion benefits the circular economy through the creation of renewable energy whilst reducing methane through the storage of Dairy manure as feedstock. Feasibility costings by O’Connor *et al.*, 2020, highlight its application and need for further financial incentive from the Government of Ireland. A detailed and up to date study portraying SSAD its potential to the rural economy and direct impact in saving GHG emissions will further reinforce this necessity and help fast track its implementation.

Pyrolysis in its application produces the by-product of biochar and its benefit in terms of manure additive, Biocover and fertiliser saving has been highlighted in this study. However, in their study, Dougherty assessed the Ammonia saving from the use of a Biocover and yielded varied results of reduction over the control of no cover. To reinforce the potential of biocovers derived from biochar as a potential end use of Irish Biochar, specific study regarding Methane saved will need to be conducted. Study is also required regarding biochar as an additive for stockpiled manure in the creation of a product available at scale to treat the underutilised area of manure management in dry form. Furthermore, greater work will be needed to identify the reason of variation among differing biochar types and the impact biochar produced from the new pyrolysis site in Offaly will have on localised Dairy farm emissions.

Ultimately, the fate of methane emissions targets lays with the primary producer to implement. It is apparent through Shorthalls study that farmers want to operate environmentally and deem it best practice. However, further work is required in their education, guidance, implementation and encouragement of best practices highlighted by Industry.

References

1. A.P. Puga, C.A. Abreu, L.C.A. Melo, L. Beesley, Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium, *J. Environ. Manage.* 159 (2015) 86–93
2. Abbasi T, A Brief History of Anaerobic Digestion and "Biogas". *SpringerBriefs in Environmental Science* 2 11-23 (2011).
3. Agathe Auer, Nathan H Vande Burgt Agricultural anaerobic digestion power plants in Ireland and Germany: policy & practice Teagasc (2021).
4. Ali, K., Arif, M., Jan, M. T., Khan, M. J., and Jones, D. L. (2015). Integrated use of biochar: a tool for improving soil and wheat quality of degraded soil under wheat-maize cropping pattern. *Pak. J. Bot.* 47, 233–240.
5. Amon, B., Kryvoruchko, V., Amon, T., Zechmeister-Boltenstern, S., 2006. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. *Agric. Ecosyst. Environ.* 112, 153–162. <http://dx.doi.org/10.1016/j.agee.2005.08.030>
6. Babalola Aisosa Oni, Olubukola Oziegbe, Obembe O. Olawole *Annals of Agricultural Sciences* 64 (2019) 222–236
7. Baldé, H., VanderZaag, A.C., Burt, S.D., Wagner-Riddle, C., Crolla, A., Desjardins, R.L., MacDonald, D.J., 2016b. Methane emissions from digestate at an agricultural biogas plant. *Bioresour. Technol.* 216, 914–922. <http://dx.doi.org/10.1016/j.biortech.2016.06.031>
8. Banks, C.J., Zhang, Y., Jiang, Y. and Heaven, S. (2012): Trace element requirements for stable food waste digestion at elevated ammonia concentrations. *Bioresour. Technol.* Vol. 104, 127–135.
9. Baral, Khagendra R, Guillaume Jégo, Barbara Amon, Roland Bol, Martin H. Chantigny, Jørgen E. Olesen, S. O. P. 2018. Greenhouse gas emissions during storage of manure and digestates: Key role of methane for prediction and mitigation. *Agricultural Systems*
10. Berg, J.M., Tymoczko, J.L. and Stryer, L.: *Biochemistry*. W.H. Freeman and Company, New York,
11. Berglund, M.; Börjesson, P. Assessment of energy performance in the life-cycle of biogas production. *Biomass Bioenergy* 2006, 30, 254–266.
12. Bioenergy Training Center. Introduction to Anaerobic Digestion Course - Types of Anaerobic Digesters, Available online: <https://farm-energy.extension.org/types-of-anaerobic-digesters/> (accessed on 28 July 2022).
13. Blades, L., Morgan, K., Douglas, R., Glover, S., De Rosa, M., Cromie, T., & Smyth, B. (2017). Circular Biogas Based Economy in a Rural Agricultural Setting. *Energy Procedia*, 123, 89-96
14. Boyle, W.C. Energy recovery from sanitary landfills. In *Microbial Energy Conversion*; Schlegel, H.G., Barnea, J., Eds.; Pergamon Press: Oxford, UK, 1977; pp. 119–138.
15. Bryman, A. *Social Research Methods*; Oxford University Press: Oxford, UK, 2001
16. Burton, R.J.F.; Forney, J.; Stock, P.; Sutherland, L.-A. *The Good Farmer: Culture and Identity in Food and Agriculture*; Routledge: Abingdon, UK, 2021.

17. C.E. Brewer, V.J. Chuang, C.A. Masiello, H. Gonnermann, X. Gao, B. Dugan, L.E. Driver, P. Panzacchi, K. Zygourakis, C.A. Davies, New approaches to measuring biochar density and porosity, *Biomass Bioenerg.* 66 (2014) 176–185.
18. Cammack KM, Austin KJ, Lamberson WR, Conant GC, Cunningham HC. 2018. Ruminant nutrition symposium: tiny but mighty: the role of the rumen microbes in livestock production. *J. Anim. Sci.* 96: 752-770.
