Optimisation of Methane Production from Anaerobically Digested Cow Slurry Using Mixing Regime and Hydraulic Retention Time

Submitted by

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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

Signature of Author: …………………………………………………………..

Abstract

AD is regarded as a sustainable technology that could assist the UK Government meet internationally agreed GHG emission targets by 2050. However, the mature status of the technology is based on expensive systems that rely on high energy feedstock to be profitable. Meanwhile, the natural biodegradation of cow slurry is a recognised contributor to climate change despite having a relatively low CH_4 potential because of the large volumes produced. Economic mixing is essential to the cost-effectiveness of farm AD but techniques applied are not always appropriate as slurry is a shear thinning thixotropic Herschel-Bulkley fluid and therefore challenging to mix. The apparent viscosity of slurry and the shear stress induced was most influenced by solids content (exponential change) followed by temperature (linear). Most shear thinning occurred before a rising shear rate of $20s^{-1}$ was achieved with the fluid acting near-Newtonian above. Thixotropic recovery occurred within 1 hour of resting. Rheological values were also much higher than previously reported. Highest CH_4 production occurred in the first 10 days of the batch process using a range of mixing regimes with different shear rates and rest periods. During fed-batch operations, changing shear rate had a minimal effect on CH_4 production using a 30-day HRT whereas shorter rest periods increased production. Specific CH_4 production rate was highest when feeding and mixing coincided. However, when HRT was reduced (OLR increased) the CH_4 produced by all mixed regimes significantly increased with highest values being achieved using high intensity mixing rested for short periods. Lower HRTs also requires smaller digesters. Parasitic mixing energy invariably had the most influence on net energy production. Signs of instability were evident after 20 days using the low HRT. Significant microbial adaptation was also observed as the experiments progressed. The research outcomes demonstrate that mixing regime and HRT can be managed to maximise net energy production whilst reducing capital expenditure.

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Declaration

The author confirms that the following manuscript is original and has not been submitted elsewhere.

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List of Abbreviations

Abbreviation	**Meaning**
AD	Anaerobic digestion
ANOVA	Analysis of variation
CAPEX	Capital expenditure
CARPT	Computer automated radioactive particle tracking
CFD	Computerised fluid dynamic (modelling)
CHP	Combined heat and power
CMC	Sodium carboxymethyl cellulose
CO_2e	Carbon dioxide equivalent
CSTR	Continuously stirred tank reactor
CV	Calorific value
DPIV	Digital particle image velocimetry
EPS	Extracellular polymeric substance
ERT	Electrical resistive tomography
GHG	Greenhouse gas
HRT	Hydraulic retention time
K (K-value)	Rheological consistency index
LDA	Laser-doppler anemometry
LDV	Laser-doppler velocimetry
LRLC	Large rotor large cup
LRSC	Large rotor small cup
MSW	Municipal solid waste
n (n-value)	Flow behavioural index
NFU	National Farmers Union
OBR	Oscillatory baffle reactor
OLR	Organic loading rate
OPEX	Operational expenditure
PLC	Programmable Logic Controller
pLIF	planar laser induced fluorescence
Re_i	Reynolds number (at impeller)
Rpm	Revolutions per minute
RTD	Residence time distribution
SRLC	Small rotor large cup
SRSC	Small rotor small cup
SRT	Solids retention time
SSRP	Standard shear rate profile
TS	Total solids
UASB	Up-flow anaerobic sludge blanket
UV	Ultraviolet
VFA	Volatile fatty acid
VS	Volatile solids
w/w	Weight for weight

Introduction

As part of the global initiative to address climate change, the UK Government has agreed to reduce UK greenhouse gas (GHG) emissions by at least 80 percent by 2050 relative to 1990 levels (DECC, 2010). Achieving that target is likely to be a compromise between reducing energy demand and de-carbonising energy supply. In response to the challenge, alternative pathways have been identified by which the ambitious reductions can be achieved (DECC, 2010). As early as 2009, the UK Government Department for Environment, Food and Rural Affairs (DEFRA) set out a clear ambition to increase the uptake of anaerobic digestion (AD) in England (DEFRA, 2009). In response, the National Farmers Union (NFU) declared a target of 1000 on-farm digesters to be operational by 2020 (Royal Agricultural Society of England, 2011). On-farm digesters are likely to be fed with animal waste/slurries, crop/animal feed residues or purposely grown crops such as maize with the energy value of each feedstock being different. Slurry has a relatively low energy value compared to maize grain and other energy crops on a weight for weight (w/w) basis (Andersons Centre, 2010) but the high volumes produced daily by the dairy industry imply substantial potential to produce useful energy. However, AD systems for dairy farm applications tend to be relatively expensive and not financially viable when fed with low energy feedstock alone. As a result, the uptake of the technology is unlikely to improve unless financial viability increases (Mezzullo, 2010).

The volumetric biogas potential of an AD plant is a major economic metric as biogas generation determines the ratio of production of saleable energy and the capital invested in the volumetric capacity of the plant (Banks & Zhang, 2010). Therefore, AD system design should ideally support high biogas yields whilst maximising organic loading rate (OLR) in the shortest hydraulic retention time (HRT) (Ward et al., 2008). However, rates of biogas production are higher at the beginning of the degradation cycle with production levelling off towards the end of the process (Andersons Centre, 2010). Bensmann et al. (2013) suggest that in some circumstances the specific methane (CH_4) production rate for a given configuration should be the key design consideration for a digester rather than attempting to maximise cumulative yield. Indeed, if the intention is to process low cost feedstock, sizing a digester to achieve complete substrate degradation may not be the most cost-effective option. The subsequent potential decrease in HRT could reduce digester volume, and thus capital costs of installation as well as associated mixing energy and costs. Before an AD process can be optimised and inhibition avoided the feedstock, whether a waste stream or intentionally grown, must be understood (Chen et al., 2008). Many measures can be implemented to improve process performance with varying degrees of success. However, appropriate, economic and responsive mixing is fundamental if microbial kinetics are to be optimised at all times.

The choice of mixing system and the approach to effective management can provide optimum environmental conditions for the microbial communities to ensure process stability. To do so requires a better understanding of the effects of mixing on microbial communities embedded in a substrate than has been available. If that is to be achieved, the rheology of the host substrate when subjected to key environmental factors also needs to be better understood.

Effective mixing relies on the appropriate level of shear rate being applied to the substrate for the time necessary to achieve a required level of homogeneity throughout the digester. The system of choice must also minimise any detrimental effect mixing may have on the microbial community on which the AD process and hence the quality and quantity of the products relies. However, the application of shear force influences the non-Newtonian characteristics of the intended substrate so the substrate’s rheological response to handling must first be characterised. Identifying extremes of shear stress and apparent viscosity will improve the understanding of issues associated with mixing and provide valuable information to assist in equipment selection. The rheological response of a feedstock to key influences experienced when mixed can also be used to design experiments to identify the effect of those influencing factors on methanogenesis by monitoring the CH_4 produced for various mixing regimes.

If an appropriate mixing technique is assumed then the effects of mixing intensity and resting (mixing regime) on microbial kinetics and hence CH_4 production can be explored and balanced against the parasitic energy demanded to produce it.

A mixing regime that maximises net energy gain can then be used as a basis to identify the effects of reducing HRT on system performance.

Thesis Aims, Objectives and Structure

The aims of this research are to:

1. Identify the rheological properties of common cow slurry when subjected to conditions experienced during daily farm operations and when processed anaerobically.
2. Apply the rheological outcomes to demonstrate the effects of a range of mixing regimes on CH_4 production during batch and fed-batch AD processes.
3. Compare energy generated with parasitic energy used to provide a mixing hierarchy based on net energy gain.
4. Demonstrate how HRT can be managed to maximise the rate of CH_4 production per unit of digester volume to optimise digester capacity.

The objective of the research is to inform the design, operation and management of farm-scale AD systems to improve the financial viability of the technology in the dairy industry.

The thesis begins with a current review of AD literature with particular emphasis on those aspects that influence the application of the technology in the dairy industry. Chapter 2 presents a rheological analysis of cow slurry when subjected to key variables commonly experienced on dairy farms and in the AD process. Extreme shear stress and apparent viscosity values are captured to inform both industry and the academic community. A suitable substitution fluid for cow slurry is also analysed. A description of how the rheometer design was adapted and calibrated to accommodate and measure the rheological properties of cow slurry without compromising sample integrity is captured as an appendix. The rheological outputs of chapter 2 inform the experimental design of chapter 3 which investigates the effect of shear rate and resting on methanogen communities by measuring the rate of CH_4 production and overall yield using a batch process. The outcomes are used to refine the experimental method used in chapter 4 where larger lab-scale digesters are intermittently fed in 2 separate experiments to identify the individual effects of shear rate and resting on methanogen activity when the HRT is 30 days. Again, CH_4 production rate and cumulative yield are the main outcomes. Chapter 5 explores the effects of reducing HRT on CH_4 production and process stability when subjected to the same fed-batch technique. The results of chapters 4 and 5 are compared in chapter 6 to highlight the financial and operational benefits of optimising HRT when processing cow slurry. Chapter 7 summarises the research and suggests further research that may improve the financial viability of AD on dairy farms through appropriate mixing.

Scope of Work

The scope of work relied on the following assumptions being made and research boundary identified.

Assumptions

To ensure that clarity of scientific reasoning was maintained whilst producing evidence to inform the design and operation of a financially-viable baseline dairy farm AD solution, the following assumptions were made:

- Dairy cattle slurry would be the sole feedstock.
- The sample of dairy cattle slurry used was representative of that commonly produced.
- Separation of solids greater than 10mm did not influence the rheology when working at lab-scale.
- No pre-treatment methods would be practiced.
- The mixing system eventually used would be efficient in terms of mixing effect and energy use.
- CH_4 produced added to the overall mixing effect.
- The process would be appropriately monitored and controlled.
- Biogas output was not purified but used to fuel a CHP generator.

System Boundary

The research boundary is defined as the internal mechanical, environmental and chemical processes that occur during AD. However, substrate rheology influences all stages of substrate management so extreme values of variables in all pumping/mixing conditions were investigated, where possible. For clarity, influencing factors are presented as those internal and external to the system.

Factors Internal to the System

The following factors are fundamental to understanding the effects of mixing on the AD process and so included in the research:

- Type of feedstock and the calorific value (CV) of the embedded VS.
- Substrate rheology of the primary/major feedstock.
- OLR.
- Process temperature.
- Effectiveness of mixing technique.
- HRT.
- Rate of CH_4 production.
- CH_4 yield.
- Parasitic energy demand.

External Factors

To isolate the effects that mixing has on the AD process and ensure that results are not influenced by advanced techniques and practices, the following subject areas are excluded from the research:

- Digester design.
- Geographical influence of digester location.
- Digester operating practices beyond mixing and feeding.
- Implications and benefits of co-digestion.
- Using feedstock external to the farm, such as food waste.

- Environmental regulation.
- Product application post-digestion.

Project Aims

The aims of this project are to:

- Identify, test and calibrate a suitable rheometer to analyse cow slurry.
- Carry out a full rheological analysis of cow slurry representative of dairy farm operations in the UK and central Europe.
- Identify differences in gross and net CH_4 production when slurry is subjected to a range of mixing regimes under batch process conditions.
- Identify differences in gross and net CH_4 production when slurry is subjected to a range of mixing regimes in a fed-batch process and different HRTs applied.
- Provide information to inform mixing regime and HRT selection when financially modelling system design and operation.

CHAPTER 1 – ANAEROBIC DIGESTION IN AGRICULTURE

1:1 Background

Bioenergy is recognised as a serious renewable energy alternative to fossil fuels (Cherubini & Strømman, 2011). In turn, AD provides a very effective method of turning waste products into useful energy (Royal Agricultural Society of England, 2011) whilst reducing the potential for GHG emissions to atmosphere (Amon et al., 2006). However, one of the main barriers to the uptake of farm-scale AD in the UK dairy sector is the lack of financial viability (Mezzullo, 2010).

1:1:1 Environmental Pollution from Agriculture

If left untreated or poorly managed, animal manure becomes a major source of air and water pollution (Holm-Nielsen et al., 2009) as gaseous emissions from livestock waste significantly contribute to CH_4, Ammonia (NH_3) and Nitrous Oxide (N_2O) entering the atmosphere (Massé et al. 2003; Amon et al. 2006; Rodhe et al. 2009). In particular, the generation of CH_4 through the aerobic and anaerobic bio-degradation of cattle manure is recognised as a major contributor to GHG emissions, particularly as CH_4 has a global warming potential of 25 times that of carbon dioxide (CO_2) (UK Government Department of Business Innovation and Skills, 2011). Meanwhile, intensification of livestock farming in developed countries is increasing the potential of environmental pollution as the slurry management burden increases.

1:1:2 Reducing GHG Emissions from Livestock

GHG emissions from UK agriculture in 2012 was estimated at 60Mt CO_2e or 10 percent of total emissions. In terms of CH_4, agriculture was credited with producing 44 percent of the country’s total emission, the majority of which came from the enteric fermentation in livestock and manure management (DEFRA, 2014). CH_4 from livestock is produced at 3 distinct stages in the feed cycle: when food is digested within the ruminant gut and when slurry and farm effluent are left to aerobically or anaerobically bio-degrade. When reviewing the potential to influence production within the gut, Patra (2012) concluded a lack of long-term experimental evidence to support mitigation measures such as dietary supplements and immunisation against methanogens. However, the use of AD to reduce CH_4 emissions from farm slurry and effluent is a common practice although more research is required before the benefits of the technology can be fully understood (Bernet & Béline, 2009). In 2014, just one percent of all UK farms processed slurries using AD which had changed little from 2008 (DEFRA, 2014).

1:2 Anaerobic Digestion

AD can accommodate a wide range of feedstock with different characteristics, processing challenges and management issues. As a result, the extensive research that informs the industry is naturally diverse and not necessarily balanced. For example, the sewage and waste water industry has attracted continuous attention over recent decades as outcomes have a global and direct effect on human health. Conversely, research into improving AD of cow manure has been limited. Technical solutions can be widely adopted or specific to address a particular problem in one sector. As a result, this research has drawn on outcomes from all aspects of the industry, including the treatment of sewage and waste water, municipal solid waste (MSW), industrial waste, energy crops and livestock manures. In addition, relevant outcomes from other industries, particularly those that inform or address the rheological challenges of managing fluids, have also been captured, where appropriate.

1:2:1 The Process

AD is a micro-biologically mediated process during which organic carbon, present in bio-polymers and other degradable compounds, is converted to a most reduced form (CH_4) and most oxidised form (CO_2) in the absence of oxygen (Madsen et al., 2011). The multi-stage process follows 2 main bio-degradation pathways after the polysaccharides, fats and proteins are solubilised to monomers by extracellular enzymes (Madigan et al., 2012). Some monomers ferment to either acetate, H_2 or CO_2 whilst others form intermediate fatty acids such as butyrate and formate or alcohols such as ethanol, lactate and succinate. The flow of carbon through the pathways depends on H_2 concentrations. Acetogens consume intermediates to produce acetate, formate, CO_2 and H_2. The methanogens then consume the acetate and H_2 to produce CH_4 (Schink, 1997). Temperature is the most important physical condition for bacterial growth, whereas HRT determines the length of time that the substrate is retained in the digester (Doran, 2013). Meanwhile, solids retention time (SRT) is the time that solids are made available to the microbes that carry out the digestion (Appels et al., 2008). Common process temperatures are mesophilic (37.5˚C) and thermophilic (55˚C) and digesters can be either continuously fed or processed as a batch or a fed-batch. The microbial process is regulated by pH (Wu, 2012b). The digestion process is regarded as 'wet' if the total solids (TS) content is less than 15 percent (%TS) and 'dry' above that figure (Li et al., 2011). Cow slurry tends to be treated using 'wet' techniques due to low %TS content.

1:2:2 Products

If handled correctly, animal manure can be converted from an environmental burden to a valuable source of renewable energy through the production of (Holm-Nielsen et al., 2009):

- Biogas consisting of approximately 55 to 65 percent CH_4, with the remainder primarily consisting of CO_2 accompanied by small amounts of H_2S, and H_2. Biogas can be used to provide electricity and heat through a combined heat and power (CHP) unit or purified to biomethane standard (98 percent CH_4). Pure CH_4 has an upper calorific value of $39.8MJm^{-3}$ (equivalent to 11.06 $kWhm^{-3}$) (Jørgensen, 2009). Cow slurry takes approximately 30 days to bio-degrade at mesophilic temperatures (Khanal, 2008) with the majority of the biogas being produced in the first 10 days (Andersons Centre, 2010).
- Digestate, a natural organic nutrient-rich and relatively low viscosity fluid containing Nitrogen (N), Phosphorus (P), Potassium (K) and Magnesium (Mg). The major benefit of digestate is the high proportion of Ammonium Nitrogen ($NH_4^{+-}N$) that the digestate contains which can be directly taken

up by plants (Schnurer & Jarvis, 2010) although Möller & Müller (2012) observed that this was only the case if applied correctly. If done so, the benefits of appropriate application of digestate could be used to offset the overall N_2 needs of the farm that are often met by importing inorganic fertiliser. The quality and therefore value of the digestate is directly influenced by the variables that affect the process (Schnurer & Jarvis, 2010) so will vary with processing technique and efficiency. Digestate can be further refined and the benefits enhanced if the solid and liquid fractions are separated prior to land application. Unfortunately, the value of digestate is not always appreciated even though including the benefits in financial modelling could improve the net energy output of a plant (Mezzullo, 2010). For example, digestate offers less obvious benefits over slurry including an increased spreading window, reduced crop taint, a decrease in grazing times and vastly reduced watercourse pollution potential (Royal Agricultural Society of England, 2011).

1:2:3 Maintaining Process Stability

The success of digester design is particularly related to the digester’s ability to retain high microbial concentration (biomass), often via the formation of dense granules or biofilm (Pevere et al., 2006). Such methods can be a particularly effective way of microbes resisting physical forces that would otherwise remove cells weakly attached to a surface (Madigan et al., 2012). Temporal distribution techniques, such as batch processing can be adopted to retain biomass in the digester (Bensmann et al., 2013). OLR can also effect process stability (Kim et al., 2002) if the metabolic response of the microbial community is delayed causing an accumulation of feedstock. This can be a common occurrence as the microbes that make up a diverse community have various rates of metabolism that can result in digester acidification. However, process stability may be recovered through long-term adaptation by the microbial community (Jian et al., 1997).

1:2:4 Process Optimisation

When a stable temperature is maintained, AD processing of animal slurry is primarily influenced by the HRT of the substrate in the digester (Keshtkar et al., 2003) and the degree of molecular contact between incoming substrate and the microbial population. The latter is heavily influenced by the effectiveness of the mixing system, the optimisation of which has attracted much debate (Karim et al., 2005c). Spatial distribution of the hydrolysis/acidogenesis and methanogenesis stages has also been found to significantly improve process stability and optimise the operation (Nasir et al., 2012). Bensmann et al. (2013) performed an extensive model-based qualitative comparison of a range of digester configurations using ADM1[1]. When compared to a single continuously-stirred tank reactor (CSTR), most techniques using spatial and temporal distribution outperformed single CSTR operations. CH_4 yields were calculated whilst substrate throughput in the form of a dilution rate (the inverse of HRT) was increased until microbial washout was achieved. A theoretical compromise between maximum CH_4 yield and rate of production was then identified so a process could be optimised for a particular feedstock. The study went on to de-couple SRT from HRT to highlight the benefits of biomass retention, including the potential to significantly increase CH_4 yield with minimal reductions in substrate throughput. Model validation through practical experimentation was recommended.

1:2:5 Parasitic Energy Demand

The main energy demands of the AD process are heat to maintain temperature and pumping/mixing energy to distribute and homogenise substrate. As most AD systems are used to generate electricity using a CHP unit, excess heat is often readily available so the parasitic energy required to heat will not be considered further. In this study, pumping and mixing are combined for simplicity.

Measuring the energy demanded by a mixing system is relatively simple but extrapolating when scaling up is difficult as the volume/power relationship to

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[1] ADM1 is a mathematical model that was produced by the IWA in 2002. The model was a harmony of the slightly different versions used in AD analysis at the time. Formulated for CSTR modelling, the AD process is described by dynamic balance equations, kinetic equations and acid-based equilibria.

achieve the same degree of mixing is not linear and will be specific to the mixing system used (Doran, 2013). Any comparison of parasitic energy demand should therefore be restricted to digesters of the same size and design and using similar mixing systems.

1:2:6 Limitations and Issues

The choice of bedding used for livestock can have a detrimental effect on an AD system (Karim et al., 2008). The use of sand can be particularly problematic due to the resultant accumulation of silt and increased wear and tear on components with no biogas gain (Al-Seadi, 2001). Various techniques to remove sand from the process have been attempted but the approach preferred by most plant manufacturers is to use an alternative digester-friendly bedding material. Meanwhile, the choice of feedstock, type of process and adopted bio-degradation pathway will define the quantity of unwanted products such as CO_2 and H_2S. The former is relatively harmless if included in a combusted biogas mix but high levels of H_2S can damage an internal combustion engine (Deublein & Steinhauser, 2011).

1:3 Opportunities for Dairy Farm-scale AD

1:3:1 Current Position

Dairy manure is an abundant farm waste that can pose handling, storage, disposal and environmental challenges. However, effective slurry management can turn a farm waste into a valuable renewable energy source and provide essential nutrients for agriculture (Holm-Nielsen et al., 2009). In 2013, there were 50 farm-based AD plants reported as operating in the UK (Waste and Resources Action Programme (WRAP), 2014). In June 2013, cow numbers in the UK totalled 1.78 million, with the average dairy herd consisting of 123 lactating cows plus heifers and calves (DairyCo, 2014). Latest figures released by DairyCo quote 9,914 UK milk producing farms at the beginning of 2015 (DairyCo, 2015) so the potential for AD is significant.

However, digesters tend to be designed to process complex waste streams on a much larger scale that that required by most UK farms. Consequently, the wide range of proven AD solutions available in the marketplace are often inappropriate and too costly for small-scale farm operations (Royal Agricultural Society of England, 2011). DEFRA is keen to encourage the farming industry to embrace the technology, particularly small-scale AD (DEFRA, 2013). However, whilst the Government introduces policy and financial incentives to encourage the uptake of the technology, providers must also be encouraged to design systems that are attractive to farmers by being:

- Modular.
- Easy to integrate into the farm operation.
- Automated to minimise operator interaction.
- Inexpensive enough to not require the importing of waste to be cost-effective.
- Preferably constructed using equipment and components familiar to farmers.

1:3:2 Benefits

The benefits of embracing AD on farms include (Zglobisz et al., 2010):

- De-centralised energy generation from renewable sources.
- Assisting in the abatement of GHG emissions.
- Increasing energy security, nationally and locally.
- Production of low impact fertiliser.
- Facilitating adherence to the EU policy principles of proximity of treatment, self-sufficiency in resource use and in waste disposal.

Meanwhile, financial savings can be realised by:

- Minimising reliance on expensive imported energy.
- Avoiding fluctuating energy prices.
- Reduced dependence on inorganic fertiliser.

1:3:3 Barriers

The greatest sensitivities for farm-scale AD are the capital expenditure (CAPEX) of the plant and the cost of the feedstock (National Non-Food Crop Centre, 2011). The latter can be high if energy crops are imported or minimal if restricted to livestock slurry. Energy crops have higher embedded energy potential whereas manure has relatively low energy potential per unit mass which is why manure is relatively costly to process per unit volume (Atandi & Rahman, 2012). Moreover, on many farms large volumes of slurry are often only available for the 6 to 7 cooler months of the year as cattle are grazed during warmer weather (Royal Agricultural Society of England, 2011). High fuel prices also encourages farmers to grow their own animal feed, thereby reducing the land available to cultivate alternative high energy crops that could increase biogas yield through co-digestion (Royal Agricultural Society of England, 2011). Initiating biogas production must also take into account social acceptability to the local community (Mezzullo, 2010).

1:3:4 Importance of Appropriate System Design

Digester design has a significant impact on system performance (Nasir et al., 2012). To be fit for purpose a digester must (Ward et al., 2008):

- Maximise the degradation of volatile solids (VS) [within the design HRT].
- Provide a physical environment to optimise CH_4 production (including adequately mixing).
- Accommodate a high and sustainable OLR.
- Minimise HRT to reduce reactor volume.