19. Céline Vaneeckhaute, Viooltje Lebuf, Evi Michels (UGent) , Evangelina Belia, Peter A Vanrolleghem, Filip Tack (UGent) and Erik Meers (UGent) (2017) WASTE AND BIOMASS VALORIZATION. 8(1). p.21-40
20. Central Statistics Office. Farm Structure Survey 2016. Available online: <https://www.cso.ie/en/releasesandpublications/ep/p-fss/farmstructuresurvey2016/> (accessed on 10 August 2022)
21. Chynoweth, D.P. (1996): Environmental impact of biomethanogenesis. *Environmental Monitoring and Assessment*. Vol. 42, 3–18.
22. Clauss M, Hofmann RR. 2014. The digestive system of ruminants, and peculiarities of (wild) cattle. *Ecology, evolution and behaviour of wild cattle: Implications for conservation*. pp. 57-62
23. Clemens, J., Trimborn, M., Weiland, P., Amon, B., 2006. Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry. *Agric. Ecosyst. Environ.* 112, 171–177. <http://dx.doi.org/10.1016/j.agee.2005.08.016>.
24. Commission for Regulation of Utilities. Fuel mix disclosure 2016; Commission for Regulation of Utilities: Dublin, Ireland, 2017.
25. 'Connor, S.; Ehimen, E.; Black, A.; Pillai, S.C.; Bartlett, J. An overview of biogas production from smallscale anaerobic digestion plants on European farms; In *Proceedings of the Energy Technology Partnership (ETP) Annual Conference*, University of Strathclyde, Glasgow, UK, 29 October 2018.
26. DAFM. Food Harvest Food Harvest 2020: A Vision for Irish Agro-Food and Fisheries; DAFM: Dublin, Ireland, 2010
27. Dahal R K, Acharya B and Farooque A 2018 Biochar: a sustainable solution for solid waste management in agro-processing industries *Biofuels* 1-9
28. Dalby, F.R., Hafner, S.D., Petersen, S.O., VanderZaag, A.C., Habtewold, J., Dunfield, K., Chantigny, M.H., Sommer, S.G., 2021. Understanding methane emission from stored animal manure: a review to guide model development. *J. Environ. Qual.* 50 (4), 817–835. <https://doi.org/10.1002/jeq2.20252>.
29. Daniel-Gromke, J., Liebetrau, J., Denysenko, V., Krebs, C., 2015. Digestion of bio-waste – GHG emissions and mitigation potential. *Energy. Sustain. Soc.* 5, 1–12. <http://dx.doi.org/10.1186/s13705-014-0032-6>.
30. De Dobbelaere, A.; De Keulenaere, B.; De Mey, J; Lebuf V.; Meers E.; Ryckaert, B.; Schollier C.; Van Driessche J. Small scale anaerobic digestion: Case studies in Western Europe, *Enerpedia: Rumbeke*, Belgium, 2015.
31. De la Fuente G, Yañez-Ruiz DR, Seradj AR, Balcells J, Belanche A. 2019. Methanogenesis in animals with foregut and hindgut fermentation: a review. *Anim. Prod. Sci.* 59: 2109-2122
32. De Paor Consultancy, Review of the Irish Agri-food industry 2017-2018, *Irish Farmers Monthly: Ireland*, 2018.

33. Demirel, B. and Scherer, P. (2011): Trace element requirements of agricultural biogas digesters during biological conversion of renewable biomass to methane. *Biomass and Bioenergy*. Vol. 35, No. 3, 992–998.
34. Department of Communications Climate Action & Environment. Support Scheme for Renewable Heat Scheme Overview, Department of Communications Climate Action & Environment: Dublin, Ireland, 2018.
35. Department of Communications Energy and Natural and Resources. Renewable Energy Feed in Tariff: A competition for electricity generation -from Biomass Technologies 2010-2015; Department of Communications Energy and Natural and Resources: Dublin, Ireland, 2013.
36. Deublein D and Steinhauser A, Biogas from waste and renewable resources: an introduction. John Wiley & Sons, (2011).
37. Doris Läßle, Colin A. Carter, Cathal Buckley (2020) EU milk quota abolition, dairy expansion, and greenhouse gas emissions *Agricultural Economics*
38. Dougherty et al 2020 Biochar as a cover for dairy manure lagoons: reducing odour and gas emissions while capturing nutrients. Oregon State University.
39. Duan Yun-Feng, Sabine Reinsch, Per Ambus, Lars Elsgaard, and Søren O Petersen. 2017. Activity of Type I Methanotrophs Dominates under High Methane Concentration: Methanotrophic Activity in Slurry Surface Crusts as Influenced by Methane, Oxygen, and Inorganic Nitrogen. *J. Environ. Qual.* 46:767-775. DOI: 10.2134/jeq2017.02.0047
40. Ehimen, E.A.; Connaughton, S.; Sun, Z.; Carrington, G.C. Energy recovery from lipid extracted, transesterified and glycerol codigested microalgae biomass. *GCB Bioenergy* 2009, 1, 371–381.