Internationally, the last decade has seen impressive advances in terms of maturation of biogas technologies and improvements in economic sustainability for small and large biogas plants (Holm-Nielsen et al., 2009). Techniques vary from basic passive biogas capture from slurry lagoons to the common CSTR. Hybrid reactors such as the up-flow anaerobic sludge blanket (UASB) and the anaerobic membrane bioreactor (AMB) offer high rates of bio-degradation and hence low HRT potential. The UASB is by far the most popular AD technique in use as approximately 80 percent of the waste water treatments of the world are serviced by them (Abbasi & Abbasi, 2012). Each technique offers particular benefits but also limitations, particularly when the rheology of the intended feedstock is considered. Examples of extremes include the UASB which is particularly effective at processing low %TS fluids as found in the sewage and textile industries where the majority of solids are removed in the form of sludge or particulate debris prior to anaerobic processing. By doing so, the substrate is generally well below 5%TS content and therefore demonstrates Newtonian fluid characteristics (Achkari-Begdouri & Goodrich, 1992). Conversely, the processing of energy crops such as maize augmented with cow slurry has a much higher solids content with the substrate adopting more non-Newtonian characteristics as the %TS increases. The CSTR tends to be the preferred method in such circumstances, as demonstrated by countries such as Germany and Denmark. That said, hybrid digesters have been reported as successfully processing animal slurry with impressive CH_4 yields but the slurry has usually been sieved/screened prior to entering the digester as in the case of Demirer & Chen (2005). Generally, conventional high-rate digesters do not process animal manures with high %TS very effectively (Yilmaz & Demirer, 2008). Due to the nature of dairy farm operations and the quantities of slurry generated on a daily basis, intermittently fed (fed-batch) systems are more common.

1:3:5 System Optimisation

Many AD systems are simple in design yet operate below their design OLR to ensure stable performance is maintained (Nasir et al., 2012). A comparison of 13 agricultural biogas plants across Europe found that process efficiency varied with some plants showing considerable capacity to improve performance (EU-Agrobiogas, 2008). Main areas of concern included the high levels of parasitic energy demanded by some processes, the general lack of effective monitoring on which control relies and the under-utilisation of electrical capacity often due to the over-sizing of CHP units. Splitting the digestion process by configuring 2 or more digesters in series has shown positive results (Kaparaju et al., 2009; Boe & Angelidaki, 2009) as adopting the method allows the specific and sometimes conflicting needs of each process to be attended (Ward et al., 2008). However, increasing the number of digesters can increase costs. Optimising the process for production rate rather than overall yield may provide an opportunity to reduce CAPEX as the approach may increase the viability of reducing HRT and hence digester volume and cost (Bensmann et al., 2013). Such an approach may also provide opportunities to reduce operational expenditure (OPEX) associated with mixing. CAPEX and OPEX may also be effected by the rheology of the substrate to be mixed as the apparent viscosity of the fluid will influence the rating and size of mechanical components required to induce flow and the parasitic energy required to operate them. Hence, system sizing, design and optimisation are key to financial viability.

1:3:6 System Selection

AD projects are generally funded using revenue realised from the products of the process, the main product being energy derived from the biogas produced. Net energy gain of the system will therefore be key to financial viability so selecting an appropriate system and optimising the process is essential. The likelihood of this being achieved is increased if the system is matched to the intended feedstock. To do so requires an understanding of how the feedstock will respond to the physical mechanisms (such as mixing) on which process success relies.

1:4 Technical Challenges of AD System Design and Operation on Dairy Farms

1:4:1 The Substrate

Cow slurry is “a biological suspension of particles having irregular shapes and various sizes that change with time and environmental conditions” (Karim et al., 2007). Karim, Hoffmann, et al. (2005a) identified slurry ‘as excreted’ to consist of approximately 12%TS and 10.5%VS. Such wastes exhibit strong non-Newtonian characteristics (Achkari-Begdouri & Goodrich, 1992) but slurry can vary, depending on the amount of forage in the diet of the livestock (Wu, 2012a) which will also influence the biogas potential of the slurry. Wu defined manure slurry as being non-Newtonian above 2.5%TS.

1:4:1:1 Rheology

Rheology is the study of deformation and flow of materials when forces are applied (Brambilla et al., 2013). When a fluid is subjected to a shear force that encourages molecules to move in relation to one another, shear stress is induced within the fluid. The relationship (ratio) between the shear stress (τ) induced in a fluid when a shear rate (ý) is applied quantifies the fluid's viscosity (μ) or resistance to motion (Doran, 2013).

$$\mu = \frac{\tau}{\acute{y}} \qquad \text{Equation 1}$$

Viscosity is the principal parameter that characterises the flow properties of fluids such as liquids, semi-solids, gases and even solids (Howard, 1991). As viscosity increases, mass transfer and distribution of heat within a fluid reduces as the fluid's opposition to movement increases. In fermentation fluids, viscosity is [further] affected by the presence of cells, substrates, products and gas (Doran, 2013). Viscosity is also referred to as dynamic viscosity.

1:4:1:2 Newtonian Flow

A fluid is defined as Newtonian when the ratio between shear stress and shear rate remains linear when different shear rates are applied. The gradient of the linear relationship represents the viscosity of the fluid (Figure 1). A fluid that requires a shear stress to be achieved before flow is induced (the yield stress point) is called a Bingham plastic (Figure 2) (Howard, 1991). The size and shape of embedded particulates can influence the rheological characteristics of a fluid as observed by Erdoğan et al. (2008) when analysing cement suspensions.

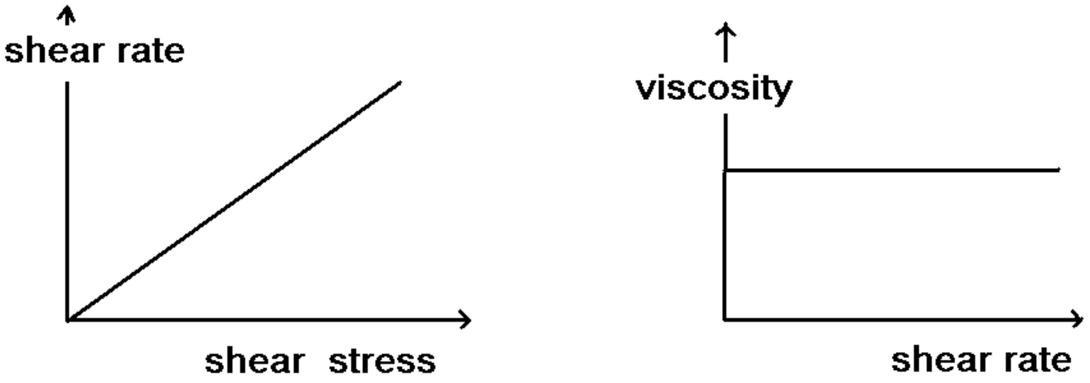


Figure 1 – Relationship between shear rate, shear stress and viscosity in Newtonian fluids

1:4:1:3 Non-Newtonian Flow

The vast majority of fluids do not exhibit a constant shear rate:shear stress ratio so are referred to as non-Newtonian (Brookfield, 1999). Cross (1964) succinctly captured the property declaring “flocculation behaviour provides a qualitative explanation of pseudo-plastic flow. If a system contains elements which are capable of assuming some structural formation which is wholly or partially disrupted by shear one may expect a corresponding viscosity/shear dependency”. An increasing gradient on a graphical representation of the ratio indicates an increasing viscosity as shear rate is increased. These fluids are categorised as dilatant or shear thickening (rheopectic) (Figure 2). Conversely, when the viscosity of a fluid decreases as a result of an increase in applied shear rate the fluid is considered pseudo-plastic or shear-thinning. Past research has characterised numerous non-Newtonian flow models (Seyssiecq et al., 2003; Eshtiaghi et al., 2012) with the Power Law and Herschel-Bulkley models being particular relevant to this research.

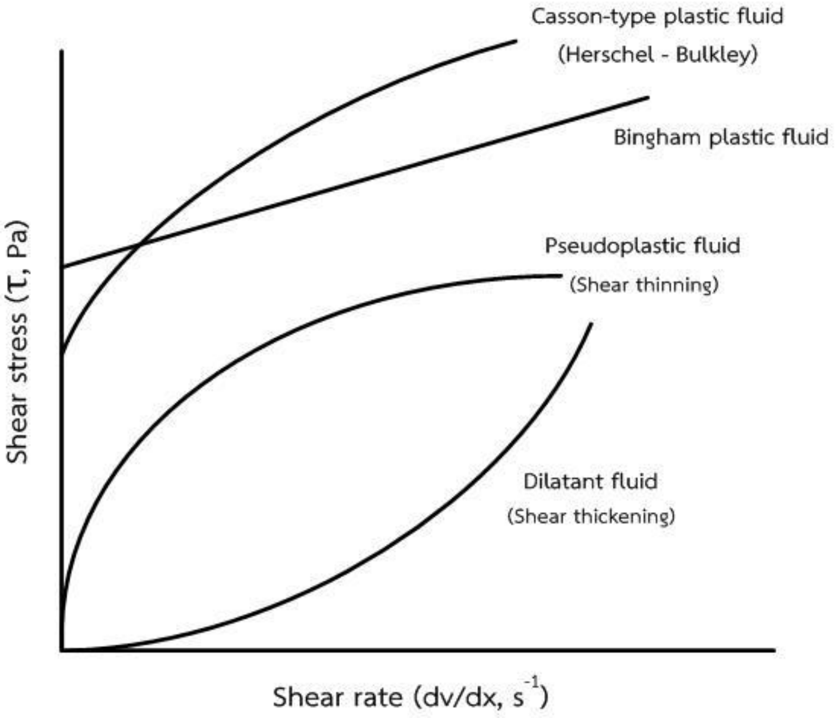


Figure 2 – Relationship between shear stress and shear rate in non-Newtonian fluids

1:4:1:4 Power Law Model

The power-law model offers a generalised basis for shear-thinning non-Newtonian flow:

$$\tau = K \cdot (\acute{y})^n \qquad \text{Equation 2}$$

where τ is the shear stress, K is the rheological consistency index, $\acute{y}$ is the applied shear rate and n is the power-law or flow behavioural index. K is reported as specific to the fluid whereas n can be influenced by other factors such as temperature (Achkari-Begdouri & Goodrich, 1992). An n-value of 1 represents a Newtonian fluid. The fluid becomes more pseudo-plastic (shear-thinning) as the n-value decreases (Eshtiaghi et al., 2012). An n-value above 1 indicates a dilatant (shear-thickening) fluid. The use of such models allow complex rheological characterisation of fluids whose rheological properties cannot be related to single value of viscosity (Baroutian et al., 2013). However, the usefulness and applicability of the technique reduces as the range of shear rates to which the values refer widens and the associated accuracy reduces (Bongenaar et al., 1973). Chen (1986) assessed that the power law model could only be applied to low %TS slurries. In a review of the art of rheology, Seyssiecq et al. (2003) concluded that the choice of rheological model was highly dependent on experimental conditions such as the applied shear rate range and the type of sludge. Also, sample handling and storage prior to characterisation had a significant impact on sludge rheology. If enough shear rate is applied viscosity can eventually reach a point where maximum shear thinning is achieved which is referred to as limit viscosity (Pevere et al., 2006). Limit viscosity is strongly influenced by %TS (Tixier et al., 2003).

1:4:1:5 Herschel-Bulkley Model

The Herschel–Bulkley flow model describes a shear-thinning fluid that requires a yield stress to be reached before flow is induced. The model is described as:

$$\tau = \tau_y + K \cdot (\acute{y})^n \qquad \text{Equation 3}$$

τ_y represents the yield stress necessary to induce fluid movement and tends to increase as %TS increases (Seyssiecq et al., 2003; Baroutian et al., 2013). Mbaye et al. (2014) found that agricultural waste demonstrated power law characteristics below 10%TS and Herschel-Bulkley above. Particle interaction may explain the introduction of a yield point at which the weak solid state of the fluid experiences structural breakdown, allowing the fluid to flow. Removal of the shear rate then allows the particles to re-associate over time (Eshtiaghi et al., 2012). These characteristics are similar to those observed in primary sewage sludge (Markis et al., 2014; Baroutian et al., 2013). A fluid that experiences shear-thinning as a result of a constant shear rate being applied over a prolonged period is known as thixotropic. The structure of thixotropic fluids progressively breaks down on shearing and slowly rebuilds at rest in a reversible process (Barnes, 1997; Baudez, 2006). Indeed, understanding the thixotropic nature of a fluid is essential if mixing intermittently. As the viscosity of a non-Newtonian fluid is always directly related to a specific shear rate being applied, the term apparent viscosity (μ_a) is used to distinguish the fluid as non-Newtonian. Apparent viscosity can be estimated using the formula:

$$\mu_a = \mathrm{K} \cdot (\acute{y})^{n-1} \qquad \text{Equation 4}$$

It is clear that if processes that involve non-Newtonian fluids are to be optimised rheological characterisation of the fluids involved is essential. Only by doing so can the structure and inter-particle interactions within the microbial communities/biomass that make up bacterial flocs be understood and used to inform process design (Seyssiecq et al., 2003). The review of rheological analysis techniques by Seyssiecq et al. (2003) further explains how a fluid can also be characterised by the complex modulus which can in turn be divided into viscous forces and elastic components. They are used to describe factors that influence strain within a fluid prior to yielding and subsequent flow. As this study concentrates on the rheology of fluids undergoing mixing and therefore already flowing the complex modulus of cow slurry is not considered further as knowing the yield point is sufficient.

1:4:2 Implications of Rheology of Cow Slurry as an AD Feedstock

The characteristics of a fluid can have a substantial impact when attempts are made to manipulate fluid flow. Hence, knowledge of the rheology of AD wastes is essential to inform the design of the processes needed to handle them (Mbaye et al., 2014), a design challenge that is increased if the fluid in question is non-Newtonian. Rheological behaviour [of a fluid] can be complex and affected by multiple parameters such as concentration, shape, density and surface properties (Nguyen et al., 2013). If the fluid is shear-thinning, the viscous forces governing the rheology of the substrate are particularly sensitive to shear rate distribution of a mixing configuration (Sossa-echeverria & Taghipour, 2014). Complexity increases further if continuous-flow mixing is intended (Patel et al., 2014). Continuous mixing of Newtonian fluid can also be imperfect, particularly at scale-up (Deublein & Steinhauser, 2011) so empirical evidence is often relied upon to minimise risk of failure. The continuous flow mixing of Newtonian fluids is well documented; however, documented research into effects on the flow patterns of Herschel-Bulkley fluids has been reported as limited by some (Patel et al., 2014) and extensive by others (Pevere et al., 2006). Pevere's (2006) analysis of sieved granular sludge sheared at 500s^{-1} highlighted the significance that TS had on the rheology of a substrate. Hence, any reduction in solids content by microbial metabolism will directly influence the rheology of the host substrate. This in turn could influence the shear stress within the substrate, the effectiveness of mixing and hence digester performance.

Dairy farm livestock slurries are shear-thinning, thixotropic fluids. When rested, they recover their original state in a period specific to the fluid and temperature

(Plochl et al., 2009). Such fluids tend to consist of flocs of relatively solid matter suspended in the fluid. A typical slurry excreted by a lactating cow is approximately 12.5%TS (Roos, 2007). Hashimoto & Chen (1976) found that when flocculated slurry was subjected to shear forces. The fraction of the slurry with the larger flocs required higher shear force to induce movement than the un-flocculated fraction. This was thought to be due to higher levels of internal friction being experienced in the flocculated slurry resulting in lower mechanical energy dissipation. Predicting the shear stress induced in the fluid was found to be challenging as floc volume was difficult to estimate. In spite of the reported rheological similarities between cow slurry and sewage sludge, particularly with the latter attracting global research attention, wastewater sludge is still regarded as unpredictable and is scientifically poorly understood (Baudez et al., 2011). Meanwhile, Seyssiecq et al. (2003) observed an “important lack of unity in literature” that characterises the hydrodynamics of fluids in relation to process optimisation which can reduce the value of such research. Interestingly, Eshtiaghi et al. (2012) questioned the value of sludge rheology as reference material for industrial process design due to the tendency of rheological characteristics to change through ageing and microbial activity. Instead, the value of stable substitute fluids was stressed. One could argue that both have a part to play in the design, sizing and operating of equipment. Specific parameters such as apparent viscosity may change but knowledge of the boundaries of the metrics of that property is essential to avoid over/under-specification of system components. For example, rheological properties of the fluid will determine the size, type and power rating of a slurry pump whereas apparent viscosity could be used as a process control parameter (El-Mashad et al., 2005).

1:4:3 Microbial Community Dynamics

Maintaining microbial communities in a digester is important to process performance and treatment capacity (Zheng et al., 2012) and the range of microbial types involved in the process are extensive (Krakat et al., 2010). Microbes responsible for AD are generally classified as hydrolytic, fermentative, acetogenic and methanogenic (Li et al., 2011). Physical digester characteristics such as velocity distribution (the velocity of a substrate in relation to geographical location within a digester) and turbulence intensity within the substrate can significantly affect the composition of microbial communities and hence biomass activity. This will in turn effect the rate of biodegradation of the host substrate and hence substrate rheology (Pevere et al., 2006). Microbial composition may be governed by the type of substrate as well as process temperature (Sundberg et al., 2013), although temperature is commonly regarded as the most important physical condition for bacterial growth (Wu, 2012b). Bio-activities, such as extracellular polymeric substance (EPS) production and environmental adaptation by bacteria should also be considered dominant factors affecting biomass resilience rather than considering hydrodynamic forces in isolation. EPS reduces negative charge, regulates hydrophobicity of cell structures and increases the availability of electrostatic binding sites, thereby reducing electrostatic repulsion (Schmidt & Ahring, 1993; Siren & Kosapac, 1993). However, a review by Mahmoud et al. (2003) reported that the major components of EPS (protein and carbohydrates) varied depending on process and substrate.

1:4:3:1 Community Symbiosis

Methanogenesis is a typical terminal electron-accepting (reduction) metabolic activity that relies on syntrophic relationships between partner bacteria with neither player able to operate without the other (Schink, 1997). The degree of mutual dependence varies but latter members of the food chain (methanogenic archaea) always depend on the products of earlier ones before they can perform. Methanogenesis is the least exergonic of all anaerobic respirations which may be the reason why this is the last step to occur after the other electron acceptors have been reduced. Also, methanogens take a relatively long time to reproduce compared to hydrolytic and acidogenic bacteria (Deublein & Steinhauser, 2011). Deublein & Steinhauser (2011) identified H_2 partial pressure as being essential to the biological reaction so a narrow special symbiosis is required between H_2-producing and H_2-consuming bacteria, the acetogenic conversion of H_2 and CO_2 to acetic acid being a good example. However, too much H_2 surrounding acetogenic bacteria can deprive them access to suitable feedstock and stop them metabolising. Ghanimeh et al. (2012) made a similar conclusion when attributing inadequate hydrogenotrophic diversity to poor mixing during a comparison of start-up performance of mixed and unmixed digesters fed on MSW. More research is required to better understand these symbiotic relationships and the microbial community dynamics that they influence so that existing AD models may be improved (Appels et al., 2011).

Methanogen characteristics and requirements vary (McMahon et al., 2001). Acetoclasts such as *Methanosarcina* are generalists that also consume CO_2 and H_2. They enjoy high rates of growth and prefer higher acetate concentrations. They perform better when propionate turnover is high. Meanwhile, specialists like *Methanosaeata concilli* have a high affinity to acetate giving them a competitive advantage in stable environments with low levels of acetate. When considering H_2 consumers, high populations of hydrogenotrophic methanogens such as *Methanomicrobiales, Methanobacteriacea* and *S. wolinii* allow syntrophic VFA oxidisers to grow and consume intermediates such as propionate more quickly. McMahon found that as the AD process de-stabilised and digester acidity increased, *Methanosarcina* and *Methanobacteriacea* populations increased substantially. This basic comparison offers a simple insight into the complexities of methanogen co-existence.

Successful microbial metabolism may also be influenced by location. When researching gas metabolism in lake sediments and sewage sludge Conrad et al. (1985) concluded that the bulk of interspecies H_2-transfer occurred between juxtapositioned microbial associations within flocs and consortia. In short, methanogens were regarded as more likely to take electrons from a local donor than from a H_2 pool, [kinetically favourable circumstances that we aim for as juxtapositioning is difficult to manage]. Batstone et al. (2004) observed that acetotrophic methanogens and syntrophic acetogenic clusters occupied the same region of a UASB digester rather than forming distinct layers. McMahon et al. (2001) argued that the stability of the AD process was reliant on the balanced co-existence of hydrolytic-fermentative bacteria, proton-reducing bacteria, hydrogenotrophic methanogens and acetoclastic methanogens. Kim et al. (2002) suggested that non-mixing maintained microbial consortia proximity and produced more biogas. Madigan et al. (2012) also stresses the importance of microbial proximity in a symbiotic relationship.

1:4:3:2 Microbial Response to Shear Stress

Although the application of shear force is necessary to mix, high levels of shear stress induced by inappropriate mixing technique and intensity can disrupt spatial associations between syntrophic microbes within a consortia thereby affecting their function, effectiveness and productivity (Stroot et al., 2001). Whilst evaluating microbial population dynamics when digesting MSW and sewage sludge McMahon et al. (2001) concluded that “mixing appeared to inhibit the syntrophic oxidation of VFAs by disrupting the spatial juxtaposition of syntrophic bacteria and their methanogen partners”. Intensive mixing could disrupt the syntrophic relationship thereby interfering with any balance in microbial activity resulting in lower levels of CH_4 production. Indeed, Liu & Tay (2002) argued that hydrodynamic shear force played a crucial role in the formation of biofilm and granules. Mohle et al. (2007) agreed but also noted that biomass formation depended on the concentration of the substrate feedstock as well as the shear force experienced at the biofilm surface.

Biomass morphology and the dynamics of biomass formation can differ significantly in response to changes in applied shear stress (Park et al., 2011). Under ideal conditions where optimum stress is applied an irregular EPS network structure was found to provide a mechanical shield against high-pressure fluid flow. When analysing waste water sludge, Ren et al. (2009) observed that the size, shape, structure and density of biomass granules could be limited by the rate of microbial population/cell growth and biomass loss due to shear stress experienced at the granule surface. Ren observed that shear stress experienced by larger granules was greater than that experienced by smaller ones with similar biomass density. As a result, biomass loss increased as granules increased in size. Also, granules subjected to lower levels of shear stress were less dense and hence more fragile. Rochex et al. (2008) called the process biofilm maturation and credited shear stress with maintaining young biofilm. But shear stress was also found to affect microbial community composition with biodiversity decreasing as shear stress increased. Biomass communities in slurry also experience high levels of shear stress although there is no evidence that the communities form granules. Nevertheless, if shear stress affects microbial kinetics in whatever form, the metric could be used to influence, manage and control the composition of a microbial community. Indeed, increasing the elasticity of communities using conditioning is another means of improving community resilience to stress (Wang et al., 2011). Tian et al. (2013) observed that a non-agitated digester had a higher microbial diversity with several methanogen species being evident whereas the agitated digester favoured *Methanosaeta*-related methanogens. Hoffmann et al. (2008) on the other hand observed an increase in *Methanosarcina spp* population in response to increasing shear stress. Tian et al. (2014) later confirmed that induced shear stress through agitation could influence microbial composition. Levels of methanogens and syntrophic bacteria were found to be much lower in an agitated digester whereas the bacterial genera *Acetanaerobacterium* and *Ruminococcus* were relatively abundant. The evidence therefore suggests that shear stress can have negative and positive effects on microbial diversity. In turn, microbial diversity will influence the range and quantity of the products of metabolism and hence process stability (Madigan et al., 2012).

The way shear stress is applied has also been observed to influence biomass robustness. Wu et al. (2012) found that microbial granular communities subjected to a range of shear stress levels were more resilient to increases in shear rate if the shear rate was introduced in large steps between long dormant periods (10 days), rather than smaller increments every day yet totalling the same increase overall. Allowing adequate recovery time between increases in shear rate was regarded as essential to microbial granular strength, allowing bio-activities such as EPS replacement. Although the research related to low %TS UASB operations, the shear rate thresholds identified provides a guideline for future research. Hence, the effects of resting when intermittently mixing is worthy of further investigation.

1:4:3:3 Metabolic Stability

A history of poor digester performance can promote the establishment of microbial communities better equipped to deal with extreme organic overload conditions (McMahon et al., 2004). This may be because good performing digesters enjoy stability resulting in low levels of microbial populations that are key to process recovery after trauma. Therefore, microbial diversity should be encouraged in good digesters to aid process recovery should trauma occur.

1:4:3:4 Biomass Washout

Digestate withdrawal will invariably result in biomass being inadvertently removed, a process termed biomass washout. Digesters in series can reduce the potential for washout. The enhanced hydrodynamics relied on by high-rate digesters to accelerate mass transfer and improve the processing efficiency can cause biomass washout due to limited granular settling opportunities, if too high and introduced too often (Wu et al., 2012). Re-circulation of effluent can re-introduce biomass into the process thereby increasing SRT, particularly where biofilm fixing techniques are not appropriate (Yadvika et al., 2004). Biomass washout also increases the VS content and hence the rheology and handling characteristics of the digestate as solids content will increase. Meanwhile the biogas potential of the remaining substrate is reduced. Biomass washout can be reduced by combining techniques such as appropriate positioning of the digestate outlet and timely/appropriate mixing (Doran, 2013).