41. El-Naggar, A., El-Naggar, A. H., Shaheen, S. M., Sarkar, B., Chang, S. X., Tsang, D. C., et al. (2019). Biochar composition dependent impacts on soil nutrient release, carbon mineralization, and potential environmental risk: a review. *J. Environ. Manage.* 241, 458–467. doi: 10.1016/j.jenvman.2019.02.044
42. Enerblu Cogeneration. Combined heat and power (CHP) specifications, Available online: <http://www.enerblu-cogeneration.com/products/80-impianti-biogas.html> (accessed on 12 July 2022)
43. European Commission & United States of America. “Global Methane Pledge” (2021. <https://www.ccacoalition.org/en/resources/global-methane-pledge>) (accessed July 16, 2022).
44. European Commission 2020, Circular Economy Action Plan For a cleaner and more competitive Europe available at https://ec.europa.eu/environment/pdf/circular-economy/new_circular_economy_action_plan.pdf accessed 23 July 2022
45. European Commission 2020, COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS on an EU strategy to reduce methane emissions available at https://ec.europa.eu/commission/presscorner/api/files/attachment/866544/Methane_GreenDeal_EN.pdf accessed 23 July 2022
46. Facchin, V., Cavinato, C., Fatone, F., Pavan, P., Cecchi, F. and Bolzonella, D. (2013): Effect of trace element supplementation on the mesophilic anaerobic

- digestion of foodwaste in batch trials: The influence of inoculum origin. *Biochemical Engineering Journal*. Vol. 70, 71–77.
47. Fageria, N. K., and Baligar, V. C. (2005). Enhancing nitrogen use efficiency in crop plants. *Adv. Agron.* 88, 97–185. doi: 10.1016/S0065-2113(05)88004-6
 48. FAO. 2006. In: Steinfeld H, Gerber P, Wassenaar T, Castel V, Rosales M, de Haan C (eds) *Livestock's long shadow. Environmental issues and options*. Food and Agriculture Organization of the United Nations, Rome, ISBN: 978-92-5-105571-7
 49. Food and Agricultural Organization of the United Nations, (FAO). "FAOSTAT Statistical Database of the Food and Agricultural Organization of the United Nations" (FAO, 2019; <https://www.fao.org/faostat/en/#home>) (accessed July 16, 2022)
 50. Gesetz für den Vorrang Erneuerbarer Energien (Erneuerbare-Energien-Gesetz EEG) sowie zur Änderung des Energiewirtschaftsgesetzes und des Mineralölsteuergesetzes, Bundesgesetzblatt, Jahrgang 2000 Teil I Nr. 13 vom 31.03.2000 (2000).
 51. Gilsenan, E. Map: 2019 County-by-County Dairy Cow Numbers. Available online: <https://www.agriland.ie/farming-news/map-2019-county-by-county-dairy-cow-numbers/> (accessed on 25 June 2022)
 52. Glanbia (2021) Making the most of Grazed grass available at: <https://www.glanbiaconnect.com/farm-advice/detail/article/making-the-most-of-the-grazed-grass> Accessed 8 July 2022.
 53. Glanbia (2021) Peak Supply Management Policy to be introduced at Glanbia Ireland Available at <https://www.glanbiaconnect.com/news/peak-supply-management-policy-to-be-introduced-at-glanbia-ireland> Accessed 13 August 2022.
 54. Glanbia (2022) Glanbia Ireland launches €18 million annual Sustainability Action Payment for family farms Available at <https://www.glanbiaireland.com/our-story/news/glanbia-ireland-launches-eu18-million-annual-sustainability-action-payment-for-family-farms> Accessed 14 August 2022.
 55. Gomez, Claudius da Costa, 2013. 1 – Biogas as an energy option: an overview. *The Biogas Handbook, Science, Production and Applications*. Woodhead Publishing Limited, pp. 1–16. <http://dx.doi.org/10.1533/9780857097415.1>.
 56. Government of Ireland, 2022 Programme for Government Our Shared Future available at <https://assets.gov.ie/130911/fe93e24e-dfe0-40ff-9934-def2b44b7b52.pdf> accessed 23 July 2022
 57. Government of Ireland, Fact sheet on Irish agriculture - January 2018. Available online: <https://www.agriculture.gov.ie/media/migration/publications/2018/January2018Factsheet120118.pdf> (accessed on 10 July 2022)
 58. Grainger, C.; Beauchemin, K.A. Can enteric methane emissions from ruminants be lowered without lowering their production? *Anim. Feed Sci. Tech.* 2011, 166–167, 308–320.
 59. Gupta D K, Gupta C K, Dubey R, Fagodiya R K, Sharma G, Keerthika A, Mohamed M N, Dev R and Shukla A 2020 *Biochar Applications in Agriculture and Environment Management: Springer*) pp 141-65

60. H. Li, X. Dong, E.B. da Silva, L.M. de Oliveira, Y. Chen, L.Q. Ma, Mechanisms of metal sorption by biochars: biochar characteristics and modifications, *Chemosphere* 178 (2017) 466–478.
61. Hackmann TJ, Spain JN. 2010. Invited review: ruminant ecology and evolution: perspectives useful to ruminant livestock research and production. *J. Dairy Sci.* 93: 1320-1334
62. Han, S. H., An, J. Y., Hwang, J., Kim, S. B., and Park, B. B. (2016). The effects of organic manure and chemical fertilizer on the growth and nutrient concentrations of yellow poplar (*Liriodendron tulipifera* Lin.) in a nursery system. *For. Sci. Technol.* 12, 137–143. doi: 10.1080/21580103.2015.1135827
63. Harrison, Si Gao, Melinda Gonzales, Touyee Thao, Elena Bischak, Teamrat Afewerki Ghezzehei, Asmeret Asefaw Berhe, Gerardo Diaz, and Rebecca A. Ryals *Environmental Science & Technology* 2022 56 (15), 10987-10996 DOI: 10.1021/acs.est.2c03467
64. He L, Zhong H, Liu G, Dai Z, Brookes P C and Xu J 2019 Remediation of heavy metal contaminated soils by biochar: Mechanisms, potential risks and applications in China *Environmental pollution* 252 846-55.
65. Heilig GK. 1994. The greenhouse gas methane (CH₄): sources and sinks, the impact of population growth, possible interventions. *Popul. Environ.* 16: 109-137
66. Höglund-Isaksson, L.; Gómez-Sanabria, A.; Klimont, Z.; Rafaj, P.; Schöp, W. Technical potentials and costs for reducing global anthropogenic methane emissions in the 2050 timeframe - results from the GAINS model. *Environ. Res. Commun.* 2020, 2, No. 025004
67. Hrad, M., Piringer, M., Huber-Humer, M., 2015. Determining methane emissions from biogas plants – operational and meteorological aspects. *Bioresour. Technol.* 191, 234–243. <http://dx.doi.org/10.1016/j.biortech.2015.05.016>
68. Hutchinson, G. L.; Mosier, A. R. Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Sci. Soc. Am. J.* 1981, 45, 311–316.
69. IPCC. Chapter 2: Stationary Combustion. In 2006 IPCC Guidelines for National Greenhouse Gas Inventories; Eggleston, S.; Buendia, L.; Miwa, K.; Ngara, T.; Tanabe, K., Eds.; Institute for Global Environmental Strategies: Hayama, 2006; pp 2.1–2.47.
70. J. Huang, C. Liu, H. Tong, W. Li, D. Wu, Theoretical studies on pyrolysis mechanism of xylopyranose, *Comput. Theor. Chem.* 1001 (2012) 44–50.
71. J. Wei, C. Tu, G. Yuan, Y. Liu, D. Bi, L. Xiao, J. Lu, B.K.G. Theng, H. Wang, L. Zhang, X. Zhang, Assessing the effect of pyrolysis temperature on the molecular properties and copper sorption capacity of a halophyte biochar, *Environ. Pollut.* 251 (2019) 56–65.
72. J.I. Osayi, S. Iyuke, S.E. Ogbeide, Biocrude production through pyrolysis of used tyres, *J. Catal.* 2014 (2014) 1–9.
73. Janssen PH, Kirs M. 2008. Structure of the archaeal community of the rumen. *Appl. Environ. Microbiol.* 74: 3619-3625
74. Jenkins, T.C.; Wallace, R.J.; Moate, P.J.; Mosley, E.E. Board-invited review: Recent advances in biohydrogenation of unsaturated fatty acids within the rumen microbial ecosystem. *J. Anim. Sci.* 2008, 86, 397–412

75. Jordan, E.; Kenny, D.A.; Hawkins, M.; Malone, R.; Lovett, D.K.; O'Mara, F.P. Effect of refined soy oil or whole soybeans on intake, methane output, and performance of young bulls. *J. Anim. Sci.* 2006, 84, 2418–2425
76. Kampman, B.; Leguijt, C.; Scholten, T.; Tallat-Kelsaite, J.; Brückmann, R.; Maroulis, G.; Lesschen, J.P.; Meesters, K.; Sikirica, N.; Elbersen, B. Optimal use of biogas from waste streams - An assessment of the potential of biogas from digestion in the EU beyond 2020; European Commission, Strasbourg, France, 2017.
77. Kariyapperuma, K.A.; Johannesson, G.; Maldaner, L.; Vanderzaag, A.; Gordon, R.; Wagner-Riddle, C., 2017. Year-round methane emissions from stored liquid dairy manure from a commercial farm in a cold climate. *Agric. Forest Meteorol* (Special Issue, Greenhouse gas and ammonia emissions from livestock production systems
78. Khan MA, Basir A, Fahad S, Adnan M, Saleem MH, Iqbal A, Amanullah, Al-Huqail AA, Alosaimi AA, Saud S, Liu K, Harrison MT and Nawaz T (2022) Biochar Optimizes Wheat Quality, Yield, and Nitrogen Acquisition in Low Fertile Calcareous Soil Treated With Organic and Mineral Nitrogen Fertilizers. *Front. Plant Sci.* 13:879788. doi: 10.3389/fpls.2022.879788.
79. King GM, Ecological aspects of methane oxidation, a key determinant of global methane dynamics, in: *Advances in Microbial Ecology*, Springer, pp. 431-468 (1992).