1:4:3:5 Intermittent Feeding (Fed-Batch)

Intermittent feeding and digestate removal can result in a high turnover of substrate embedded with nutrients as well as biomass. This is referred to as short-circuiting and occurs when nutrients are allowed to exit the digester before coming into contact with the biomass and being metabolised. Hence, HRT determines the duration of microbial digestion (Wu, 2012b). Residence time distribution (RTD) is an effective technique for identifying short-circuiting within a digester (Olivet et al., 2005). Keeping mixing to a minimum can reduce short-circuiting (Ward et al., 2008) but can also reduce homogeneity on which the process relies. Poor homogeneity can also result in extensive short-circuiting of feedstock before bio-degradation of the embedded VS can occur (Monteith & Stephenson, 1981) affecting system process.

1:5 Mixing

1:5:1 Fundamentals

Mixing is one of the most important operations in process technology (Zlokarnik, 2008), the key objective of which is to maximise the degree of homogeneity of a property such as concentration, viscosity, colour and temperature (Patel et al., 2014). Doran (2013) termed the 3 physical processes that capture the stages required for effective mixing as:

- Distribution (macro-mixing).
- Dispersion (micro-mixing).
- Diffusion (classified as macro-mixing or micro-mixing depending on the scale of the fluid motion).

Micro-mixing cannot exist without macro-mixing as the latter is essential to overcome substrate segregation within the fluid (Cheng et al., 2012). Furthermore, when mixing multi-phase substrates variations in density, particle size, gas flow rate, and aggregation will affect success.

1:5:2 Laminar Versus Turbulent Flow

For laminar flows, a Reynolds number (Re_i) of less than 10 is required at the impeller [or point of mixing]; for turbulent flows, the Re_i must generally be greater than 10^4 (Doran, 2013). Laminar flow is associated with an orderly arrangement of velocity vectors parallel to the tank wall, whereas turbulent flow is regarded as chaotic (Wu, 2012a). Generally, turbulent flow is required to effectively mix (Brambilla et al., 2013) although techniques such as those used in oscillatory baffle reactors (OBR) manipulate laminar flow through design to mix the internal fluid (Ni et al., 2003; Stonestreet & Harvey, 2002). Transition from laminar to turbulent flow requires a higher Re_i as viscosity increases (Pinho & Whitelaw, 1990).

1:5:3 The Need to Mix

Rising biogas and thermal convection due to heating of the substrate can provide some degree of mixing (Fleming, 2002) but is not sufficient to ensure adequate mixing [at full scale] (Appels et al., 2008). Incomplete mixing can jeopardise the efficiency of the treatment process (Bello-mendoza & Sharratt, 1998) and result in large dead zones forming within which the access to new feedstock is limited (Monteith & Stephenson, 1981). Deublein & Steinhauser (2011) succinctly captured the requirements of appropriate mixing in AD, as follows:

- Individual microorganisms should be given ample opportunity to metabolise fresh feedstock. Benbelkacem et al. (2013) and Gómez et al. (2006) agreed.
- Products of metabolism need to be distributed without disrupting microbial symbiosis.
- Biogas must be removed.
- Temperature gradients within the substrate must be minimised.
- Floating/sinking layers must be avoided (Rico et al., 2011).
- Energy consumption should be minimised.
- Short-circuiting should be prevented.

Mixing also aids the release of trapped H_2 from the liquid phase to the gas headspace (Clark et al., 2012). Mixing can also help reduce particle size [and therefore microbial access to nutrients] but more research is required to better understand the effects of mixing intensity and duration as literature can be contradictory (Karim et al., 2005a). Unmixed digesters, particularly plug-flow, can experience reduced pH due to the accumulation of organic acids caused by the concentration of new feedstock loading at the front end of the digester at high OLR (Kobayashi & Li, 2011). Mixing is also essential to breaking up crusts and re-suspending solids before emptying storage tanks and channels (Schofield, 1984).

1:5:4 When to Mix

When reviewing the effects of mixing on AD, Lindmark et al. (2014) concluded that a lower degree of mixing can be beneficial at start-up to encourage methanogenic biomass growth; McMahon et al. (2004) agreed. Mixing of high %TS substrates is particularly necessary for efficient convective mass [and heat] transfer, to homogenise soluble compounds and to prevent sedimentation and floating layers caused by differing densities (Benbelkacem et al., 2013). Indeed, biogas production can be impaired in substrates above 12%TS (Deublein & Steinhauser, 2011). Karim, Hoffmann, et al. (2005a) agreed that mixing and the mode of mixing became more influential as %TS increased but also noted that the action of mixing was not beneficial during start-up. Abbassi-Guendouz et al. (2012) analysed fluids up to 30%TS and confirmed a reduction in liquid/gas mass transfer when mixing as %TS increased.

1:5:5 Benefits of Mixing on Biogas Production

Biogas (and H_2) yield increases when digesters are mixed (Clark et al., 2012). When comparing mesophilic and thermophilic processes using 4 lab-scale digester configurations Kim et al. (2002) found that non-mixed digesters produced the most biogas at both temperatures. Conversely, Ghanimeh et al. (2012) found that ‘gentle’ mixing of a thermophilic digester fed on MSW produced 20 percent more biogas than a similar but unmixed digester. Mixing also improved treatment efficiency and process stability whilst reducing the start-up period; a 20 percent increase in OLR was also accommodated. Karim, Hoffmann, et al. (2005a) compared 5, 10 and 15%TS cow slurries in unmixed and gas/substrate/impeller mixed lab-scale digesters. Start-up was found to be quicker in the unmixed digester but long-term biogas yields were lower. Moreover, the role of mixing had little statistical significance at 5%TS (w/w) but increased in importance as %TS increased. However, mixing is also known to disturb microorganisms thus ultimately reducing gas output (Deublein & Steinhauser, 2011). Sindall et al. (2013) suggested that there is a velocity gradient threshold within a digester above which mixing becomes counter-productive and biogas production falls. Wu (2012b) used CFD modelling to demonstrate that “CH_4 yield remains almost unchanged while energy efficiency decreases with increasing mixing power in a complete-mix digester”. On reviewing previous CFD research Wu also concluded that no inherent relationship between mixing and CH_4 yield had been revealed. Tian et al. (2013) reported lower yield and rates of production using mixed digesters than that produced by unmixed. Others (Hoffmann et al., 2008) observed no difference. Such confliction may be due to variations in the process temperatures, agitation method, mixing intensities used or differences between batch and intermittent feeding techniques.

1:5:6 Mixing Techniques

Mixing techniques common to AD include mechanical mixing and the re-circulation of substrate or biogas in the digester. Each have their benefits and drawbacks so the selection of appropriate agitation equipment is fundamental to ensuring mass and heat transfer and the disruption of agglomerated particles/flocs required of a bio-degradation process (Nguyen et al., 2013). In some cases, mixing highly viscous fluids may not be achievable for mechanical and/or economic reasons (Doran, 2013). Although impellers are effective and often reported as demanding the lowest energy of all mixing techniques (Paul et al., 2004), internal fittings and equipment can make the maintenance [of mechanically mixed digesters] difficult during digester operation (Karim et al., 2005c). As an alternative, re-circulation mixing equipment can be mounted external to the digester.

1:5:7 Selecting a Mixing Technique

When comparing 5, 10 and 15%TS cow slurries in unmixed and gas/substrate/impeller mixed lab-scale digesters, Karim, Hoffmann, et al. (2005a) observed that substrate re-circulation of 10%TS slurry produced 29 percent more biogas than an unmixed digester, whereas mixing by impeller achieved 22 percent and gas re-circulation 15 percent. Gas pipework experienced fouling at 15%TS, although this may not be a factor on scale-up. Whatever the constraints, the choice of mixing technique must be matched to the demands of the rheology of the substrate so that kinetic energy can be employed effectively and economically to influence the movement and hence molecular interaction of the fluid. This is particularly relevant if the fluid is non-Newtonian. However, care must be taken when scaling up as lab-scale results do not always directly translate, particularly where mixing time and power consumption are concerned (Doran, 2013). Indeed, a major part of published research about mixing in AD relates to lab-scale experiments the results of which should be approached with caution until demonstrated at full-scale.

1:5:8 Mixing Intensity (Shear Rate)

Mixing intensity decreases as %TS is increased (Wu, 2010). Kaparaju et al. (2008) demonstrated that high levels of agitation can be detrimental when processing cow manure anaerobically as CH_4 production may not only be reduced but also delayed. Vavilin & Angelidaki (2005) observed that when the methanogenesis stage of an AD process was the rate-limiting step a gentle mixing regime was beneficial for CH_4 production and special methanogenic zones could develop [around the digester]. However, where hydrolysis was the rate-limiting step, an intense mixing regime resulted in the highest bio-degradation. Furthermore, intensive mixing when OLR was high resulted in acidification but at low OLR mixing intensity had no significant effect on the process. But if digester stability and in turn process efficiency are directly affected by mixing intensity (Stroot et al., 2001), biogas production will in turn be directly influenced by the degree of mixing success. By accepting that the mixing intensity (shear rate) and the length of time that shear rate is applied by an effective mixing system defines the degree of mixing achieved, then shear rate can be regarded as a tool to control the biodegradation process.

1:5:9 Mixing Period and Intermittency

Time to achieve homogeneity of a substrate is more critical in some industries than in others (Doran, 2013). Interrupting hydrodynamic flow in an AD substrate (by resting the fluid) can increase a microbial community’s resilience to increases in shear stress (Wu et al., 2012). Resting can also provide time for granular cohesion to strengthen thereby increasing opportunities for symbiosis between microbes whilst reducing the chance of washout by hydrodynamic forces. Intermittent mixing has been found to produce the same amount of gas and even improve gas production compared to a continuously mixed system while decreasing the maintenance and energy demand of the process (Lindmark et al., 2014). Rico et al. (2011) agreed that continuous mixing may not improve biogas production. The risk of foaming can also be lowered by reducing the mixing period although mixing itself may not be a primary cause of foaming (Subramanian & Pagilla, 2014).

1:5:10 Parasitic Energy Demand of Mixing

The efficiency of a mixing process can be determined by the power consumed and the time taken to mix, 2 factors that define homogenisation energy (Ochieng & Onyango, 2008). Excessive mixing increases power consumption, deteriorating the energy balance (Deublein & Steinhauser, 2011). Generally, energy required to mix cow slurry to a specific degree of homogeneity in a given time depends on the manure type and %TS with thicker slurries requiring more mixing energy (Hashimoto & Chen, 1976; Wu, 2012a). However, mixing substrates above 12%TS can cause undue wear and tear on pumping systems (IBBK, 2008) with attendant cost implications.

The average power consumption required to mix industrial bio-reactors ranges from 10kWm^{-3} for small vessels (approximately 0.1m^{3}) to between 1.1-2kWm^{-3} for larger vessels (approximately 100m^{3}) (Doran, 2013). Karim, Hoffmann, et al. (2005b) criticised the lack of availability of clear information and threshold limits for mixing, citing the US Environmental Protection Agency’s recommendation of a maximum power input of 8Wm^{-3} as the only available guide. Predicting the power required to mix non-Newtonian fluids is difficult, particularly if the fluid includes a gaseous volume. Substrate re-circulation can require high levels of energy to achieve the necessary flow rates in high %TS fluids (circa 12%TS) (Appels et al., 2008). Indeed, whilst CFD modelling substrate re-circulation mixing Wu & Chen (2007) found that when scaling up, power input to maintain fluid flow patterns increased logarithmically. Moreover, even a small drop in mixing efficiency can lead to the need for substantially larger and more costly equipment (Bello-mendoza & Sharratt, 1998). Care should therefore be applied when extrapolating the net energy production of a system when scaling up as although the increase in gas yield may be linear the additional power required to mix will not (Doran, 2013).

1:5:11 Factors Affecting Mixing

Predicting the effects of fluid flow and mixing when scaling-up from bench-scale to commercial scale can be inherently difficult (Cheng et al., 2012) as local hydrodynamic characteristics in industrial vessels can be very different from small-scale versions. Rheological properties of substrates will also complicate scale-up (Seyssiecq et al., 2003). System overdesign to address mixing shortfalls can result in excessive CAPEX that is not outweighed by corresponding decreases on OPEX (Monteith & Stephenson, 1981). Also, mixing above 8%TS can experience difficulties in mass flow, scum formation and dead zones (Rivard et al., 1989).

Using xanthan gum, Patel demonstrated that increases in fluid stress and flow rate can have a significant effect on channelling, re-circulation and dead zoning (Patel et al., 2012). The zone of influence of the mixing system may be well mixed whereas distant fluid, such as that around the walls of a stirred tank, may remain relatively stagnant. These regional effects were also observed by Arratia et al. (2006). Also, impellers can be particularly susceptible to a phenomena known as ‘caving’ where, in extreme cases, fluid around the point of mixing can thin to such a degree that the fluid loses contact with the impeller in the form of a vortex, the outcome being ineffective heat and mass transfer (Patel et al., 2014). Increasing temperature can also affect a substrate’s rheology. The yield stress and apparent viscosity of digested sewage sludge was found to reduce in response to an increase in temperature (Baudez et al., 2013).

Whatever the environmental conditions to which a substrate is subjected, non-ideal flows caused by substrate rheology, mixer configuration and system geometry can substantially influence the performance of continuous flow mixing of these more challenging fluids (Ein-Mozaffari et al., 2003). Moeller & Torres (1997) went further, recognising that the implications of a substrate's rheology must also be taken into account when considering the need for effective mass and heat transfer when mixing and even when designing pipework. Therefore, the relative lack of understanding of flow dynamics of non-Newtonian fluids needs to be improved if difficulties associated with system design are to be addressed and the effects of scale-up accurately predicted (Arratia et al., 2006).

1:5:12 Other Ways of Enhancing Mixing

Mixing/pumping can also be enhanced through digester design and operational practices, often with no additional energy being required. Common techniques include:

- Shaping the digester floor can enhance mixing (Wu, 2010) although changing the floor shape does not necessarily enhance digester performance at lower %TS (Karim et al., 2005b) yet can reduce dead space (Vesvikar & Al-Dahhan, 2005). A comparison between a 25 and a 60 degree inclined floor in similar digester configurations observed an increase in the accumulation of biomass and inert matter at the base outlet of the digester with the steeper floor as a result of settling. Karim et al. (2007) used mathematical modelling of a draft tube mixing system to compare the effects of 25 and 60 degree inclined floors observing only a 4 percent reduction in the poorly mixed zone although the effect was enhanced if baffles were also introduced. However, this was based on an earlier linked study (Karim et al., 2005c) using only 5%TS dairy cow manure.
- Pre-treatment with enzymes has been used successfully to enhance fluidity (Plochl et al., 2009) by accelerating hydrolysis (Nguyen et al., 2013), particularly if fibrous material is encountered.
- Biomass content of effluent was found to be higher if taken from the base of a digester due to the effects of settling (Karim et al., 2005b) so the positioning of substrate removal/introduction points can enhance mixing.

- The removal of inert matter such as sand and debris from the digester may improve mixing as they have no calorific value yet can reduce effective digester volume; issues that can be exacerbated at scale-up (Karim et al., 2005b). Settling/deposition was observed to affect inert matter more than biomass, particularly as %TS increased. Removal of embedded inert material prior to injecting the substrate into the digester was recommended as the chances of removing valuable biomass if attempting to remove inert matter at a later stage are reduced.
- Baffles are standard features in stirred tanks as they induce turbulence by disrupting circular flow generated by impellers [or pumps]. Digesters used to process viscous fluids tend to have baffles mounted perpendicular to but clear of the wall to avoid stagnant zones and sedimentation along the inner edge of the baffle (Doran, 2013). The need for baffles is reduced when mixing is achieved using rotating jets as liquid flow continuously changes direction with jet movement (Kold, 2010). Karim et al. (2007) mathematically modelled fluid flow in a draft tube mixing system based on 5%TS cow slurry and reduced the poorly mixed zone by combining a hanging baffle near the tube outlet with a 45 degree conical digester base.
- Computerised fluid dynamic (CFD) modelling has much to offer the development of bioenergy systems by informing the optimisation of the physical environment within a digester (Wu, 2013).

1:6 Monitoring and Control

Effective monitoring and control is essential to ensure process stability whilst optimising process performance and hence the economics of the system (Boe, 2006), particularly if OLR is high (Li et al., 2014). Indeed, the need for effective monitoring and control is essential if the mixing system is to be optimised for biogas production. In general, monitoring and control systems vary depending on the intended application and associated requirement (Bakeev, 2010). Research and development requires versatile process instrumentation whereas on-site plant needs robust and automated process instrumentation solutions. In terms of complexity, a small single-feedstock rural AD plant may survive with simple titration augmented by the occasional visit by a consultant whereas larger operations may warrant a much more sensitive, comprehensive and reliable approach (Madsen et al., 2011). However, the cost of monitoring equipment continues to reduce thereby improving the affordability of monitoring and control for smaller operations although robustness and simplicity will always be key requirements when deployed in the potentially harsh environment of a farm.

The usefulness of the wide range of metrics that can be measured varies (Boe et al., 2010) but key parameters tend to be pH, alkalinity, VFA concentration and biogas flow rate and composition (Appels et al., 2008). Biogas production is a relatively easy way to measure reactor performance but does not indicate the chemical stress being experienced by the digester. The pH of a fluid is also relatively easy to monitor. But many digesters are run below OLR design capacity to address poor process monitoring and the associated risk of inhibition (Ward et al., 2008). Also, reliability can vary significantly with widespread anecdotal evidence of systems under-performing (The Soil Association, 2011). This may be due to the difficulties associated with on-line monitoring (Liu et al., 2004). More recently, the application of modern sensor technology and multivariate data analysis of the outputs [have addressed many monitoring issues and] have been observed to keep a process within tolerances (Madsen et al., 2011). Meanwhile, other software sensor techniques require further development to increase their accuracy and reliability (Ward et al., 2011b). In fact, the transfer of knowledge and skills from the well-established fermentation, pharmaceutical and food science industries offers great potential.

1:7 Summary

AD is regarded as an environmentally-friendly mature technology yet the industry lacks small-scale financially viable solutions appropriate for dairy farm applications when fed on slurry alone. The low energy potential of cow slurry is often cited as the reason why dairy farm AD is not viable without co-digestion with energy crops or waste streams. Meanwhile, a lack of knowledge and understanding in key areas such as the rheology and mixing of non-Newtonian slurry can have a detrimental influence on system design and operation. Process optimisation is heavily dependent on effective mixing but an economic and effective mixing technique is far from being common to systems, particularly those fed on cow slurry. As a result, additional parasitic energy is often applied to address mixer shortfalls increasing OPEX whereas appropriate design and operating could improve the net energy balance and hence system viability. The effects of shear stress on the syntrophic microbial communities essential to CH_4 production is also far from understood. Also, systems often lack effective process monitoring and control mechanisms without which optimisation is not possible.

Identifying the effects of mixing intensity and resting on methanogen productivity and net energy output would inform system design and optimisation. The study of CH_4 production rate over the degradation period could also identify opportunities to optimise HRT selection and therefore digester volume.

1:8 Analytical Approach

A progressive approach was adopted with each research step reliant of the outcomes of the previous one. Detailed methodology relating to each step is captured in the relevant chapter with supporting technical information provided as an appendix. The overall approach was structured as follows:

1. Adaptation and calibration of a TA Instruments AR2000 rheometer to accommodate an appropriately-sized sample of cow slurry without affecting sample integrity. Independent variables were selected to reflect environmental conditions to which slurry could be exposed during handling before, during and after the digestion process. Conversion coefficients were calculated to convert system measurements into shear stress and apparent viscosity values from which realistic rheograms could be produced.
2. A full rheological analysis of cow slurry when subjected to the environmental parameters used in Step 1.
3. Application of the same environmental inputs to identify the suitability of an inert transparent non-Newtonian fluid (Sodium Carboxymethyl Cellulose) to act as a substitution fluid for cow slurry.

4. Application of the CMC analysis to inform ERT experiments to identify mixing times required to achieve acceptable levels of homogeneity when mixing cow slurries of different solids content using key shear rates.
5. Application of the outcomes of the rheological analysis and CMC modelling to investigate the effects of key shear rates and resting on CH_4 rates of production and cumulative yield over 21 days using 42 x 600ml lab-scale batch digesters. The analysis was to identify trends in CH_4 production rates over the period to indicate times of maximum specific production. Cumulative yield was compared and parasitic energy demand measured to calculate net energy gain of each mixing regime to provide a net energy hierarchy.
6. Application of the outcomes of the batch analysis to refine mixing regimes to be used in a fed-batch experiment using 6 x 2000ml digesters. The objective was to identify the effect of different mixing regimes on CH_4 production profiles over a 30-day HRT commonly used in mesophilic systems digesting cow slurry. Effluent recycling techniques were not included. Overall yield was also to be quantified so that the net energy gain of each regime could again be compared to provide a net energy hierarchy.
7. Application of the outcomes of the batch analysis to inform research into the effects of HRT reduction on CH_4 production and process stability for all selected mixing regimes when fed-batch techniques were used by reducing the feeding period without reducing the volume of the feedstock.
8. Select an optimum mixing regime/HRT configuration for processing cow slurry.

CHAPTER 2 - RHEOLOGICAL ANALYSIS OF COW SLURRY

2:1 Introduction

The measurement of apparent viscosity of dairy cow slurry presents a range of analysis challenges, the most difficult being the 3-phase nature of each sample (solid, liquid and gas), the solids content and inconsistency between samples. This particular analysis was further complicated by the need to identify the rheological response of the complex fluid to changes in a wide range of key variables, including shear rate, temperature and time exposed to shear forces. These key metrics are important as they have the potential to influence the handling characteristics of cow slurry during farm operations and the success of any AD process to which the slurry is subjected. For example, a slurry re-circulation pump may have to deal with a low temperature, high viscous fluid when starting up a digester yet relatively low stress conditions once the substrate reaches operating temperature or when thixotropic effects are established. Hence, knowing the extreme rheological values that may be encountered throughout the slurry handling process is important when selecting equipment, designing digesters and managing slurry. The rheology of a substrate will also influence the mixing time required to achieve the desired degree of homogeneity necessary to support a stable AD process. Conversely, changes in the effectiveness of a mixing system will effect digester performance and hence the rheology of the substrate being processed and digestate removed (Doran, 2013).

2:1:1 Aims

The aims of this chapter are to:

- Carry out a full rheological analysis of a range of %TS (w/w) dairy cow slurries representative of typical dairy farm operations to identify extremes of shear stress and apparent viscosity values when subjected to common individual and combined influencing variables associated with dairy farm AD operations.

- Compare the rheological characteristics of a range of CMC concentrations to identify a suitable substitute for the range of %TS cow slurry encountered in later research experiments.
- Use the CMC analysis outcomes to model the time required to mix cow slurry when subjected to shear rates applied in later batch and fed-batch experiments.

2:2 Materials and Method

2:2:1 Analysis Period

Slurry collection and analysis was carried out between 12 February and 18 April 2013.

2:2:2 Slurry Collection, Storage and Preparation

Cow slurry was sourced from a non-organic modern dairy farm located in the South West of the UK. The cattle were fed a diet of grass, barley, maize and sugar beet with food nutrients and additives introduced as part of the feed. The following operational practices were observed:

- Cows were housed for 10 months of the year in a covered barn and parlour so slurry dilution due to water ingress was minimal.
- Powdered paper bedding was used to supplement rubber mat beds, further reducing the water content of the slurry although the volumes used were minimal.
- Slatted barn floors removed slurry which was then macerated prior to entering the AD system. Samples were taken after the maceration stage to ensure homogeneity, minimise the size of accumulations of mass and represent slurry on entering a digester.
- A single slurry sample was collected at the beginning of the rheology analysis period and sieved using a mechanically agitated 10mm sieve before being stored at 4˚C until required.
- Ten sub-samples were oven-dried at 105˚C until dry to identify the mean %TS (Deublein & Steinhauser, 2011). A mean value of 12.2%TS was identified.

- Once %TS had been identified the sub-samples were oven dried at 550˚C for 2 hours to remove all VS to determine the ash content. The %TS fraction consisted of 66.1%VS.

2:2:3 Pre-analysis Observations

Sample preparation was influenced by the following observations:

- Raw slurry included liquid, solid faecal matter as compacted mass, urine, undigested feed (including grass and grass silage), soil, animal hair and debris such as plastic and string. The inadvertent inclusion of other matter and debris was also anticipated and could include other parts of the animal such as skin, hoof, milk, flesh and blood. Indeed, debris could consist of any matter from the local environment that could be detached and transported to the animal's vicinity by weather, other animals such as rodents or through the farm operating procedure. Such debris could include stones, feed components and identification tags (Brambilla et al., 2013). Large solid matter was removed on discovery to minimise the opportunity for rheometer fouling.
- Despite collecting slurry post-maceration, pieces of grass sometimes exceeded 10mm in length. These were individually discarded to avoid fouling the rheometer.
- The 3-phase composition of slurry post-maceration remained inconsistent.