80. Kliem, K.; Humphries, D.; Kirton, P.; Givens, D.; Reynolds, C. Differential effects of oilseed supplements on methane production and milk fatty acid concentrations in dairy cows. *Animal* 2019, 13, 309–317.
81. KPMG (2021) Sustainability of Biomethane Production in Ireland Available at: <https://www.gasnetworks.ie/biomethane-sustainability-report-2021.pdf>. Accessed 14 July 2022.
82. KPMG(2021) Ireland would need to cull up to 1.3 million cattle to reach climate targets <https://www.theguardian.com/environment/2021/nov/03/ireland-would-need-to-cull-up-to-13-million-cattle-to-reach-climate-targets> Accessed 14 July 2022
83. Kumar, U., Shahid, M., Tripathi, R., Mohanty, S., Kumar, A., Bhattacharyya, P., et al. (2017). Variation of functional diversity of soil microbial community in sub-humid tropical rice-rice cropping system under long-term organic and inorganic fertilization. *Ecol. Indic.* 73, 536–543. doi: 10.1016/j.ecolind.2016.10.014
84. Kupeckia, J.; Papurelloc, D.; Lanzinic, A.; Naumovicha, Y.; Motylinska, K.; Blesznowska, M.; Santarelli M. Numerical model of planar anode supported solid oxide fuel cell fed with fuel containing H₂S operated in direct internal reforming mode (DIR-SOFC). *Appl. Energy* 2018, 230, 1573–1584.
85. Kupper, T., Häni, C., Neftel, A., Kincaid, C., Bühler, M., Amon, B., & VanderZaag, A. (2020). Ammonia and greenhouse gas emissions from slurry storage - A review. *Agriculture Ecosystems and Environment*, 300(April), 106963
86. Lanigan, G.J., Donnellan, T., Hanrahan, K., Paul, C., Shalloo, L., Krol, D., & Richards, K. (2018). An analysis of abatement potential of greenhouse gas emissions in Irish agriculture 2021–2030. Teagasc, Oak Park, Carlow. June 2018
87. Lara, R. “SB 1383 Short Lived Climate Pollutants: Methane Emissions: Dairy and Livestock: Organic Waste: Livestock” (2016. https://leginfo.legislature.ca.gov/faces/billNavClient.xhtml?bill_id=201520160SB1383) (accessed July 16, 2022).

88. Lascano CE, Cárdenas E. 2010. Alternatives for methane emission mitigation in livestock systems. *R. Bras. Zootec.* 39: 175-182
89. Lebuhn M, Munk B and Effenberger M, Agricultural biogas production in Germany - from practice to microbiology basics. *Energy, Sustainability and Society* 4:1-21 (2014).
90. Lee, K. Lee, D. Sohn, Y.M. Kim, K.Y. Park, Hydrothermal carbonization of lipid extracted algae for hydrochar production and feasibility of using hydrochar as a solid fuel, *Energy* 153 (2018) 913–920
91. Leip, A., Weiss, F., Wassenaar, T., Perez, I., Fellmann, T., Loudjani, P., Tubiello, F., Grandgirard, D., Monni, S., & Biala, K. (2010). Evaluation of the livestock sector's contribution to the EU greenhouse gas emissions. Final report. European Commission, Joint Research Centre
92. Leytem, A.B.; Dungan, R.S.; Bjorneberg, D.L.; Koehn, A.C. Emissions of Ammonia, Methane, Carbon Dioxide, and Nitrous Oxide from Dairy Cattle Housing and Manure Management Systems. *J. Environ. Qual.* 2011, 40, 1383–1394
93. Li, Y.; Samir, K.K. *Bioenergy: Principles and Applications*; John Wiley & Sons, Hoboken, NZ, USA, 2016.
94. Lia Maldaner, Claudia Wagner-Riddle, Andrew C. VanderZaag, Robert Gordon, Christopher Duke. Methane emissions from storage of digestate at a dairy manure biogas facility. *Agricultural and Forest Meteorology*, Volume 258, 2018, Pages 96-107. ISSN 0168-1923, <http://doi.org/10.1016/j.agrformet.2017.12.184>.
95. Liebetrau, J., Reinelt, T., Clemens, J., Hafermann, C., Friehe, J., Weiland, P., 2013. Analysis of greenhouse gas emissions from 10 biogas plants within the agricultural sector. *Water Sci. Technol.* 67, 1370–1379. <http://dx.doi.org/10.2166/wst.2013.005>
96. Lillis, L.; Boots, G.; Kenny, D.; Petrie, K.; Boland, T.; Clipson, N.; Doyle, E. The effect of dietary concentrate and soya oil inclusion on microbial diversity in the rumen of cattle. *J. Appl. Microbiol.* 2011, 111, 1426–1435
97. Liu, E., Yan, C., Mei, X., He, W., Bing, S. H., Ding, L., et al. (2010). Longterm effect of chemical fertilizer, straw, and manure on soil chemical and biological properties in northwest China. *Geoderma* 158, 173–180. doi: 10.1016/j.geoderma.2010.04.029
98. Lukehurst, C.; Bywater, A. Exploring the viability of small scale anaerobic digesters in livestock farming; IEA Bioenergy: Paris, France, 2015, Available online: <https://www.iea-biogas.net/files/datenredaktion/download/Technical%20Brochures/Sm>
99. Lynch, J. (2019). Agricultural methane and its role as a greenhouse gas. Food Climate Research Network, University of Oxford.
100. Lyons, T.; Boland, T.; Storey, S.; Doyle, E. Linseed Oil Supplementation of Lambs' Diet in Early Life Leads to Persistent Changes in Rumen Microbiome Structure. *Front. Microbiol.* 2017, 8, 1656
101. Manchala, K.R.; Sun, Y.; Zhang, D.; Wang, Z.W. Anaerobic digestion modelling. *Adv. Bioenergy* 2017, 2, 69– 141.
102. Martin, C.; Ferlay, A.; Mosoni, P.; Rochette, Y.; Chilliard, Y.; Doreau, M. Increasing linseed supply in dairy cow diets based on hay or corn silage: Effect on enteric methane emission, rumen microbial fermentation, and digestion. *J. Dairy Sci.* 2016, 99, 3445–3456

103. Maykut, P.; Morehouse, R. *Beginning Qualitative Research: A Philosophic and Practical Guide*; Falmer Press: London, UK, 1994.
104. McCabe et al., (2019); SYSTEMIC (2020) Mineral Concentrate; Agriculture and Horticulture Development Board Nutrient Management Guide (RB209) Organic Materials
105. McCartney, C.A.; Bull, I.D.; Waters, S.M.; Dewhurst, R.J. Technical note: Comparison of biomarker and molecular biological methods for estimating methanogen abundance. *J. Anim Sci.* 2013, 91, 5724–5728.
106. McHenry M P 2009 Agricultural bio-char production, renewable energy generation and farm carbon sequestration in Western Australia: Certainty, uncertainty and risk *Agriculture, Ecosystems & Environment* 129 1-7.
107. McInerney, M.J. and Bryant, M.P.: Basic Principles of bioconversions in anaerobic digestion and methanogenesis. In: Sofer, S.R. and Zaborsky, O.R. (Eds.): *Biomass Conversion Processes for Energy and Fuels*. Plenum Press, New York, 1981
108. Mendez, A. Gomez, J. Paz-Ferreiro, G. Gasco, Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil, *Chemosphere*. 89 (2012) 1354–1359.
109. Mortimer, C. and Müller, U.: *Das Basiswissen der Chemie*. Thieme, Stuttgart, 2007.
110. Myhre, G.; Shindell, D.; Bréon, F.M.; Collins, W.; Fuglestad, J.; Huang, J.; Koch, D.; Lamarque, J.F.; Lee, D.; Mendoza, B.; Nakajima, T.; Robock, A.; Stephens, G.; Takemura, T.; Zhang, H. 2013: Anthropogenic and Natural Radiative Forcing. In *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*; Stocker, T.F.; Qin, D.; Plattner, G.K.; Tignor, M.; Allen, S.K.; Boschung, J.; Nauels, A.; Xia, Y.; Bex, V.; Midgley P.M., Eds.; Cambridge University Press: Cambridge, UK.
111. Nguyen, D.; Gadhamshetty, V.; Nitayavardhana, S.; Khanal, S.K. Automatic process control in anaerobic digestion technology: A critical review. *Bioresour. Technol.* 2015, 193, 513–522.
112. Nielsen, M.; Nielsen, O.K.; Plejdrup, M. Danish emission inventories for stationary combustion plants. Inventories until 2011; Scientific Report from DCE–Danish Centre for Environment and Energy: Aarhus University, Aarhus, Denmark, 2014
113. O'Brien, D., Shalloo, L., Patton, J., Buckley, F., Grainger, C., & Wallace, M. (2012). A life cycle assessment of seasonal grass-based and confinement dairy farms. *Agricultural Systems*, 107, 33–46.
114. Oleszkiewicz, J.A. and Sharma, V.K. (1990): Stimulation and Inhibition of Anaerobic Processes by Heavy Metals - A Review. *Biological Wastes*. Vol. 3, No. 1, 45–67.
115. Owen, J.J., Silver, W.L., 2015. Greenhouse gas emissions from dairy manure management: a review of field-based studies. *Glob. Chang. Biol.* 21, 550–565. <http://dx.doi.org/10.1111/gcb.12687>. Park, K.H., Thompson, A.G., Mari
116. Papurello, D.; Boschetti, A.; Silvestri, S.; Khomenko, I.; Biasioli, F. Real-time monitoring of removal of trace compounds with PTR-MS: Biochar experimental investigation. *Renew. Energy* 2018, 125, 344–355
117. Pavlostathis, S.G. and Giraldo-Gomez, E. (1991): Kinetics of Anaerobic Treatment: A Critical Review.

118. PCC, "Anthropogenic and natural radiative forcing" in *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, G. Myhre et al., Eds. (Cambridge University Press, Cambridge, UK, 2013), pp. 658–740.
119. Pobeheim, H., Munk, B., Johansson, J. and Guebitz, G.M. (2010): Influence of trace elements on methane formation from a synthetic model substrate for maize silage. *Bioresource Technology*. Vol. 101, 836–839.