2:2:4 Analysis Techniques

To facilitate a thorough rheological analysis of the prepared cow slurry, a 3-stage approach was adopted using the following techniques:

- Particle sizing involving sieving using, sequentially, a 5mm, 1mm and 5 hundred micron vibrating sieve. After each stage of sieving, retrieved matter was weighed before being transferred to the next stage. Samples with particulates of 1mm and above, where photographed through a microscope.

- Laser particle analysis of the remaining sample of particles of less than 5 hundred microns.
- Rheometry of 10mm-sieved samples to measure shear stress and apparent viscosity.
- Rheometry of a range of CMC solutions to identify a suitable substitution fluid for a range of cow slurries of various solids content.
- Application of CMC analysis to support ERT trials to identify the time the mixing system used in later experiments would require to achieve desired degrees of homogeneity.

2:2:5 Rheology Issues and Practices to Address Them

Sample handling practices and rheological analysis techniques can raise the following issues:

- Measuring geometries must be appropriate for the task if analysis is to be effectively compared (Mori et al., 2006). Past analysis of dairy farm slurries has relied on a range of rheometry techniques due to the complex nature and consistency of the substrate. Chen & Hashimoto (1976) used a rotational viscometer to analyse livestock waste slurries. Cumby (1980) designed a capillary viscometer using a selection of pipes of different internal diameters. This ambitious solution had an apparatus length of over 10 metres and used fluid flow rate to induce shear rates on the fluid inside the fixed diameter pipework. The size and roughness of particulates [that can make up flocs] such as [undigested] maize or grass silage also affect viscosity (Plochl et al., 2009). El-Mashad et al. (2005) used a concentric cylinder viscometer but centrifuged samples at 3500 rpm for 10 minutes prior to analysis. This may have been to allow the geometry to accommodate the sample. In fact, the practice of pre-shearing samples to ensure homogeneity and overcome sample inconsistency prior to analysis is common (Baudez et al. 2011; Baudez et al. 2013) and has been questioned for some time (Schofield, 1984). Indeed, Schofield went further and adapted a rheometer to compare the influence of depth on apparent viscosity. Achkari-Begdouri & Goodrich (1992) chose not to pre-shear Moroccan cattle manure. Instead they sieved the 2.5 to 12.1%TS samples using a 10mm gauze. This study used a similar method to that used by Achkari-Begdouri & Goodrich (1992) to avoid overly influencing a samples' rheological characteristics to a degree where the original sample was no longer represented. Also, the choice of rheometer was paramount. Of course, differences in animal diet, husbandry and environmental conditions will also influence a fluid's rheometry (Schofield, 1984) so the same source of slurry was used throughout.

- The need for an agreed laboratory protocol to maintain uniformity of data [within this research sector] has been recognised (Eshtiaghi et al., 2013) as no consensus has yet been reached on how to perform rheological measurements (Ratkovich et al., 2013). Ratkovich et al. (2013) also noted that procedures were often not described in sufficient detail to be repeatable. On the occasions that they were, variations in approaches resulted in a wide range of measurements and models were not always validated. To avoid such criticism, this study aimed to fully describe the approach, equipment used, techniques adopted and values gained so that the work can be repeated.
- Volatile organic matter immediately begins to naturally biodegrade aerobically and/or anaerobically if environmental conditions are appropriate. The rate of bio-degradation depends on the surrounding environment, the microbial communities involved and the stage of degradation. As VS degrade to form biogas, the consistency of a substrate changes and viscosity decreases. The rate of bio-degradation is temperature dependent and can be slowed effectively by storing samples at or below 4˚C. This practice was embraced.
- Cow slurry is a shear-thinning, thixotropic non-Newtonian fluid (Plochl et al., 2009). Therefore, samples were not re-used after being subjected to mechanical stress unless the experiment required it.
- If left, slurry stratifies with time taken to stratify/settle being directly related to %TS. Samples having higher %TS tend to take longer to settle (Hashimoto & Chen, 1976). Controlled settling was an integral part of this study.
- Cow slurry is opaque so techniques to quantify degrees of homogeneity and flow patterns by visual means were not appropriate. A fluid was

identified and modelled to confirm rheological suitability as a substitute for cow slurry.

2:2:6 Measuring Accurately

Choosing an appropriate rheometer for the task is important (Eshtiaghi et al., 2013; Mori et al., 2006). As shear stress and apparent viscosity directly depend on shear rate, the ability to accurately control the shear rate applied to a non-Newtonian fluid was regarded as essential if the true nature of the fluid was to be characterised. A controlled stress/controlled rate rheometer is particularly appropriate for this task (TA Instruments, 1996b). The technique relies on a simple stator/rotor arrangement, the former housing the fluid to be measured. Controlled rotation of the rotor provides an accurate shear rate whilst the drag force being induced due to the fluid’s resistance to movement produces a torque that is directly related to the maximum shear stress being induced in the fluid. The level of accuracy is governed by the size of the gap between the stator and rotor. Plotting shear rate against shear stress provides apparent viscosity values from which rheograms are produced. A bladed rotor within a fixed cylinder can also be used should more interaction be required between rotor and fluid (TA Instruments, 1996a).

2:2:7 Equipment Used

Equipment used to carry out the analysis consisted of:

- A Bruker IRScope II microscope to provide images of up to 80x magnification. These were photographed using a Nino-eye microscopic eyepiece camera supported by Dinocapture Version 2.0 software. Samples of solids content consisting of particulates up to 10, 5 and 1mm and 500 microns were thoroughly washed then oven-dried at 105˚C until all moisture was removed. Samples were then photographed to identify the nature of the solids content at each stage of sieving.
- A Laser Particle Imager provided by Malvern Instruments. The MASTERSIZER was supported by Microplus Version 2.19 software and

was used to analyse samples after all solid matter above 500 microns had been removed.

- An adapted TA Instruments AR2000 Rheometer, supported by Rheology Advantage software was used for the rheological analysis. A full description of how the controlled stress/controlled rate rheometer was adapted and calibrated is provided at appendix 1. Details include all conversion coefficients (with associated R^2 values) identified to provide accurate shear stress and apparent viscosity values.

2:2:8 Refinement of Variables and Associated Values

To maximise the potential application of the research without operating outside of the limitations of the rheometer identified in appendix 1, variables were refined as follows:

- %TS range to capture values at which slurries start to demonstrate non-Newtonian characteristics (5%TS) (Achkari-Begdouri & Goodrich, 1992) to 13 percent. A 13%TS slurry was achieved by evaporating water off a sub-sample.
- Temperature range representing key AD process and farm operating conditions that slurry was likely to encounter:
    - 10°C – to represent slurry as collected from the parlour floor.
    - 25°C – a typical calibration value used by manufacturers and also almost mid-way between 10 and 37°C.
    - 37°C – mesophilic process.
    - 55°C – thermophilic process.
    - 70°C – pasteurisation.
- Shear rate of 0-60s^{-1}. To minimise opportunities for thixotropy during the analysis of individual sub-samples, shear rate was increased within this range at 10s^{-1} increments every 10 seconds and viscosity measured, meaning a shear rate profile would take 60 seconds to complete. This was adopted as the standard shear rate profile (SSRP).
- Substrate conditioning to provide predictable thixotropic states where measurements could be used/quoted in context. Designing an appropriate methodology was critical as the characterisation of

thixotropic properties can be the most difficult to measure as concluded by Eshtiaghi et al. (2013) when carrying out a review of the rheological characterisation of municipal sludge. Initial, pre-shear and post-shear states were selected to represent digester conditions at start-up and when subjected to intermittent or continuous/prolonged mixing.

- Resting periods of 1-12 hours (overnight) to represent various intermittent mixing regimes.

2:2:9 Experimental Procedure

Temperature control was performed in accordance with appendix 1. Testing was started at 10˚C with the cup charged with a fresh 85ml sample of 5%TS slurry. Rheology was determined using the SSRP. Once all SSRPs were completed at that temperature the procedure was repeated at the remaining temperatures before proceeding to the next %TS sub-sample.

2:2:10 Presentation of Rheology Data

Actual rheological values are presented to provide a better appreciation of actual substrate conditions. Such information is vital when considering the rating of equipment motors, the range of shear stress that is likely to be experienced and the levels of energy required to drive equipment such as pumps and mixers as viscosity changes. For ease, K and n coefficients have also been included to allow comparisons with previous and subsequent research.

2:2:11 Quantifying Homogeneity/Mixing Periods

The intended variables to be used in the analysis were likely to influence the time a mixer needed to be active to achieve the desired level of homogeneity. Hence, a method to identify mixing times in response to changes in key variables, particularly shear rate need to be identified. Reliable techniques to quantify levels of homogeneity include planar laser induced fluorescence (pLIF) and ultraviolet (UV) fluorescence (Arratia et al., 2006). Dakhel & Rahimi (2004) lists others including laser-Doppler anemometry (LDA), laser-Doppler velocimetry (LDV) and digital particle image velocimetry (DPIV). Karim et al. (2004) used computer automated radioactive particle tracking (CARPT) but such techniques require specialist equipment. More accessible and affordable ways that use visual assessment and time-lapse photography were considered but regarded as too subjective and therefore potentially inaccurate. However, as the resistance to electricity passing through water reduces as the salinity of the fluid increases and the cow slurry was predicted to contain approximately 90 percent water, electrical resistance tomography (ERT) was considered viable. Furthermore, should the technique fail to work in cow slurry, a solution of CMC could be used as a substitution fluid.

2:2:12 Electrical Resistance Tomography Procedure

ERT uses variations in electrical resistivity to provide 2-D or 3-D imaging of the structure/density of a medium (Pakzad et al., 2008). A single omni-directional transmitted electrical pulse of known current is transmitted into the medium and strategically placed receiver electrodes compare the currents received with the common transmitted pulse and provide an image based on relative resistance across the medium as demonstrated by Yousefi Amiri et al. (2011) when measuring the effects of jet mixing in a 2-phase fluid. Wang et al. (1999) also used the technique to quantify the extent of mixing of fluids with different viscosities. An electric current will find the shortest pathway between 2 electrodes in a conductive medium, in this case water. Moreover, resistance to current flow decreases as salinity increases. By introducing a concentrated saline solution of the fluid being examined at the point of mixing and placing electrodes across the region that takes the longest time to mix, homogeneity can be assumed across the remainder of the vessel once achieved in the region that takes longest to mix. Such a simple experiment would only require 2 appropriately placed electrodes as 3-D imaging was not required. However, to be valid, the vessel/mixer configuration had to be similar to the digesters to be used.

To apply the technique the region taking the longest time to mix needed to be identified. Coloured beads that remained in suspension were used to provide a means of visually monitoring fluid flow around the vessel when mixed, providing an indication of time taken for the beads to reach all regions. Beads were introduced at the point of mixing (region of highest shear rate) and their movement monitored at different shear rates. This gave an indication of the effectiveness of distribution when mixed to ensure that the placement of the electrodes would be appropriate for all mixing intensities. As cow slurry is opaque, the results of the rheological analysis of CMC (Appendix 1) was used to identify a CMC concentration capable of simulating typical %TS cow slurries (Table 1). A range of CMC concentrations were considered before a 3.5 percent concentration was selected to reflect the substrate characteristics outlined in Table 7 (10%TS). Preliminary trials indicated that a 3%CMC concentration was not viscous enough. Conversely, a 4.0%CMC solution would capture the batch start-up value of 10%TS but would not represent the fluid when thinning occurred as a result of bio-degradation.

CMC Concentration Required to Simulate %TS of Cow Slurries at 25˚C			
CMC Concentration (%)	**Condition**	**Shear Rate (s^{-1})**	**Slurry Equivalent (%TS)**
3	Initial	10	8
	Post-shear	60	10
3.5	Initial	10	8
	Post-shear	60	11
4	Initial	10	10
	Post-shear	60	12

Table 1 – Percentage concentration of CMC required to simulate %TS of cow slurry at different shear rates

Figure 3 shows a typical configuration of the 500ml digester vessel containing 400ml of 3.5%CMC concentration in water with the coloured plastic beads in suspension. The transparent AMPTS II digester allowed a course but adequate assessment to be made of regional differences in mixing effectiveness across a stirred vessel.

Figure 3 – Visual assessment of regional mixing across a digester using suspended coloured beads

2:3 Results and Discussion

2:3:1 Pre-slurry Analysis Preparation

By using the SSRP to measure shear stress and apparent viscosity a standard error of less than 5 percent was achieved. With standard error minimised, the main influences when analysing cow slurry were perceived to be:

- %TS of the slurry.
- Non-Newtonian nature of the slurry.
- Limitations of available temperature control.

2:3:1:1 Addressing Rheological Inconsistency Caused By Solids Content

Measurements were often erratic and not repeatable when sub-samples of similar solids content were subjected to the same rates of shear; particularly when samples were subjected to the SSRP for the first time. When providing guidelines for rheological analysis, Howard (1991) advocated “bringing all samples to the same level of shear stability and phase separation prior to testing”. The benefits of adopting such practices became evident as the erratic nature of values reduced as applied shear rate was increased or a fixed rate of shear was applied over time. However, such sample preparation prior to analysis would undermine one of the main objectives of the rheology mapping task which was to capture all states of substrate from initial interaction of slurry with machinery/mixers/pumps in a digester to the rheological state after prolonged exposure to shear forces. Despite values not being repeatable between samples, the shear stress and viscosity profiles induced followed similar trends when subjected to similar shear rate profiles. The interaction between the geometry and samples of varying consistency was considered the most likely cause of differences in shear stress measurements taken at similar shear rates. Likewise, the way that solids combined to produce flocs of varying shapes and size could also differ within a sample and interact with the geometry in different ways and at different times (Cross, 1964; Ratkovich et al., 2013). Indeed, the 10s sampling rate over 60s occasionally provided very high values when a particularly solid mass or piece of debris came into contact with a rotor blade as a measurement was being taken. Repeating each procedure a number of times allowed for any inconsistencies to be accounted for and provided a range of values from which a ‘mean’ profile could be obtained (Figure 4). Also, rogue readings were easily identified by comparing profiles as irregularities within a trend were obvious. However, although mean values were more representative with increased repetition, time constraints precluded prolonged experimentation. As a result, each SSRP was repeated 3 times to produce mean shear stress and apparent viscosity values and profiles.

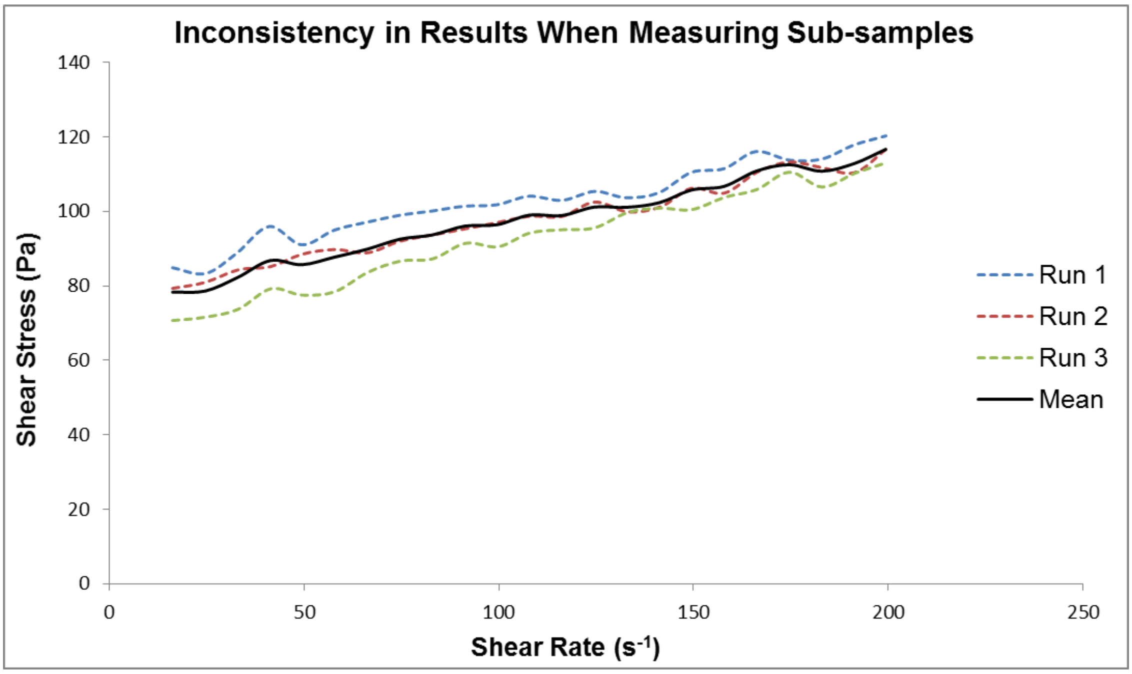


Figure 4 – Smoothing profiles by using mean values

2:3:1:2 Non-Newtonian Properties

Familiarisation trials demonstrated differences in levels of induced shear stress and apparent viscosity at similar rates of shear when a SSRP was repeated using the same sample. Measurements of both shear stress and apparent viscosity were found to reduce each time (thixotropy), as observed by Eshtiaghi et al. (2012), although the extent of the reduction reduced at each repetition (Figure 5). After carrying out repetition trials with a number of sub-samples, the following was observed:

- Highest shear stress values occurred when the sample was first subjected to shear force.
- Values reduced substantially when the SSRP was immediately re-applied.
- Differences in values reduced to relatively insignificant levels (between subsequent runs) after the sample had been subjected to the SSRP 10 times or after 15 minutes of continuous shearing at 60s^{-1}. Figure 5 shows the reducing extent of thixotropy by comparing earlier and latter runs.

Such observations were consistent with previous research using primary sewage sludge (Markis et al., 2014) and cow slurry (Plochl et al., 2009), confirming the thixotropic characteristics of cow slurry. However, the observation also highlighted that samples could not be re-used once subjected to shear forces unless the trial specifically required it.

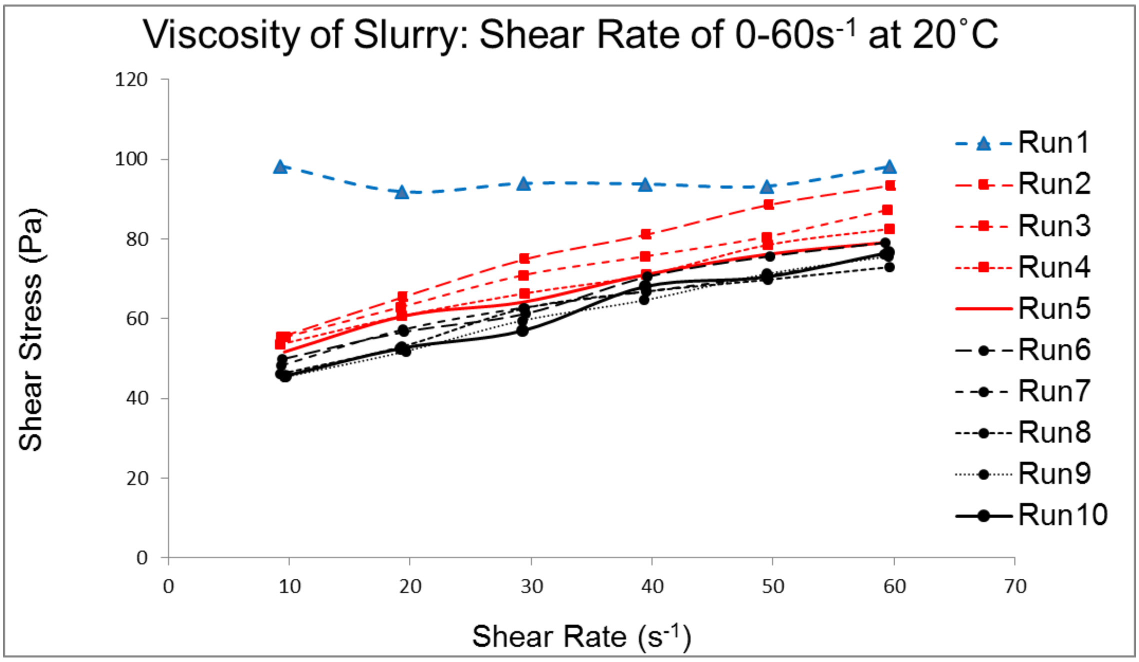


Figure 5 – Effects of shear rate over time using repetitive profiling (0-60s^{-1})

Furthermore, analysis also had to capture changes in an operational procedure that could affect the rheological characteristics of the substrate when mixing, such as continuous or intermittent agitation. To do so, a unique substrate conditioning protocol was adopted with a comparison of the typical outcome presented in Figure 6:

- An ‘Initial’ condition, when a sample was subjected to the SSRP for the first time. This ‘Initial’ exposure to shear force induced a higher rotor torque as the rotor overcame the shear stress yield point to induce fluid flow. Once flow was initiated, shear stress values remained relatively high and erratic. Indeed, shear stress (and subsequent apparent viscosity values) produced during this condition were the highest and most erratic achieved. Initial conditioning represented slurry mixed for the first time or after a prolonged rest period.

- ‘Pre-shear’ conditioning immediately followed ‘initial’ conditioning using the same sample and consisted of a repeat of the SSRP at a similar temperature. The values achieved were always lower than those gained during the ‘initial’ profile and usually less erratic. This profile represented intermittent mixing with a short rest period between mixing.
- ‘Post-shear’ conditioning again consisted of a SSRP at a similar temperature, but following a continuous applied shear rate of 60s^{-1} for 15 minutes after the completion of ‘pre-shear’ conditioning. Values were much lower and generally less erratic than those achieved during the preceding conditions. ‘Post-shear’ represented a return to mixing after prolonged agitation followed by a short rest period or continuous mixing.

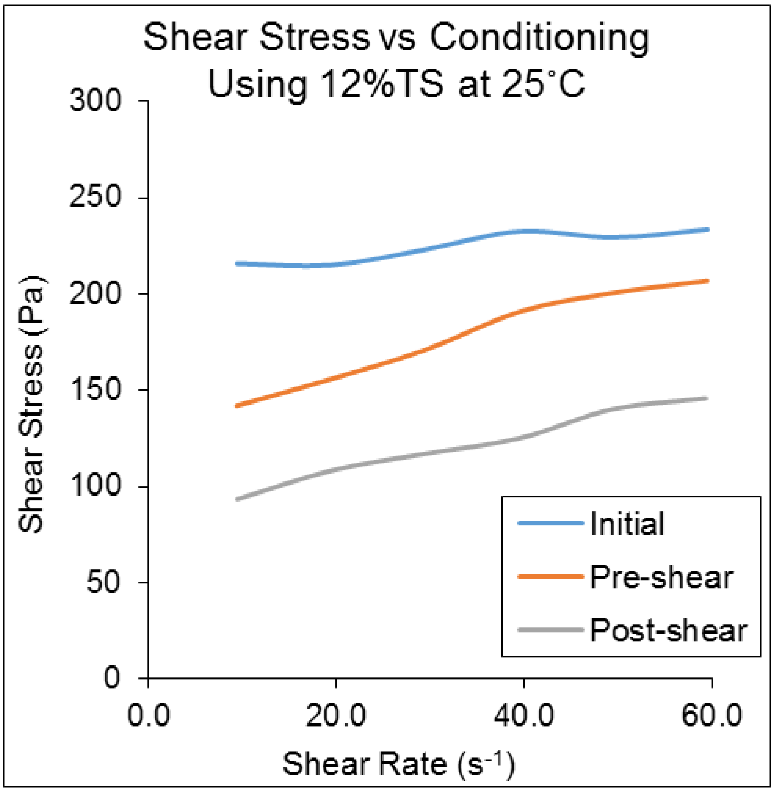


Figure 6 – Comparison of typical effects of conditioning on shear stress values when subjected to the SSRP

2:3:1:3 Temperature Control

Fixing the temperature whilst the SSRP was carried out at the 3 procedural conditions proved appropriate. Only when SSRPs had been completed at all conditions and repeated 3 times (using new samples each time), would the experiment move onto the next process temperature. Techniques and procedures adopted to manipulate temperature reflected those identified in appendix 1.

2:3:2 Slurry Analysis: Microscopic Photography

Samples were observed through a microscope to gain an appreciation of the complexity of smaller particulate matter found in cow slurry to improve understanding about how such matter may affect the viscosity of a fluid. Samples consisted of particles and pieces of material of various shapes and sizes that combine in different ways to form the solids content or flocs. The matter can exist as individual items or combine as shown in Figure 7 and Figure 8. The photographs were taken after sieving with a 5 hundred micron mesh. However, the procedure did not guarantee removal of all matter above the mesh size. Indeed, strands of grass much longer than 10 millimetres were often found in the rheology samples.