120. QUBE Renewables. Innovative small scale anaerobic digestion. Available online: <https://www.qubernewables.co.uk/> (accessed on 29 July 2022).
121. Ramsay, I.R. and Pullammanappallil, P.C. (2001): Protein degradation during anaerobic wastewater treatment: Derivation of stoichiometry. *Biodegradation*. Vol. 12, 247–257 *Critical Reviews in Environmental Control*. Vol. 21, No. 5/6, 441–490.
122. Redican, J.H. Federal Discount Rate for Fiscal Year 2019: Economic Guidance Memorandum 19-01; Army Corps of Engineers: Washington, DC, USA, 2018.
123. Redman, G. A detailed economic assessment of anaerobic digestion technology and its suitability to UK farming and waste systems; The Andersons Centre: Leicestershire, UK, 2010
124. Renewable Energy Feed in Tariff (RE-FIT 2006), Ireland Department of Communications Energy & Natural Resources (2006).
125. Rodhe, L.K.K., Ascue, J., Willén, A., Persson, B.V., Nordberg, Å., 2015. Greenhouse gas emissions from storage and field application of anaerobically digested and non-digested cattle slurry. *Agric. Ecosyst. Environ.* 199, 358–368. <http://dx.doi.org/10.1016/j.agee.2014.10.004>
126. Ryan T.; Lenehan, J.J. Chapter 48—Winter accommodation for beef animals. In *Teagasc Beef Manual*, Teagasc: Carlow, Ireland, 2016, pp. 271–284.
127. S. Mondal, K. Bobde, K. Aikat, G. Halder, Biosorptive uptake of ibuprofen by steam activated biochar derived from mung bean husk: equilibrium, kinetics, thermodynamics, modeling and eco-toxicological studies, *J. Environ. Manage.* 182 (2016) 581–594.
128. S.A. Arni, Comparison of slow and fast pyrolysis for converting biomass into fuel, *Renew. Energy* 124 (2018) 197–201.
129. Sanders, W.T.M.: Anaerobic hydrolysis during digestion of complex substrates, 2001.
130. Satchwell, A. J.; Scown, C.; Smith, S.; Amirebrahimi, J.; Jin, L.; Kirchstetter, T.; Brown, N.; Preble, C. Accelerating the deployment of anaerobic digestion to meet zero waste goals. *Environ. Sci. Technol.* 2018, 52, 13663–13669
131. Schattauer, A., Abdoun, E., Weiland, P., Plöchl, M. and Heiermann, M. (2011): Abundance of trace elements in demonstration biogas plants. *Biosystems Engineering*. Vol. 108, No. 1, January 2011, 57–65
132. Scheftelowitz M, Rensberg N, Denysenko V, Daniel-Gromke J, Stinner W, Hillebrand K, et al., Stromerzeugung aus Biomasse. Bundesministeriums für Wirtschaft und Energie (BMWi), Berlin, (2015)
133. SEAI. Domestic fuels comparison of energy costs, Sustainable Energy Authority of Ireland: Ireland, 2018, Available online: <https://www.seai.ie/resources/publications/Domestic-Fuel-Cost-Comparison.pdf> (accessed 17 July 2022).

134. Shortall, O.K. A Qualitative Study of Irish Dairy Farmer Values Relating to Sustainable Grass-Based Production Practices Using the Concept of 'Good Farming'. *Sustainability* 2022, 14, 6604. <https://doi.org/10.3390/su14116604>.
135. Singh A, Smyth BM and Murphy JD, A biofuel strategy for Ireland with an emphasis on production of biomethane and minimization of land-take. *Renewable and Sustainable Energy Reviews* 14:277-288 (2010)
136. Smith, P.H. and Mah, R.A. (1966): Kinetics of Acetate Metabolism During Sludge Digestion. *Applied Microbiology*. Vol. 14, No. 3, 368–371.
137. Sommer, S.G., Petersen, S.O., Sørensen, P., Poulsen, H.D., Møller, H.B., 2007. Methane and carbon dioxide emissions and nitrogen turnover during liquid manure storage. *Nutr. Cycl. Agroecosyst.* 78, 27–36. <http://dx.doi.org/10.1007/s10705-006-9072-4>.
138. Stambasky, J. The potential size of the anaerobic digestion industry in Ireland by the year 2030; Composting & Anaerobic Digestion Association of Ireland and The Irish Bioenergy Association: Meath, Ireland, 2016
139. Steiner, C.; Sánchez-Monedero, M. A.; Kammann, C. Biochar as an Additive to Compost and Growing Media. In *Biochar for Environmental Management: Science, Technology and Implementation*, Lehmann, L.; Joseph, S., Eds.; Routledge: New York, NY, 2015; pp 715–734.
140. Surendra K, Takara D, Jasinski J and Kumar Khanal S, Household anaerobic digester for bioenergy production in developing countries: opportunities and challenges. *Environ Technol* 34:1671-1689 (2013)
141. Taghizadeh-Toosi, A., Clough, J., Sherlock, R. R., and Condrón, L. M. (2012). Biochar adsorbed ammonia is bioavailable. *Plant Soil* 350, 57–69. doi: 10.1007/s11104-011-0870-3
142. Teagasc (2021) Cop26 and Climate Change - Focus for Farmers Available at: <https://www.teagasc.ie/news--events/daily/environment/cop26-and-climate-change---focus-for-farmers.php> Accessed 9 July 2022.
143. Teagasc (2021) Green House Gases A <https://www.teagasc.ie/environment/climate-change--air-quality/greenhouse-gases> Accessed 10 July 2022.
144. Teagasc (2022) Organic Manures Available at <https://www.teagasc.ie/crops/soil--soil-fertility/organic-manures> Accessed 8 July 2022.
145. Teagasc Dairy Manual—A best practice manual for Ireland's Dairy Farms. Teagasc: Carlow, Ireland, 2016
146. Testen J. *Microbiol. Biotechnol.* 2022.32(3):269–277
<https://doi.org/10.4014/jmb.2202.02019>
147. Thauer RK, Kaster AK, Seedorf H, Buckel W, Hedderich R. 2008. Methanogenic archaea: ecologically relevant differences in energy conservation. *Nat. Rev. Microbiol.* 6: 579-591.
148. The Engineering Toolbox. Combustion from Fuels - Carbon Dioxide Emission. Available online: https://www.engineeringtoolbox.com/co2-emission-fuels-d_1085.html (accessed on 26 June 2022).
149. Thorne, F., Gillespie, P., Donnellan, T., Hanrahan, K., Kinsella, A., & Läpple, D. (2017). The competitiveness of Irish agriculture. Dublin, Ireland: Teagasc.

150. Uddin, M.E.; Larson, R.A.; Wattiaux, M.A. Effects of dairy cow breed and dietary forage on greenhouse gas emissions from manure during storage and after field application. *J. Clean. Prod.* 2020, 270, 122461
151. Upton, J.; Humphreys, J.; Groot Koerkamp, P.W.G.; French, P.; Dillon, P.; De Boer, I.J.M. Energy demand on dairy farms in Ireland. *J. Dairy Sci.* 2013, 96, 6489–6498.
152. Van den Pol-van Dasselaar, A.; Hennessy, D.; Isselstein, J. Grazing of dairy cows in europe-an in-depth analysis based on the perception of grassland experts. *Sustainability* 2020, 12, 1098
153. Van Zijderveld SM, Gerrits WJ, Apajalahti JA, Newbold JR, Dijkstra J, Leng RA, et al. 2010. Nitrate and sulfate: effective alternative hydrogen sinks for mitigation of ruminal methane production in sheep. *J. Dairy Sci.* 93: 5856-5866.
154. VanderZaag, a.C., Wagner-Riddle, C., Park, K.-H., Gordon, R.J., 2011. Methane emissions from stored liquid dairy manure in a cold climate. *Anim. Feed Sci. Technol.* 166–167, 581–589. <http://dx.doi.org/10.1016/j.anifeedsci.2011.04.041>.
155. Vergara, S. E.; Silver, W. Greenhouse gas emissions from windrow composting of organic wastes: Patterns and emissions factors. *Environ. Res. Lett.* 2019, 14, No. 124027.
156. Walker, M.; Theaker, H.; Yaman, R.; Poggio, D.; Nimmo, W.; Bywater, A.; Blanch, G.; Pourkashanian M. Assessment of micro-scale anaerobic digestion for management of urban organic waste: A case study in London, UK. *Waste Manag.* 2017, 122, 221–236.
157. Wang, C.; Lu, H.; Dong, D.; Deng, H.; Strong, P. J.; Wang, H.; Wu, W. Insight into the effects of biochar on manure composting: *Environmental Science & Technology* pubs.acs.org/est Article <https://doi.org/10.1021/acs.est.2c03467> *Environ. Sci. Technol.* Evidence supporting the relationship between N₂O emission and denitrifying community. *Environ. Sci. Technol.* 2013, 47, 7341–7349
158. Wickham, B. Cattle Breeding in Ireland; Irish Farmers Journal: Dublin, Ireland, 2007.
159. Wilkinson, K. G. Development of on-farm anaerobic digestion. In *Integrated waste management*; Kumar, S., Ed.; InTech.: Rijeka, Croatia, 2011; Volume 1, pp. 179–194.
160. Yue Y, Guo W, Lin Q, Li G and Zhao X 2016 Improving salt leaching in a simulated saline soil column by three biochars derived from rice straw (*Oryza sativa* L.), sunflower straw (*Helianthus annuus*), and cow manure *Journal of Soil and Water Conservation* 71 467-7
161. Zhang, C.M.; Guo, Y.Q.; Yuan, Z.P.; Wu, Y.M.; Wang, J.K.; Liu, J.X.; Zhu, W.Y. Effect of octadeca carbon fatty acids on microbial fermentation, methanogenesis and microbial flora in vitro. *Anim. Feed Sci. Tech.* 2008, 146, 259–269.
162. Zhou, X, et al. 2019. Estimation of methane emissions from the U.S. ammonia fertilizer industry using a mobile sensing approach. *Elem Sci Anth*, 7: 19. DOI: <https://doi.org/10.1525/elementa.358>
163. Zuber M, Biogas to Energy. Fraunhofer Gesellschaft, Cologne, (2012).