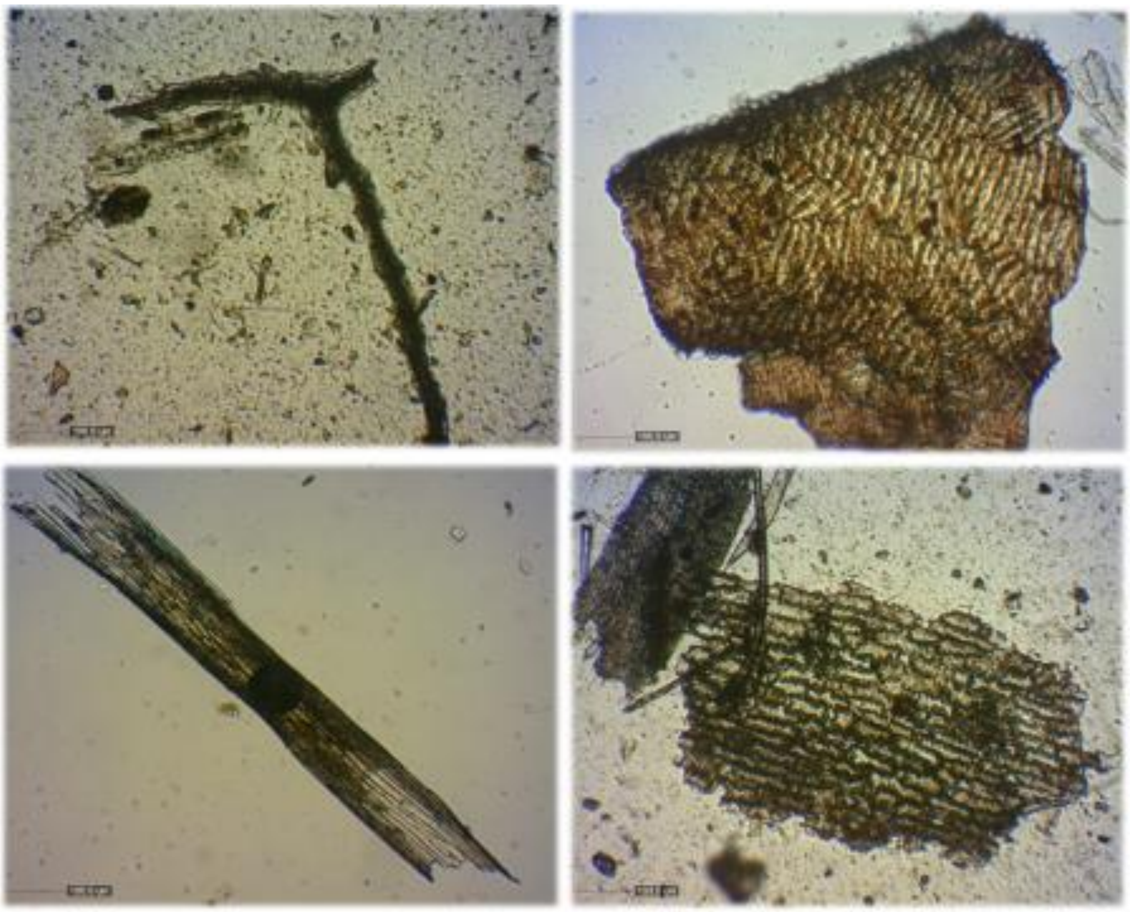


Figure 7 – Examples of particles captured after sieving using a 1mm mesh (scale bar in photograph = 0.1mm)

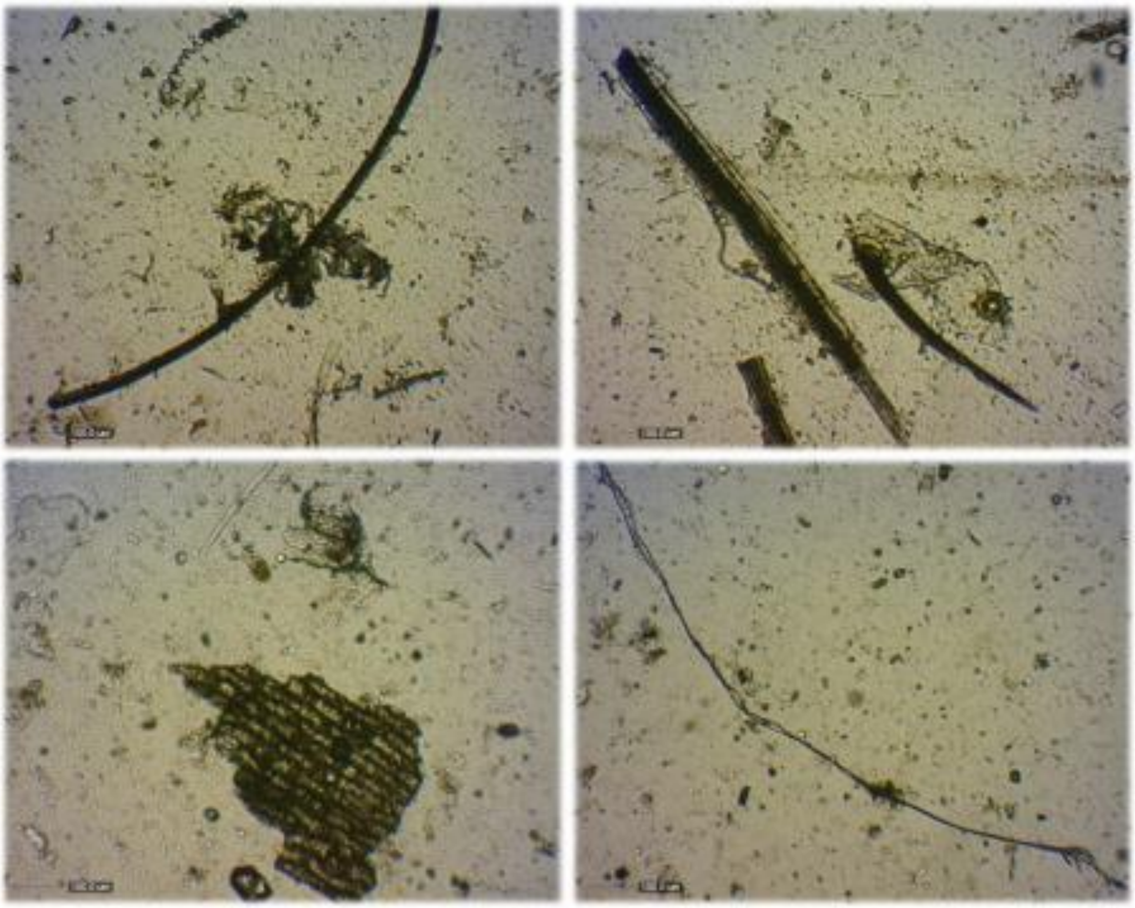


Figure 8 – Examples of particulates captured after sieving using a 500 micron mesh
(scale bar in photograph = 50 microns)

2:3:3 Slurry Analysis: Laser Particle Analysis

Laser particle sizing offered an appreciation of size distribution below 500 microns. Four independent sub-samples provided similar distribution profiles (Figure 9) indicating that particulate size distribution of slurry samples below 500 microns was consistent. Although the application of this technique provided a unique insight into the particle distribution of the slurry used the results would be sample-specific and so have limited value.

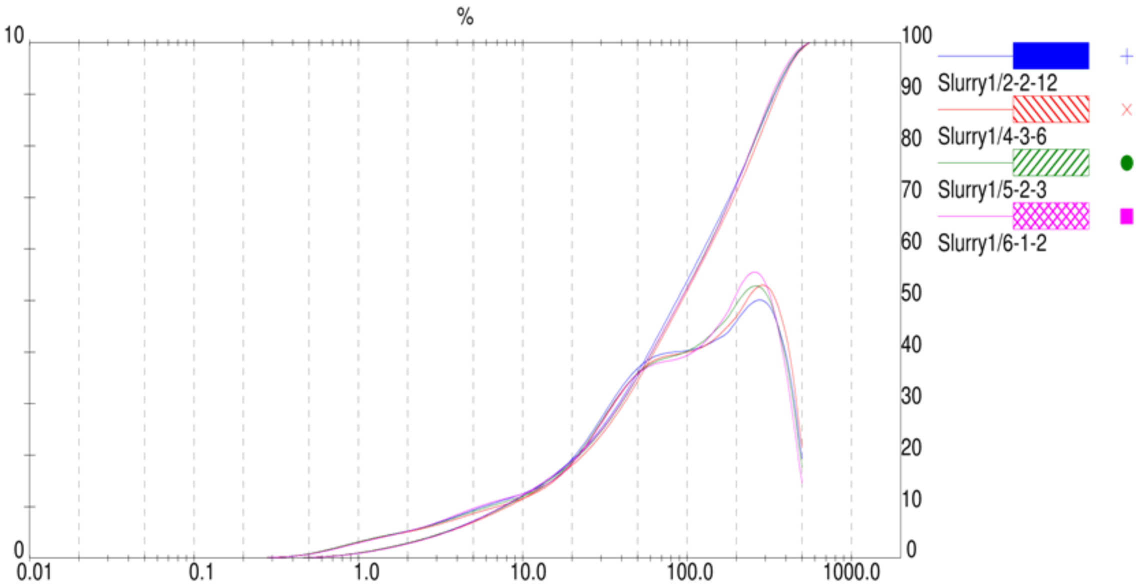


Figure 9 – Distribution by particle size of 4 independent slurry samples after sieving using a 500 microns mesh
(*x*-axis denotes laser-derived particle diameter in microns)

2:3:4 Slurry Analysis: Rheometry

Results are grouped into the effects that variables had on shear stress followed by apparent viscosity.

2:3:4:1 Limitations of shear stress values

The applied shear rate induced shear stress values between 0.07 and 524.75 Pa. The higher values were experienced when low temperature (10˚C)/high solids content (13%TS) samples where initially subjected to low shear rates (10s^{-1}). Values above 414 Pa were outside the guaranteed range of the N4000 fluid with which the equipment was calibrated. Therefore, the maximum acceptable combination of independent variables that remained within the calibration window of the fluid were achieved on initial conditioning of 13%TS at 10˚C when subjected to shear rates of 20-30s^{-1}. Conversely, lowest values occurred when high temperature (70˚C)/low solids content (5%TS) samples were initially subjected to low shear rates (10s^{-1}). Variation between extreme values across the 3 shearing conditions ranged from 11 percent between extremes of minimum values to 25 percent between extremes of maximum values. Values were much higher than those reported in previous research of cattle manure (Achkari-Begdouri & Goodrich, 1992) yet lower than those of sewage sludge of a similar %TS range (Baroutian et al., 2013). Figure 10 captures a comparison of the 3 condition/temperature combinations that embraced extreme and ‘median’ conditions. A summary of extreme values achieved can be seen at Table 2.

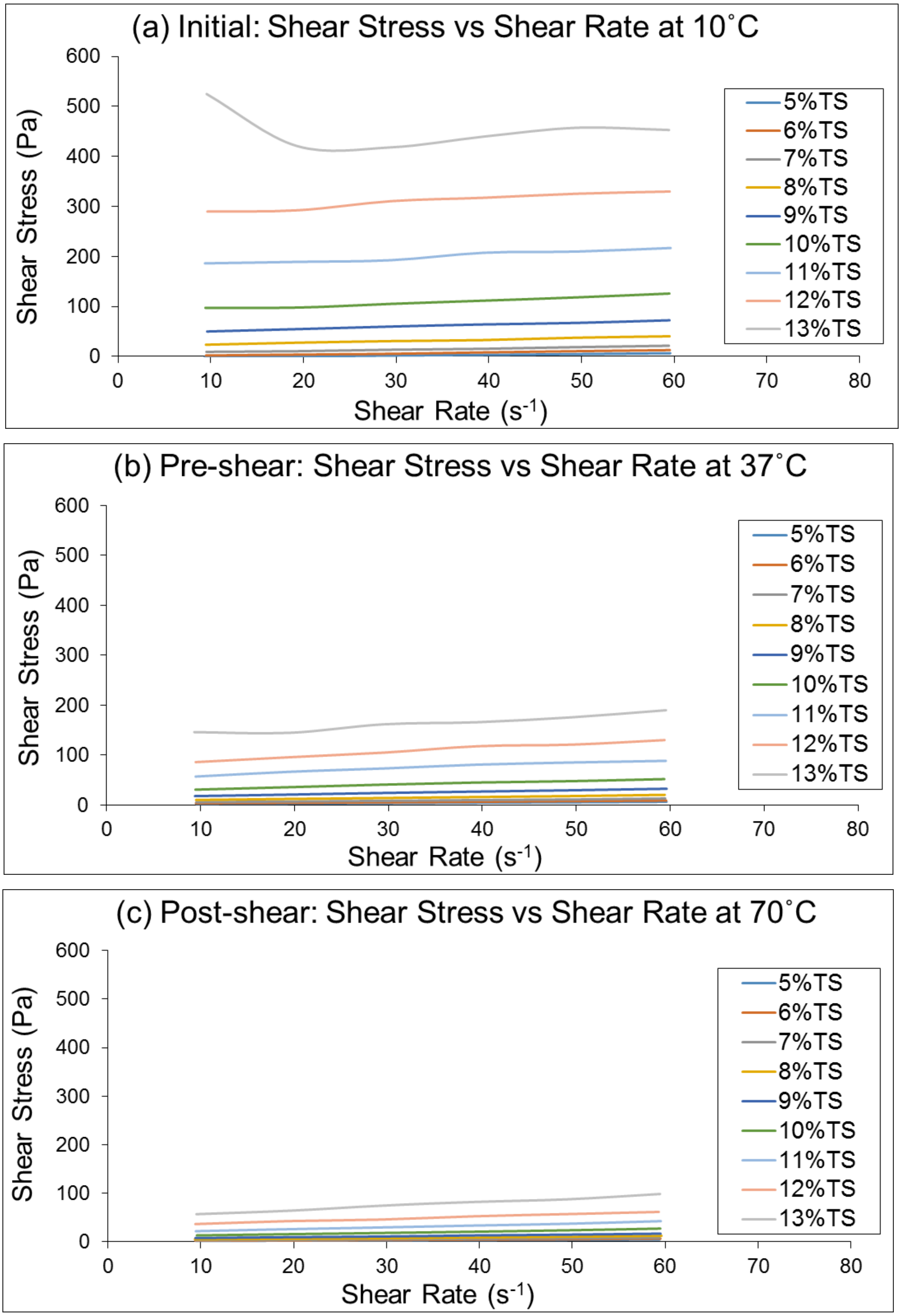


Figure 10 – Relationships between shear stress and shear rate at (a) initial conditions at 10˚C, (b) pre-shear conditions at 37˚C and (c) post-shear conditions at 70˚C

Total Solids	Shear Rate	Temp	Initial		Pre-shear		Post-shear	
			Shear Stress	Apparent Viscosity	Shear Stress	Apparent Viscosity	Shear Stress	Apparent Viscosity
(%)	(s-1)	˚C	(Pa)	(Pas)	(Pa)	(Pas)	(Pa)	(Pas)
5	10	10	*	*	*	*	1.82	0.38
		70	2.33	0.15	2.09	0.13	2.18	0.14
	60	10	6.51	0.16	6.75	0.17	6.57	0.16
		70	5.08	0.13	5.02	0.13	4.80	0.12
6	10	10	1.95	0.39	1.84	0.38	1.10	0.33
		70	3.01	0.22	2.83	0.20	2.54	0.17
	60	10	12.73	0.22	13.41	0.23	11.57	0.21
		70	7.05	0.16	6.91	0.15	6.80	0.15
7	10	10	9.32	0.82	6.48	0.66	5.18	0.58
		70	4.79	0.40	4.39	0.36	3.50	0.27
	60	10	21.51	0.31	20.93	0.30	18.98	0.28
		70	10.19	0.21	9.53	0.20	8.65	0.18
8	10	10	23.54	1.68	17.27	1.32	12.50	1.01
		70	8.14	0.71	7.01	0.61	5.66	0.48
	60	10	40.45	0.49	39.25	0.48	33.35	0.42
		70	15.01	0.28	13.88	0.26	12.65	0.24
9	10	10	49.93	3.24	37.64	2.53	26.79	1.87
		70	14.90	1.37	10.53	0.94	8.05	0.72
	60	10	72.40	0.79	71.07	0.78	57.93	0.65
		70	22.27	0.39	19.65	0.35	17.10	0.31
10	10	10	97.27	6.60	70.90	4.56	47.55	3.16
		70	28.74	2.70	17.98	1.69	13.53	1.24
	60	10	125.77	1.30	116.31	1.21	91.85	0.98
		70	36.53	0.62	31.04	0.53	27.51	0.48
11	10	10	186.24	*	126.73	9.46	88.40	5.80
		70	45.13	4.54	31.86	3.07	22.13	2.10
	60	10	216.82	2.17	205.77	2.07	150.31	1.54
		70	58.50	0.96	51.27	0.84	42.87	0.72
12	10	10	289.76	*	207.49	*	134.24	10.43
		70	77.38	8.65	46.40	4.54	36.84	3.58
	60	10	329.83	3.27	314.08	3.13	217.30	2.18
		70	87.41	1.41	75.69	1.23	61.88	1.02
13	10	10	*	*	312.64	*	203.77	*
		70	158.78	*	77.52	8.89	57.18	5.76
	60	10	*	*	*	*	310.79	3.08
		70	123.02	1.96	117.26	1.88	98.73	1.59

Table 2 – Summary of extreme values of shear stress and apparent viscosity (* denotes measurements outside guaranteed limits of calibration fluid)

2:3:4:2 Effect of Solids Content on Shear Stress

Increasing %TS increased shear stress (Figure 11). This occurred across all %TS samples repeating trends observed by Achkari-Begdouri & Goodrich (1992). The rate of change in shear stress increased exponentially as %TS increased becoming particularly significant above 9%TS, similar to observations made by Pevere et al. (2006).

Other variables had the following effect on the rate of change of shear stress caused by increasing %TS:

- Increasing temperature reduced the exponential rate of change induced by %TS (Figure 11).
- The extent of conditioning also had a reducing effect (Figure 11).
- An increase in shear rate caused a slight increase in the rate of change (Figure 14).

Noticeably, the influence of varying the %TS was greater than changes in shear stress induced by a variation in temperature or conditioning which could be a significant factor if attempting to minimise the shear stress within a digester.

The affect that other variables had on those induced by the primary variable provided a rheological insight not found in previous research which could prove useful when attempting to control a process. Indeed, the detailed technique proved unique to this study.

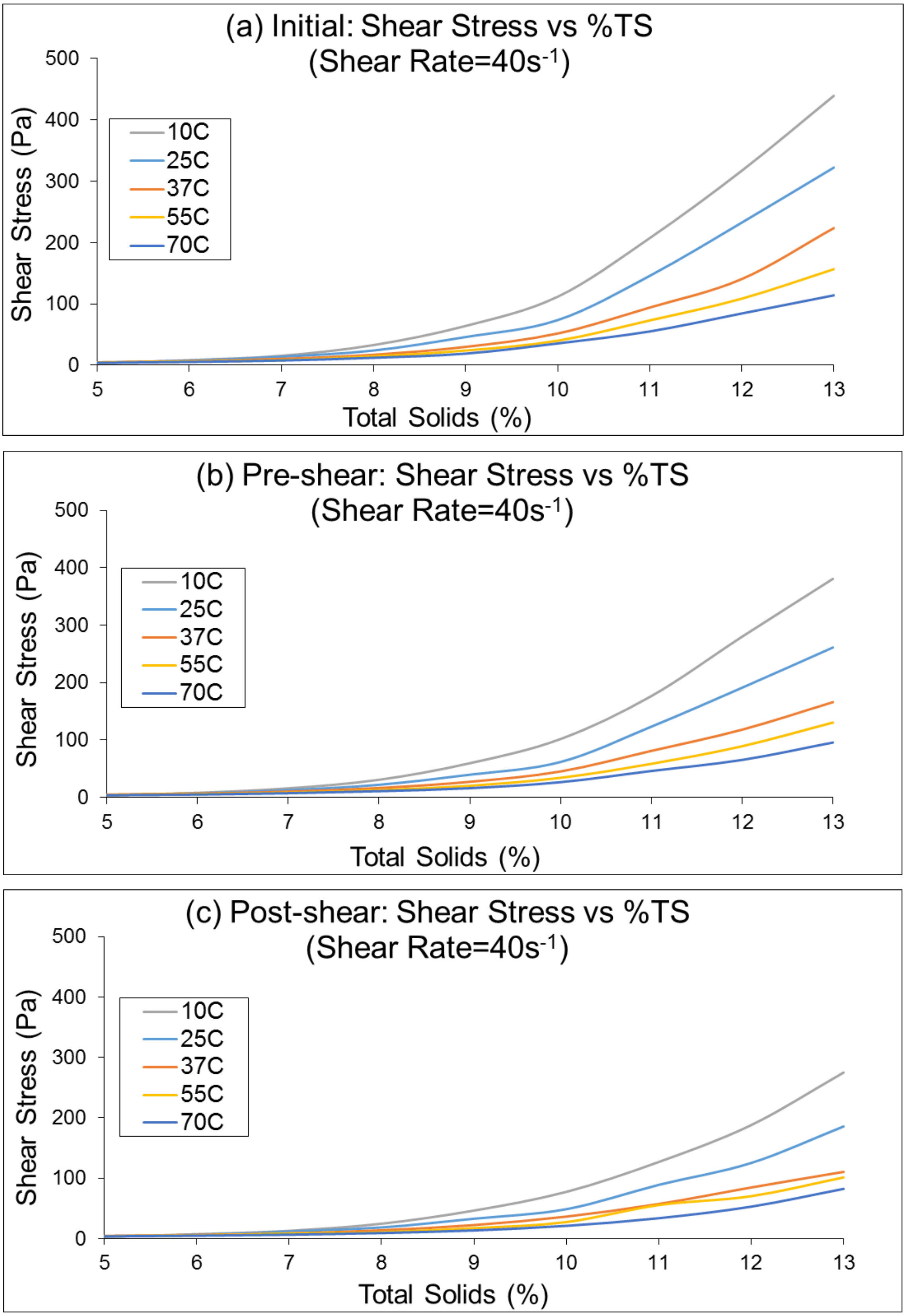


Figure 11 – Comparison of effects of solids content on shear stress when subjected to a shear rate of 40s^{-1} after (a) initial, (b) pre-shear and (c) post-shear conditioning

2:3:4:3 Effect of Temperature on Shear Stress

Shear stress decreased as temperature increased at all levels of %TS (Figure 12), similar to observations made by Baudez et al. (2013) when analysing sewage sludge. The rate of change reduced as temperature increased with the highest value achieved at low temperature and high %TS. However, in this research the rate of change was greater below 37˚C than above in all instances, a factor not previously reported yet worthy of note as both mesophilic and thermophilic processes would experience lower rates of change in response to any temperature fluctuation than processes at lower temperatures. This resulted in 2 distinct linear shear stress profiles, with the difference becoming more apparent the longer a sample was subjected to a constant rate of shear (Figure 12c). This may have been caused by the combined effects of temperature and prolonged shear, the latter resulting in thixotropy.

Other variables had the following effect on the rate of change of shear stress caused by an increase in temperature:

- An increase in %TS increased the linear rate of change (Figure 12).
- The extent of conditioning had a minimal effect (Figure 12).
- An increase in shear rate had a minimal effect (Figure 12).

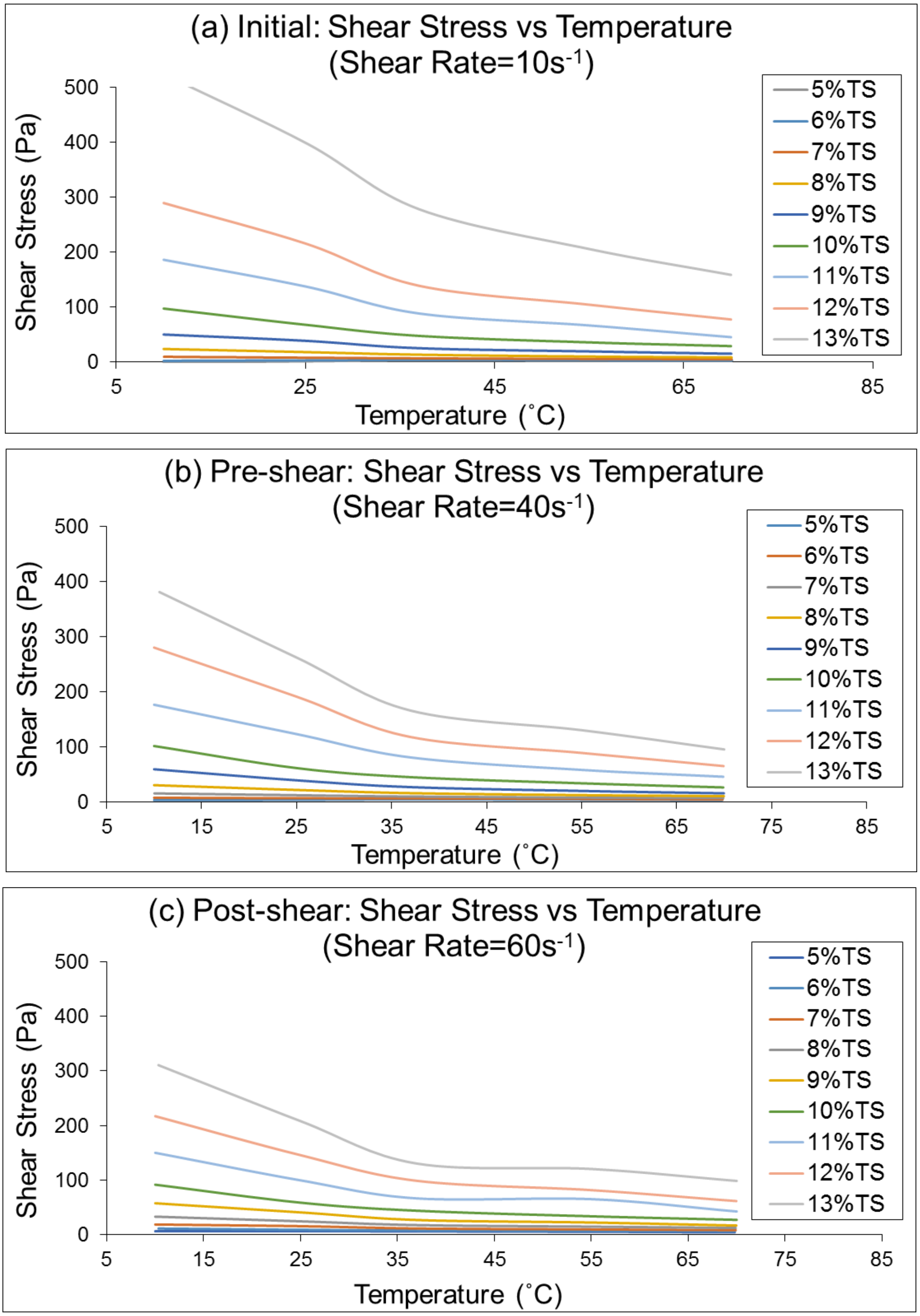


Figure 12 – Comparison of effects of temperature on shear stress after (a) initial conditioning at 10s^{-1}, (b) pre-shear conditioning at 40s^{-1} and (c) post-shear conditioning at 60s^{-1}

2:3:4:4 Effect of Conditioning on Shear Stress

Shear stress reduced the longer a sample was subjected to a rate of shear at all %TS levels (Figure 13). Moreover, the reduction could be substantial, particularly at lower temperatures (Figure 13a). This thixotropic effect was also observed in sewage sludge (Baudez, 2006; Baroutian et al., 2013). Shear stress levels were always greater on ‘Initial’ exposure. Values reduced when a sample was immediately subjected to a subsequent pre-shear routine and reduced further post-shear. Shear stress profiles adopted a slightly less inclined and straighter gradient after initial conditioning but the relationship remained linear. Moreover, the rate of change reduced as the length of exposure increased. The cause for the reduction in values may be attributed to an individual factor or a combination of the following:

- Shear-thinning.
- Thixotropy.
- Interaction of the rotor and slurry may have caused solid matter within the suspension to adopt some sort of biomass ‘order’ when flow was first initiated. This ‘order’ would then already be established at the start of any pre-shear conditioning. Such an equalising process would experience higher early shear stress values followed by a gradual decrease in resistance to flow as homogeneity increased. Hysteresis has been observed when the fluid is rested (Baudez, 2006).

Other variables had the following effect on the rate of change of shear stress caused by prolonged conditioning:

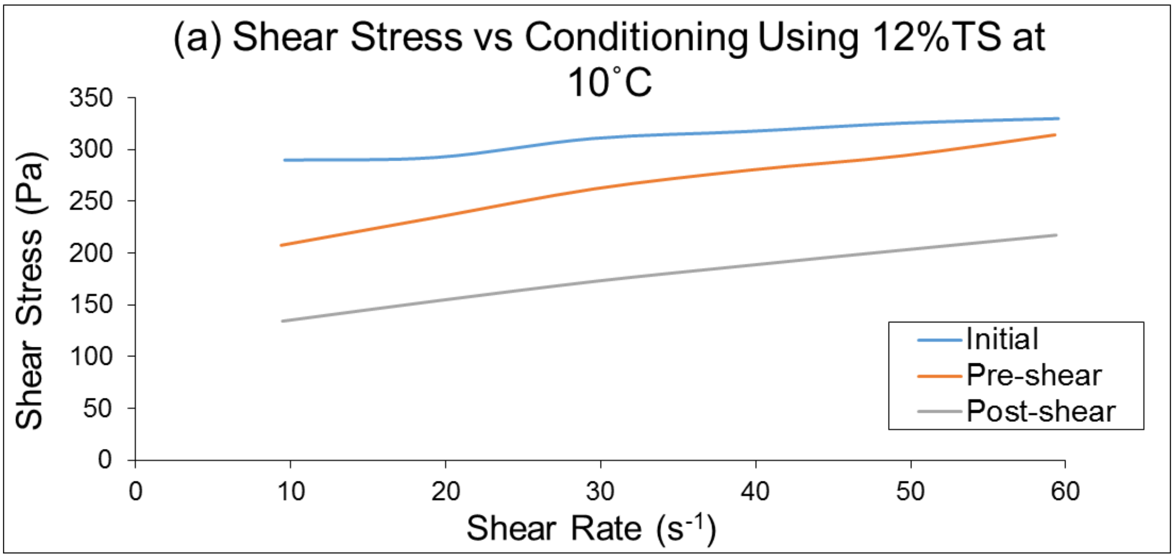
- An increase in %TS increased the linear rate of change (Figure 14).
- Increasing temperature caused a slight reduction (Figure 14).
- Increasing shear rate had a minimal effect (Figure 13).

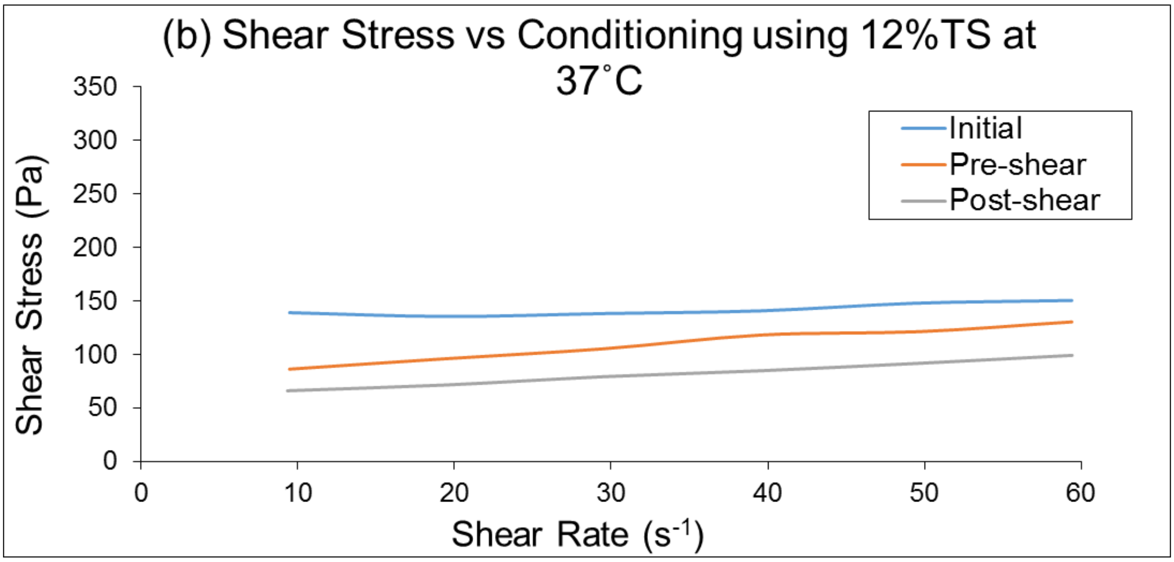
2:3:4:5 Effects of Shear Rate on Shear Stress

Shear stress increased linearly as the rate of shear increased although El-Mashad et al. (2005) only noted the relationship at higher rates of shear between

30˚C and 60˚C. However, in that study samples had been pre-sheared at 3500 rpm using a centrifuge and a much wider range of shear rate was applied (85.7 to 238s^{-1}) whereas in this study the linear relationship occurred at all levels of %TS examined (Figure 14). Similar effects had been observed in sewage sludge (Pevere et al., 2006) but literature on the rheology of cow slurry analysis is limited. Although mesophilic temperatures had been selected for the comparison, the trend was common across all temperatures. Other variables had the following effect on the rate of change of shear rate-induced shear stress:

- Increasing %TS increased the linear rate of change slightly (Figure 14).
- Increasing temperature had a minimal effect (Figure 10).
- Conditioning has a minimal effect (Figure 14).





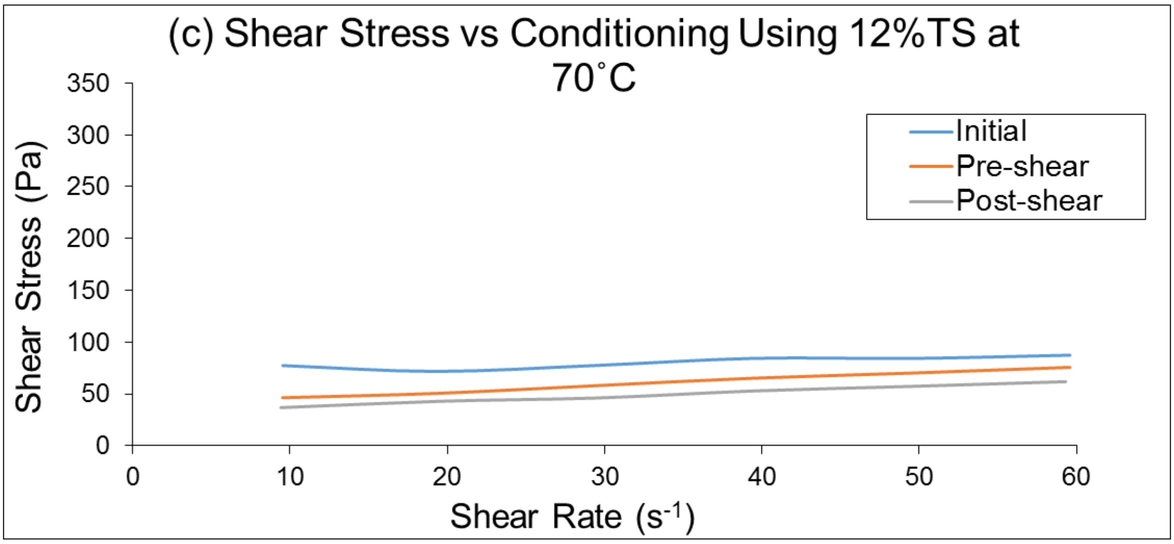


Figure 13 – Comparison of the effects of conditioning on shear stress at (a) 10˚C, (b) 37˚C and (c) 70˚C

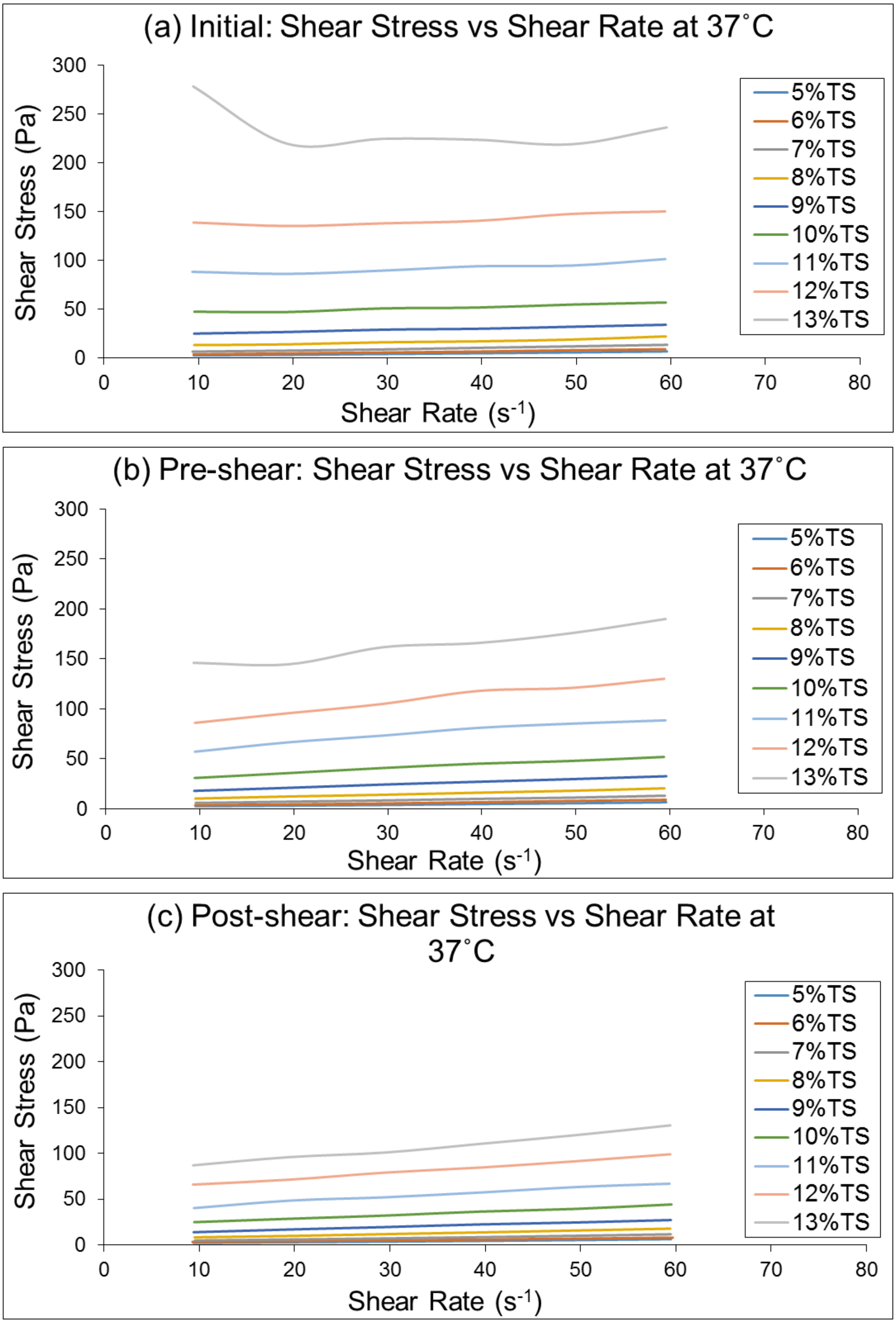


Figure 14 – Comparison of shear stress profiles when subjected to the standard shear rate profile at mesophilic process temperature after (a) initial, (b) pre-shear and (c) post-shear conditioning

2:3:4:6 Yield Stress

Detailed profiling of the effects of shear rate on shear stress in 6, 9 and 12%TS samples (Figure 15) identified a common shear rate of approximately 1.5s^{-1} at which the slurries began to flow. This Herschel-Bulkley flow model characteristic was observed at 10, 25 and 37˚C (55˚C and 70˚C were not tested). Yield stress values in 12%TS slurry ranged from approximately 45 to 122Pa at 37˚C and 10˚C, respectively and reduced as %TS reduced. At 6%TS, yield stress occurred at approximately 1 and 2.5Pa at similar respective temperatures. This conflicts with Mbaye et al. (2014) who, when analysing a range of agricultural wastes including manure, found that substrates below 10%TS did not demonstrate yield stress. However, this may have been due to all samples being pre-sheared at 600 rpm before rheological analysis was carried out.

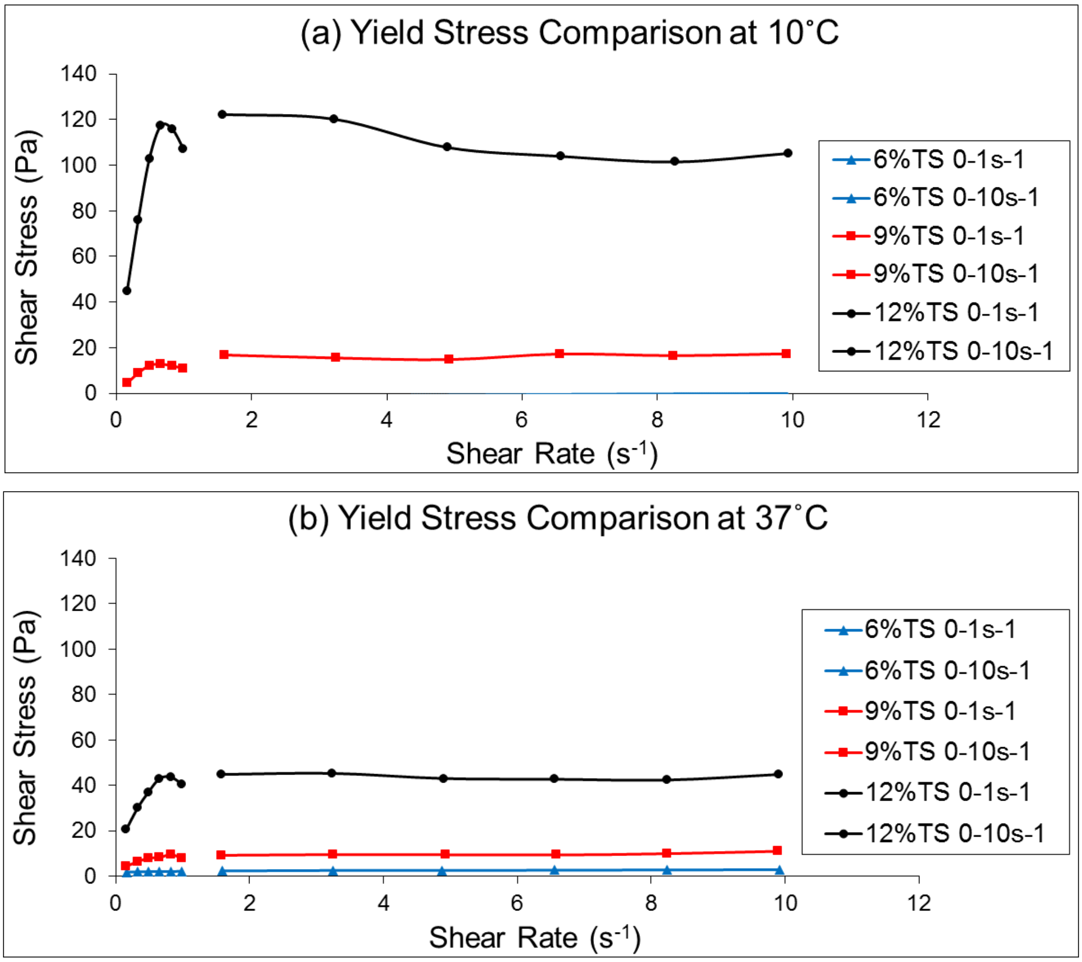


Figure 15 – Yield stress comparison of 6, 9 and 12%TS slurries at (a) 10˚C and (b) 37˚C

2:3:4:7 Response to Resting

Induced shear stress in 6, 9 and 12%TS samples recovered to original values after being rested for 1 hour and then subjected to the SSRP (Figure 16). The effect of rest was similar to that observed in sewage sludge (Markis et al., 2014) where colloidal forces intent of rebuilding the structure of the sludge were thought to compete with hydrodynamic forces responsible for keeping the slurry deflocculated. The behaviour of a substrate undergoing physical ageing whilst resting is influenced by the physical strength of the network structure of the sludge and the stress applied. Similar research into the thixotropic nature of sludge highlighted that slurry structure rebuilds over time with some evidence of hysteresis (Baudez, 2006). However, no previously published data on thixotropic recovery times for slurry was found. In this rheological analysis, investigation into the effects of resting of periods of less than 1 hour were not carried out so actual times of substrate recovery were not identified.

2:3:4:8 Consistency Co-efficient and Flow Behavioural Index

The consistency co-efficient (*K*) is specific to the fluid whereas the flow behavioural index (*n*) can be influenced by factors such as temperature (Achkari-Begdouri & Goodrich, 1992). They can certainly describe a fluid’s flow properties in terms of shear stress in response to shear rate but do not account for the additional thinning experienced by the fluid due to thixotropy as demonstrated in Figure 14. If they did, a time element indicating the length of the fluid’s exposure to that shear rate would also have to be stated. Bongenaar et al. (1973) noted that the useful application of the behavioural index reduced as the shear rate range that the technique was used to capture was widened. Yet both systems remain a popular means of presenting the non-Newtonian rheological characteristics of a fluid despite their limitations. Although such techniques have their place, the range of values identified in this study are intended to inform decision making. However, to allow these results to be compared with previous work, *K* and *n*-values have also been calculated using a log:log plot of shear rate verses shear stress as used by Achkari-Begdouri & Goodrich (1992). The y-axis intercept provides the *K*-value whereas the *n*-value is the slope of the straight line. A comparison of plots at a similar %TS but different temperatures and conditioning demonstrates how the values can vary (Figure 17). The *K*-value equates to the latter element of the formula and the *n*-value the former. High R^2 values were achieved in most cases.

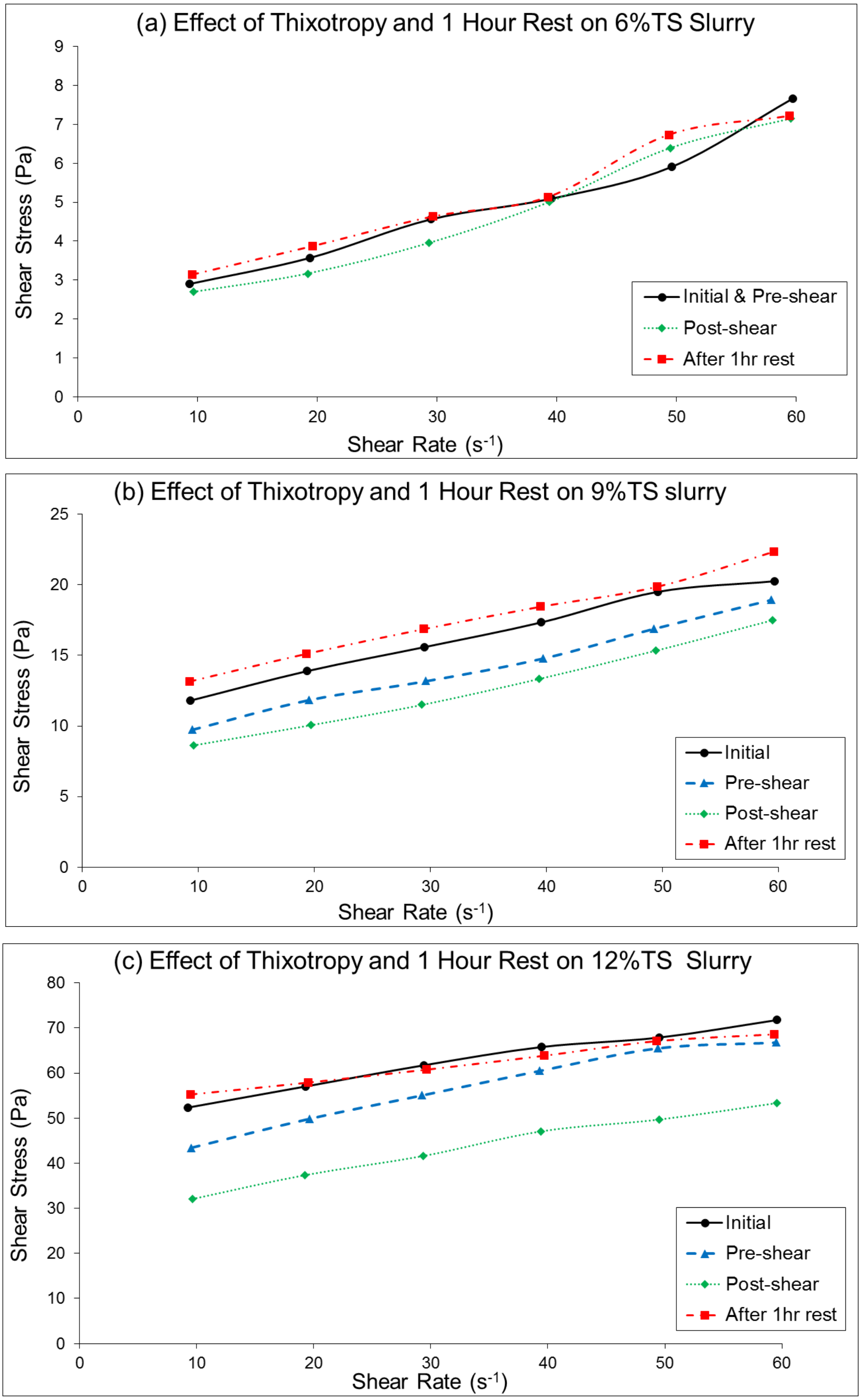
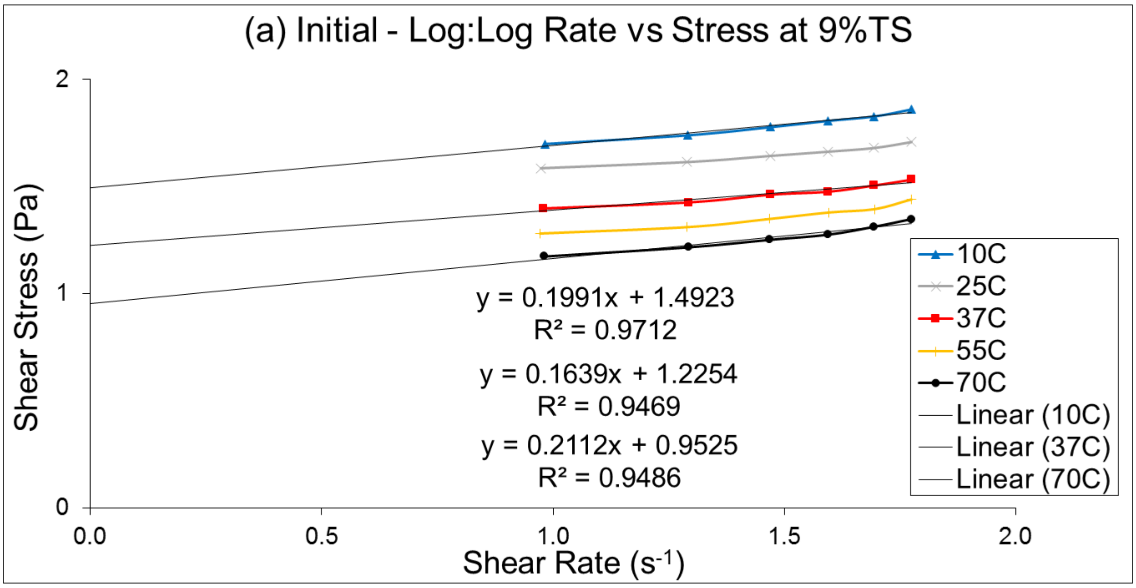
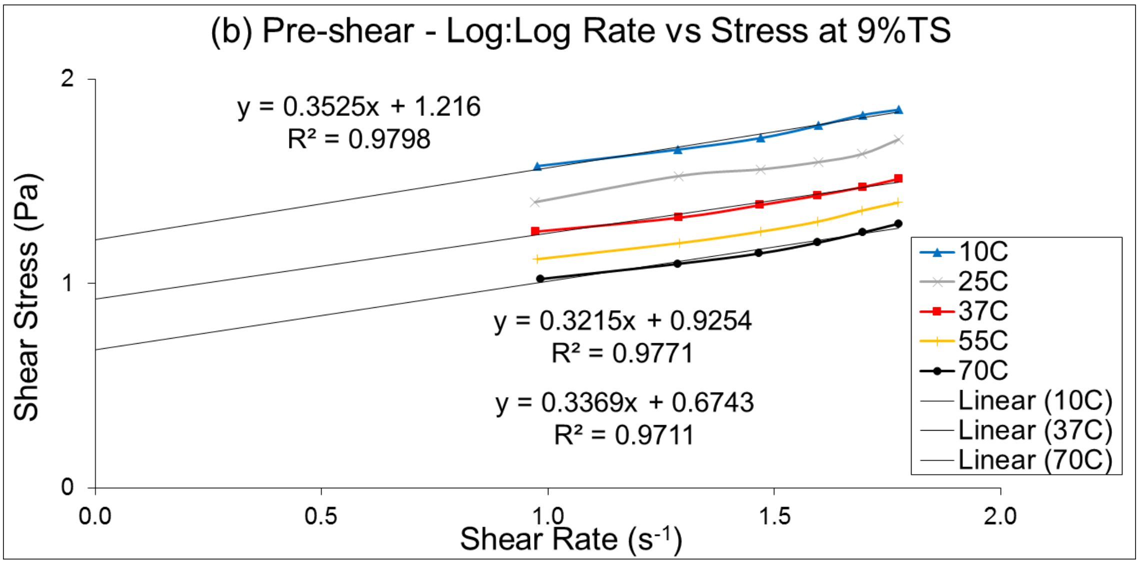


Figure 16 – Effect of thixotropy and rheological recovery on cow slurries of (a) 6, (b) 9 and (c) 12%TS after resting for 1 hour and then re-subjected to the SSRP


(a) Initial - Log:Log Rate vs Stress at 9%TS


(b) Pre-shear - Log:Log Rate vs Stress at 9%TS

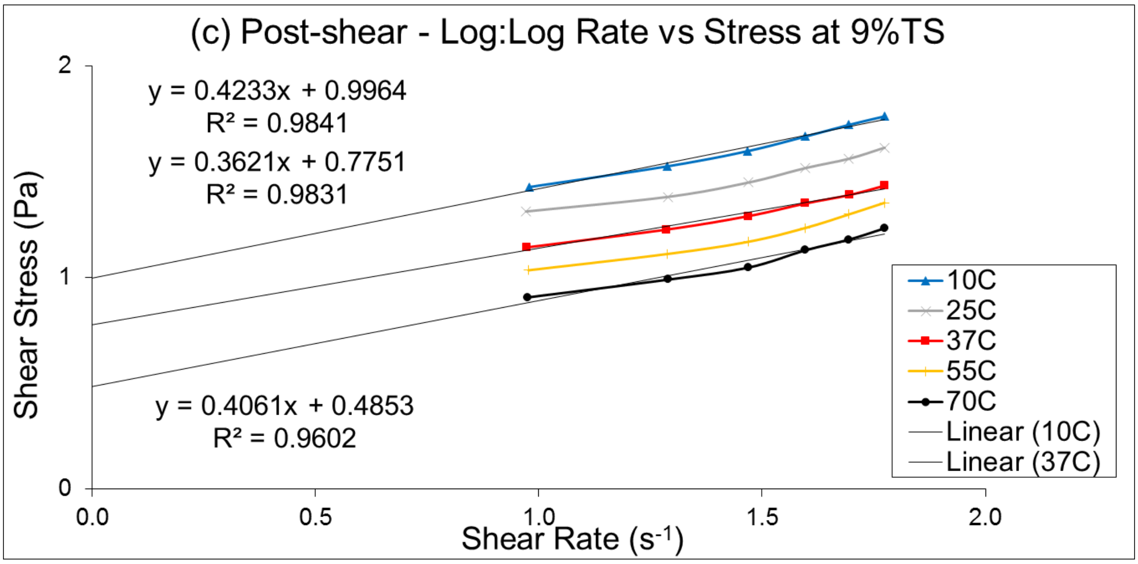

(c) Post-shear - Log:Log Rate vs Stress at 9%TS

Figure 17 – Comparison of rheological consistency coefficients and behavioural indices at differing temperatures after (a) initial, (b) pre-shear and (c) post-shear conditioning

A concise breakdown of the extremes of values encountered (Table 3) demonstrates how they can vary. For example, a 9%TS slurry at 37˚C can attract a *K*-value that may differ by over 36 percent, depending on whether the fluid is experiencing shear rate for the first time (initial) or has been sheared over a prolonged period (post-shear). This highlights a fundamental weakness of the technique and is particularly relevant if basing equipment selection on these coefficients.

Temp	**TS**	**Consistency Coefficient (K)**			**Behavioural Index (n)**		
(˚C)	**(%)**	**Initial**	**Pre-shear**	**Post-shear**	**Initial**	**Pre-shear**	**Post-shear**
10	**5**	-2.05	-1.72	-0.16	1.53	1.36	0.51
	7	0.48	0.16	-0.01	0.46	0.65	0.71
	9	1.49	1.22	1.00	0.20	0.35	0.42
	11	2.18	1.83	1.65	0.08	0.27	0.29
	13	2.74	2.30	2.07	-0.06	0.18	0.23
37	**5**	-0.13	-0.12	-0.14	0.51	0.51	0.48
	7	0.39	0.33	0.21	0.40	0.43	0.46
	9	1.23	0.93	0.78	0.16	0.32	0.36
	11	1.86	1.52	1.33	0.07	0.24	0.27
	13	2.50	2.01	1.72	-0.09	0.14	0.27
70	**5**	-0.13	-0.21	-0.11	0.46	0.49	0.43
	7	0.27	0.20	0.02	0.39	0.42	0.50
	9	0.95	0.67	0.49	0.21	0.34	0.41
	11	1.53	1.23	0.99	0.13	0.27	0.35
	13	2.24	1.67	1.45	-0.11	0.21	0.29

Notes:
1. Red indicates illogical output (< 0) or very low R2 value.
2. R2 values were erratic when undergoing 'initial' shear rate conditioning.
3. R2 values were generally above 0.95 after initial conditioning.

Table 3 – Consistency coefficients and behavioural indices for extremes of %TS, temperature and conditioning

The changing relationship becomes clearer when graphically represented. Indeed, *K*-values clearly reduced in response to thixotropy at all temperatures (Figure 18) whereas *n*-values increased as the fluid became more Newtonian (Figure 19). The range of both values were much lower than those observed by Achkari-Begdouri & Goodrich (1992) when analysing Moroccan dairy cattle manure. This was despite the solids content of both studies being similar and may be due to the broad range of shear rate applied (3-702s^{-1}) in the previous work.

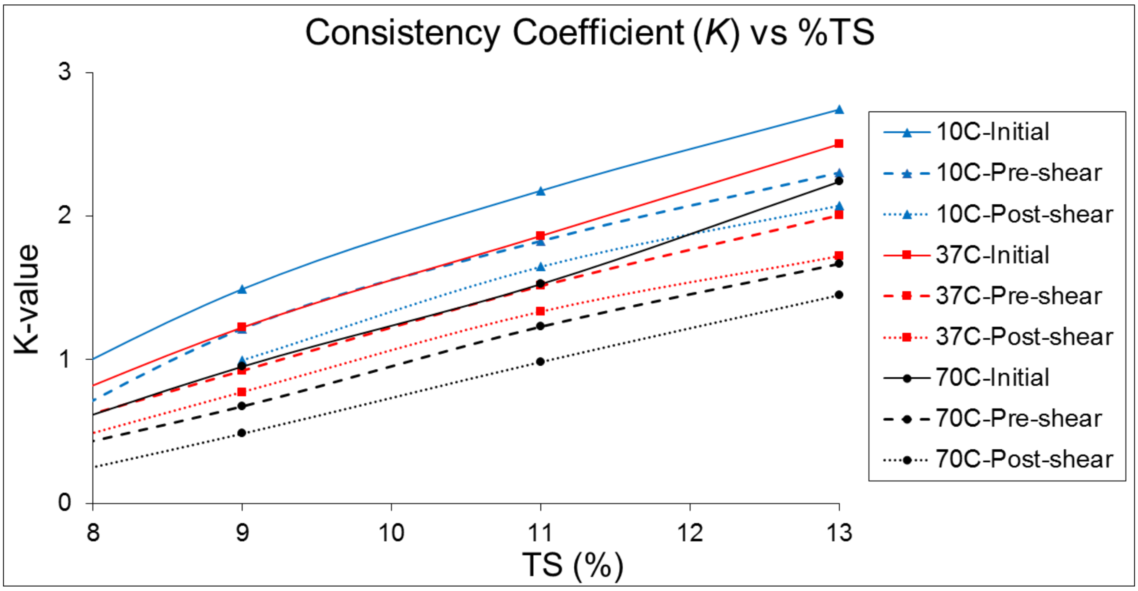


Figure 18 – Changing consistency coefficient due to thixotropy

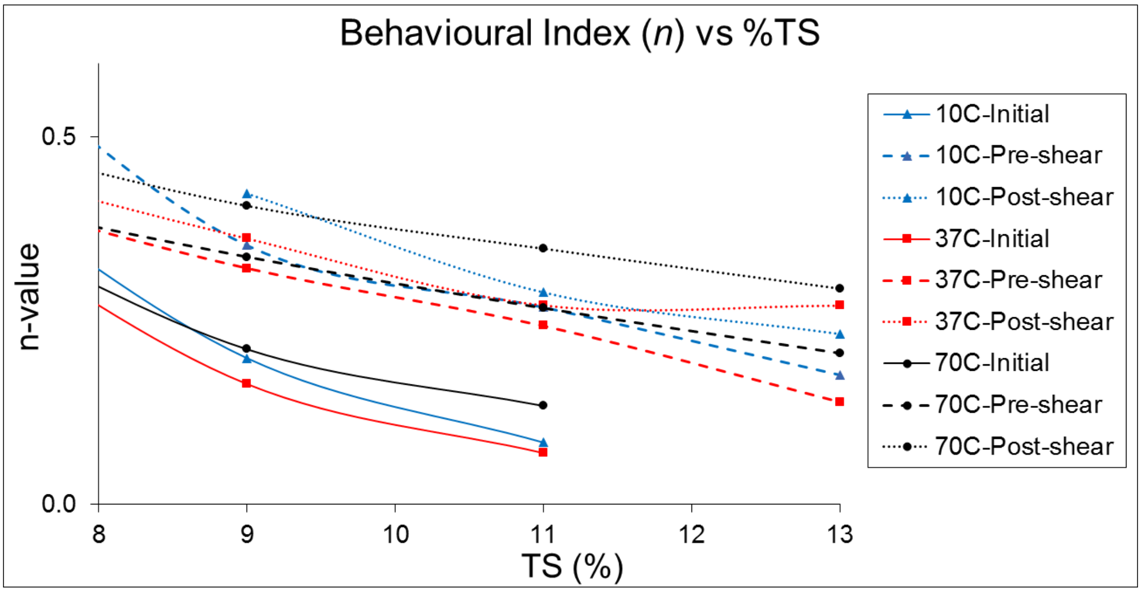
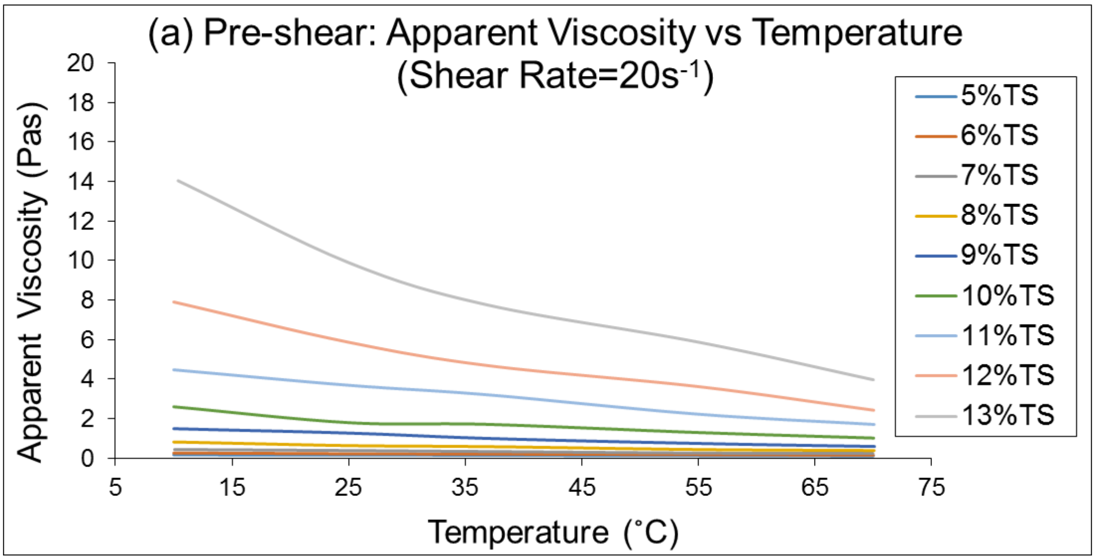


Figure 19 – Changing behavioural index due to thixotropy

2:3:4:9 Range of Apparent Viscosity Values

Viscosity is the principal parameter that characterises the flow properties of fluids (Howard, 1991). In this study apparent viscosity values ranged from 0.12 to 1748Pas. The extremely high upper value occurred when 13%TS slurry was subjected to a low shear rate at 10˚C but was outside the calibrated viscosity limits of the equipment. The maximum apparent viscosity achieved within limits was 17.3Pas and was obtained when 12%TS slurry was being pre-sheared at

25˚C using a shear rate of $10s^{-1}$. Generally, values were higher that previous research (Achkari-Begdouri & Goodrich, 1992). Considering the data trends as a whole, highest values were generally achieved when %TS was high, temperature was low and the sample was being subjected to a low shear rate for the first time. Conversely, the lowest values were achieved when near-Newtonian samples (5%TS) were sheared at high temperature (70˚C). A variation of 0.5 percent was experienced between minimum values but a comparison of variation between maximum values would be meaningless due to some values being beyond the limits of the equipment. A comparison of conditions that produced realistic extreme values is highlighted in Figure 20. Table 2 summarises the extreme apparent viscosity values achieved.



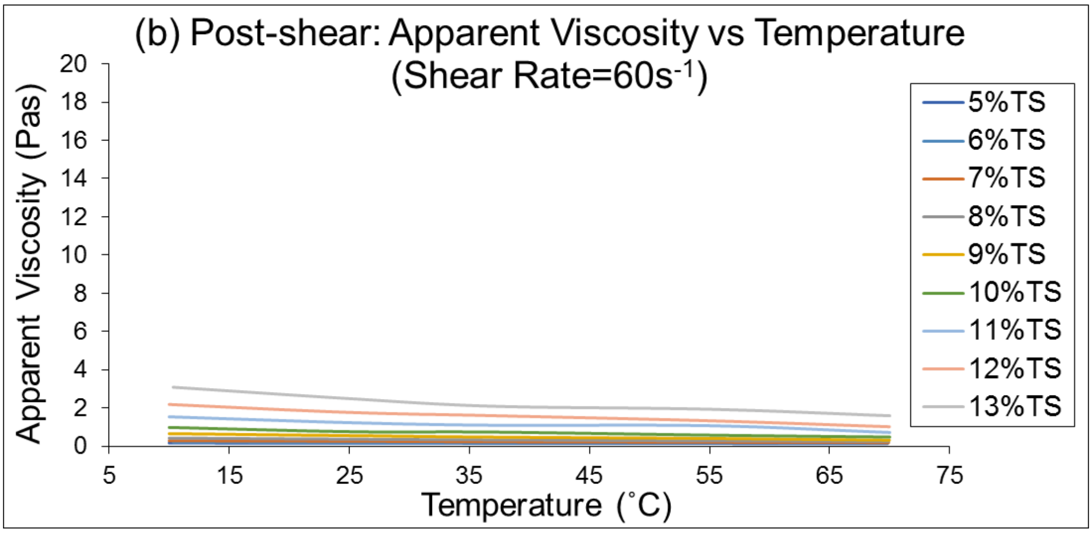


Figure 20 – Examples of variations of apparent viscosity and the conditions that cause them

2:3:4:10 Effect of Total Solids Content on Apparent Viscosity

Apparent viscosity levels increased as %TS increased, as outlined in Figure 21 and previously reported by El-Mashad et al. (2005). The resultant increase in non-Newtonian characteristics as %TS increased was similar to research outcomes by Achkari-Begdouri & Goodrich (1992). As observed in similar studies of digested sewage sludge (Baudez et al., 2011), the increase was exponential. The rate of change in apparent viscosity increased as %TS increased, becoming particularly significant above 9%TS. Limit viscosity was observed at lower solids concentration.

Other variables had the following effect on the rate of change of %TS-induced apparent viscosity:

- Increasing temperature reduced the exponential rate of change (Figure 21).
- The effects of conditioning were significant below shear rates of $30s^{-1}$ but minimal above (Figure 24).
- Lower shear rates accentuated the increase (Figure 22).

Overall, the influence of %TS on apparent viscosity was similar to that of temperature but lower than that induced by changes in shear rate and conditioning.

Capturing the enhancing effects that other key variables had on rheological responses produced by the primary was again unique to this study and provided a deeper level of understanding of the effects that multiple variables have on the rheological state of cow slurry.

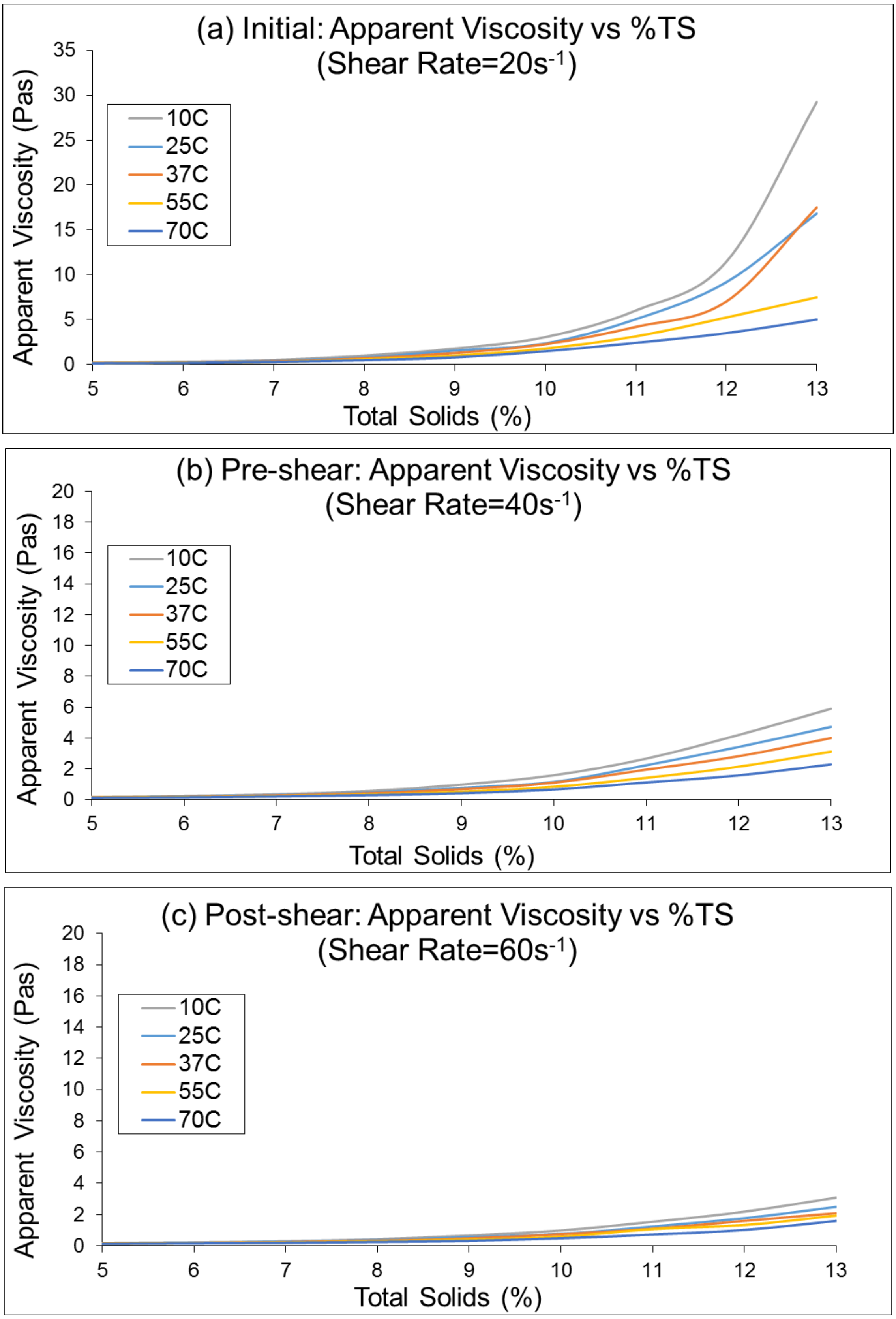


Figure 21 – Comparison of apparent viscosity across a range of solids content after (a) initial, (b) pre-shear and (c) post-shear conditioning at extremes of shear rate

2:3:4:11 Effect of Temperature on Apparent Viscosity

Apparent viscosity decreased linearly as temperature increased at all levels of %TS (Figure 22) and under all conditions. Again this was similar to the research carried out on Moroccan dairy cattle manure (Achkari-Begdouri & Goodrich, 1992). In this study, the rate of the temperature-induced decrease reduced as %TS reduced and the fluid became more Newtonian (constant viscosity). This relationship was also observed by El-Mashad et al. (2005).

Other variables had the following effect on the rate of change of apparent viscosity caused by an increase in temperature:

- An increase in %TS increased the linear rate of change (Figure 22).
- The extent of conditioning caused a further reduction (Figure 24).
- An increase in shear resulted in a further reduction (Figure 26).

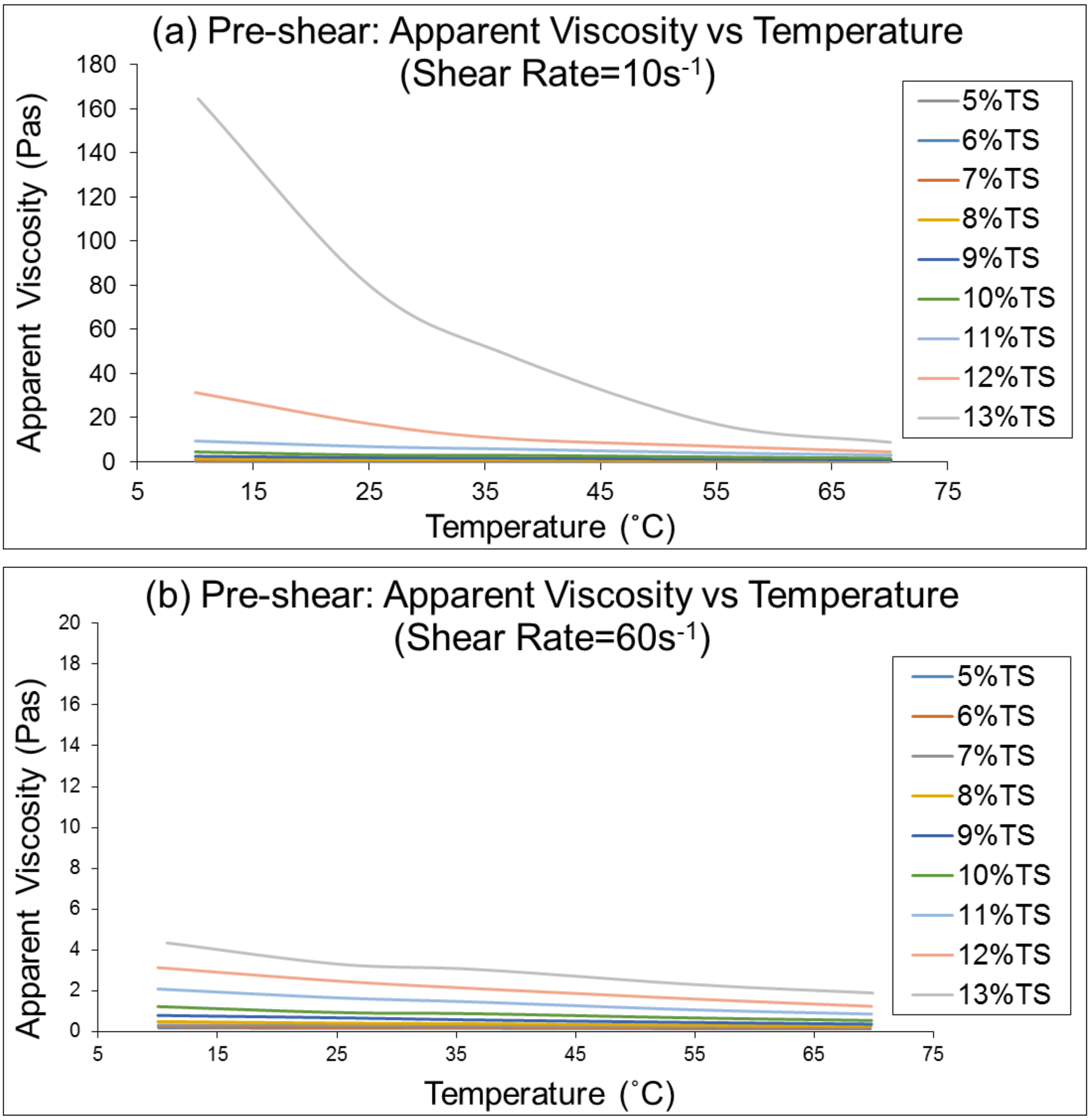


Figure 22 – Comparison of effects of temperature on apparent viscosity under pre-shear conditions at shear rates of (a) 10s^{-1} and (b) 60s^{-1}

2:3:4:12 Effect of Conditioning on Apparent Viscosity

Conditioning had a significant effect on apparent viscosity with the decrease being substantial, particularly at lower temperatures (Figure 23). Values were always greater on ‘Initial’ exposure and decreased each time a sample was subjected to additional shearing, a characteristic that was evident across all temperatures. The reduction in values was likely to be a combination of the effects of shear-thinning and thixotropy as observed in sewage sludge (Pevere et al., 2006). Such substantial reductions in apparent viscosity over time could have a major impact on the energy required to mix a fluid if low viscosity could be maintained.

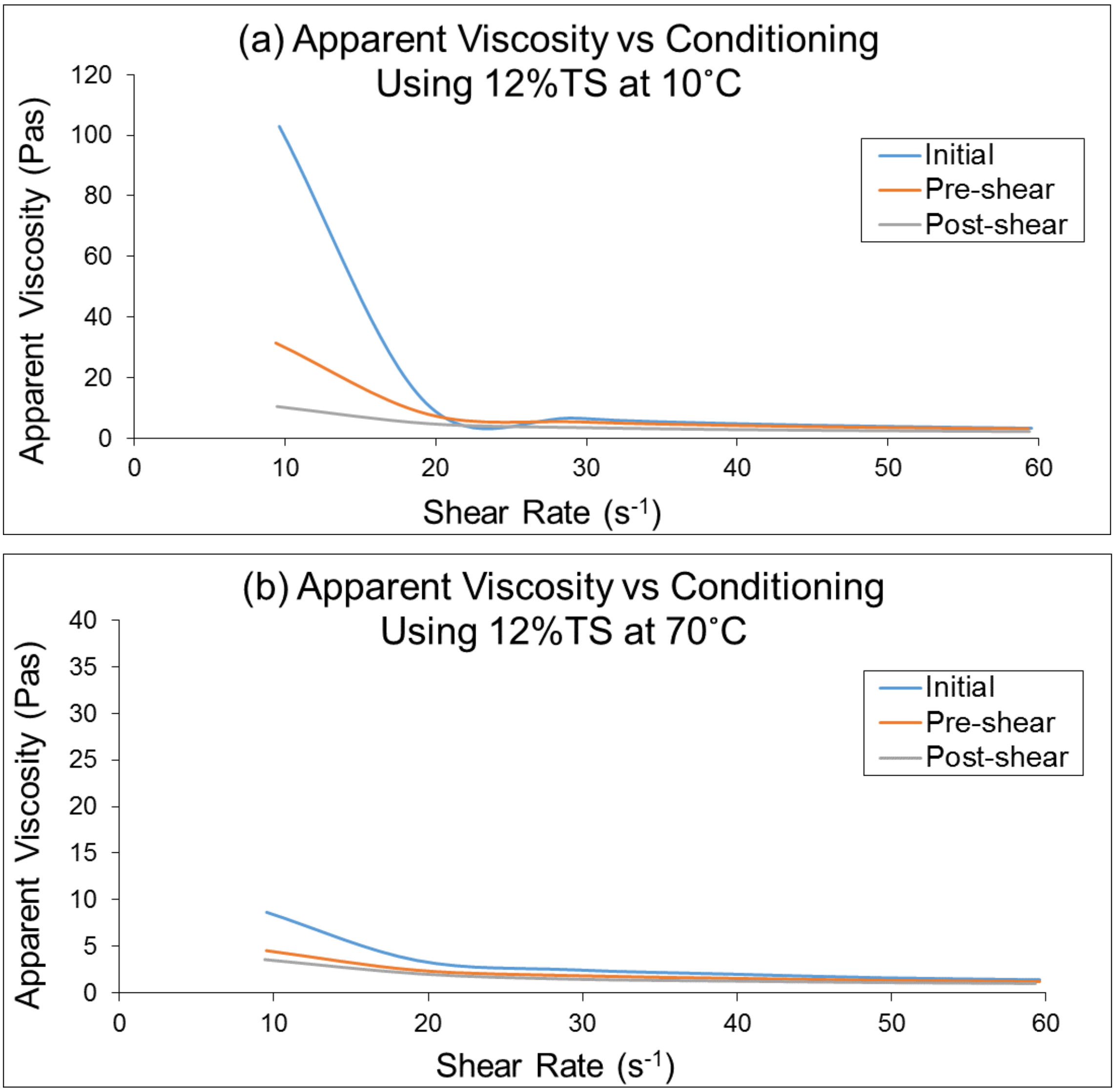


Figure 23 – Comparison of the effects of conditioning on apparent viscosity across the range of shear rates at (a) 10˚C and (b) 70˚C

In this research, a fluid was regarded as having Newtonian characteristics if the change in the apparent viscosity induced was less than 5 percent when shear rate was increased by $10s^{-1}$. When results are presented in terms of conditioning, higher %TS fluids adopt Newtonian characteristics at higher rates of shear and higher temperatures. The thresholds where this occurred are outlined in Table 4:

Boundary limitations of non-Newtonian Fluid Characteristics		
Condition	**%TS**	**Observed limit at which fluid became non-Newtonian at 25˚C**
Initial	5	< $30s^{-1}$ (reduced to < $20s^{-1}$ when heated to 37˚C or above)
	6	< $30s^{-1}$ (similar for all temperatures)
	7	< $50s^{-1}$ (reduced to < $40s^{-1}$ when heated to 37˚C or above)
	8	< $60s^{-1}$ (reduced to < $50s^{-1}$ when heated to 55˚C or above)
	9	Non-Newtonian until heated to 55˚C and $60s^{-1}$ shear rate applied
	10-13	Non-Newtonian throughout
Pre-shear	5	< $30s^{-1}$ (reduced to < $20s^{-1}$ when heated to 55˚C or above)
	6	< $30s^{-1}$ (similar for all temperatures)
	7	< $40s^{-1}$ (similar for all temperatures)
	8	< $60s^{-1}$ (reduced to < $50s^{-1}$ when heated to 37˚C and < 40 s^{-1} at 70˚C)
	9	< $60s^{-1}$ (reduced to < $50s^{-1}$ when heated to 55˚C or above)
	10-13	Non-Newtonian throughout
Post-shear	5	< $30s^{-1}$ (reduced to < $20s^{-1}$ when heated to 37˚C or above)
	6	< $30s^{-1}$ (reduced to < $20s^{-1}$ when heated to 70˚C or above)
	7	< $40s^{-1}$ (reduced to < $20s^{-1}$ when heated to 55˚C or above)
	8	< $50s^{-1}$ (reduced to < $40s^{-1}$ when heated to 55˚C or above)
	9	< $60s^{-1}$ (reduced to < $50s^{-1}$ when heated to 55˚C or above)
	10	Non-Newtonian until heated to 37˚C and $60s^{-1}$ shear rate applied
	11	Non-Newtonian until heated to 70˚C and $60s^{-1}$ shear rate applied
	12-13	Non-Newtonian throughout

Table 4 – Boundary limitations of non-Newtonian fluid characteristics of 5-13%TS samples

Other variables had the following effect on the rate of change of conditioning-induced apparent viscosity:

- Increasing temperature had a minimal effect on the linear rate of change above 37˚C but a significant effect below (Figure 22).
- Low shear rates (in the region of 10s^{-1}), when combined with ‘initial’ conditioning, resulted in a significant increase in the rate of change when solids content was above 9%TS (Figure 24). However, the impact substantially reduced to only slight after initial conditioning.

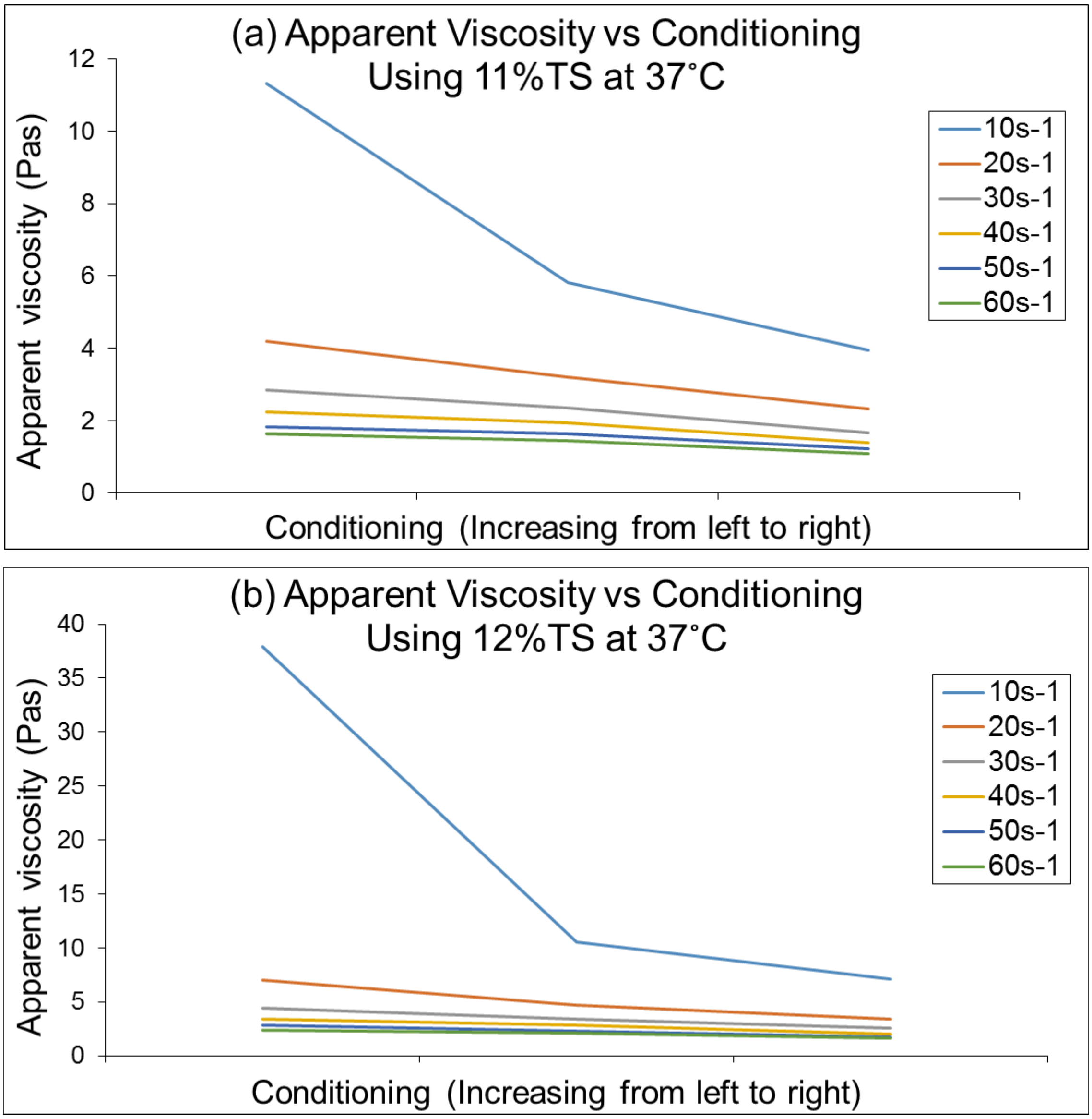


Figure 24 – Effects of conditioning on apparent viscosity when combined with solids content at (a) 11 and (b) 12%TS

2:3:4:13 Effect of Shear Rate on Apparent Viscosity

Apparent viscosity decreased as shear rate increased across all temperatures and in all slurries above 5%TS providing detailed confirmation of earlier course analysis of sieved beef cattle manure by Chen (1986) and sewage sludge by Baroutian et al. (2013). Figure 25 shows the effects of shear rate on apparent viscosity at optimum mesophilic temperature but when subjected to different conditioning. Above 9%TS, apparent viscosity profiles followed 2 distinct trends. Below 20s^{-1}, an increase in %TS produced an increase in the rate of change, becoming significant above 10%TS. Conversely, as shear rates increased above 20s^{-1} the rate of change of apparent viscosity reduced, particularly at higher shear rates. A review of literature found no reference to this key shear rate at which the rheological transition of cow slurry from demonstrating significantly non-Newtonian to near-Newtonian characteristics occurs.

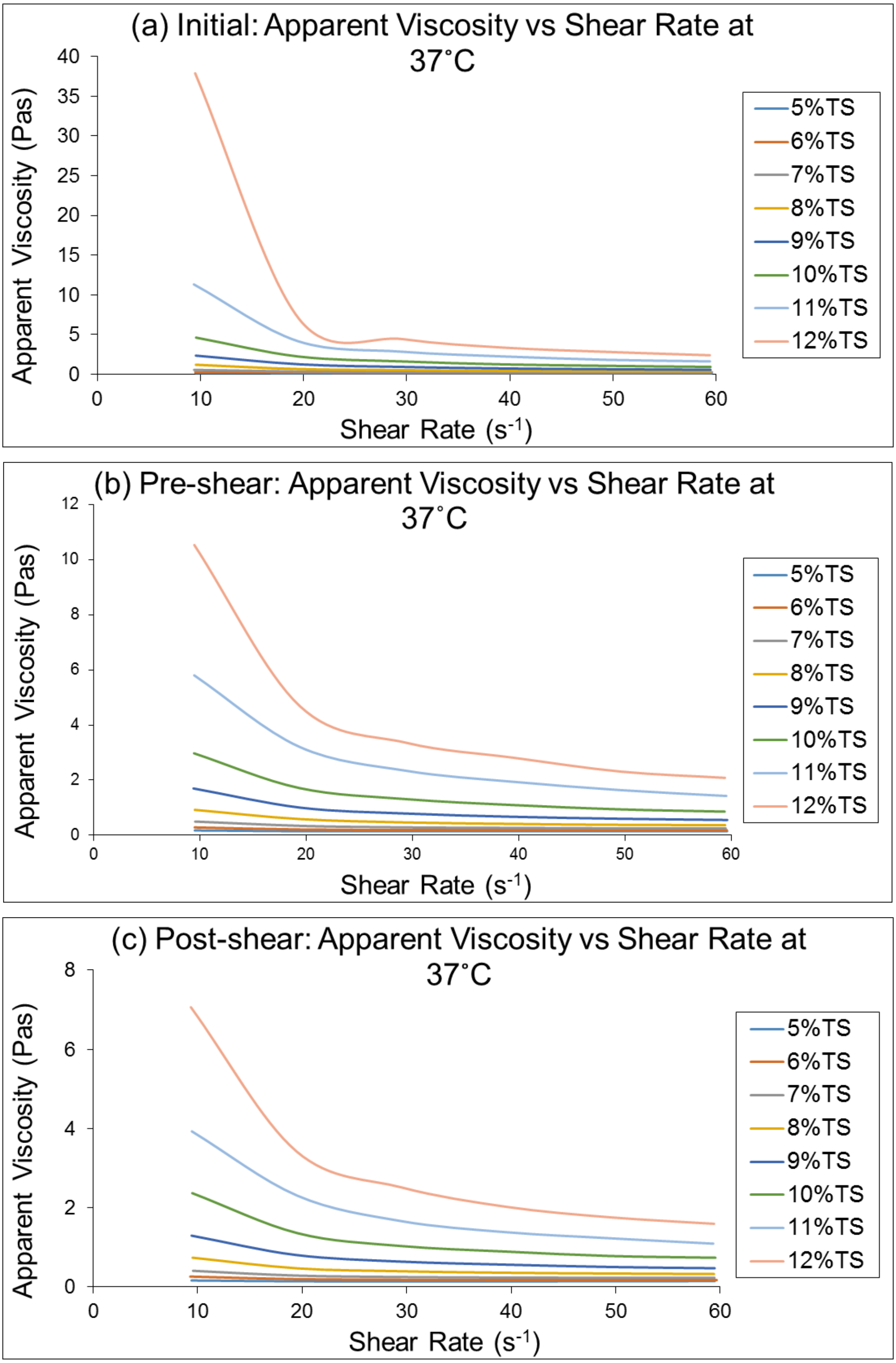


Figure 25 – Comparison of apparent viscosity profiles at similar temperatures after (a) initial, (b) pre-shear and (c) post-shear conditioning

Below 9%TS, shear rate had a relatively minor effect on apparent viscosity when shear rate was increased at extremes of temperature and conditioning, with 5%TS having relatively constant viscosity (Figure 26).

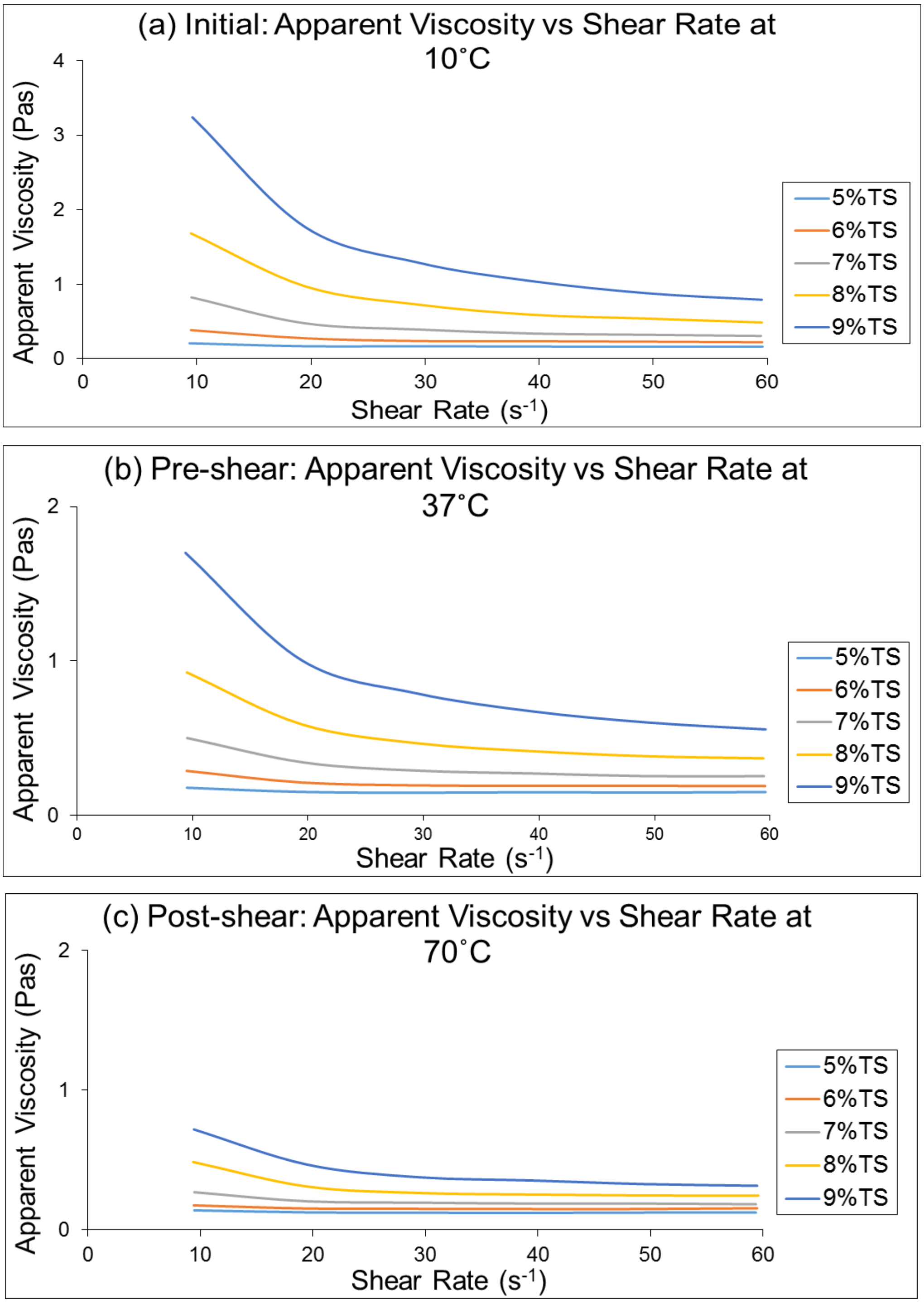


Figure 26 – Comparison of effects of shear rate on apparent viscosity at extremes of temperature and conditioning

Figure 27 compares apparent viscosity values in response to the SSRP across the temperature range, but after prolonged shearing; again a similar trend was evident with a transition shear rate around 20s^{-1}.

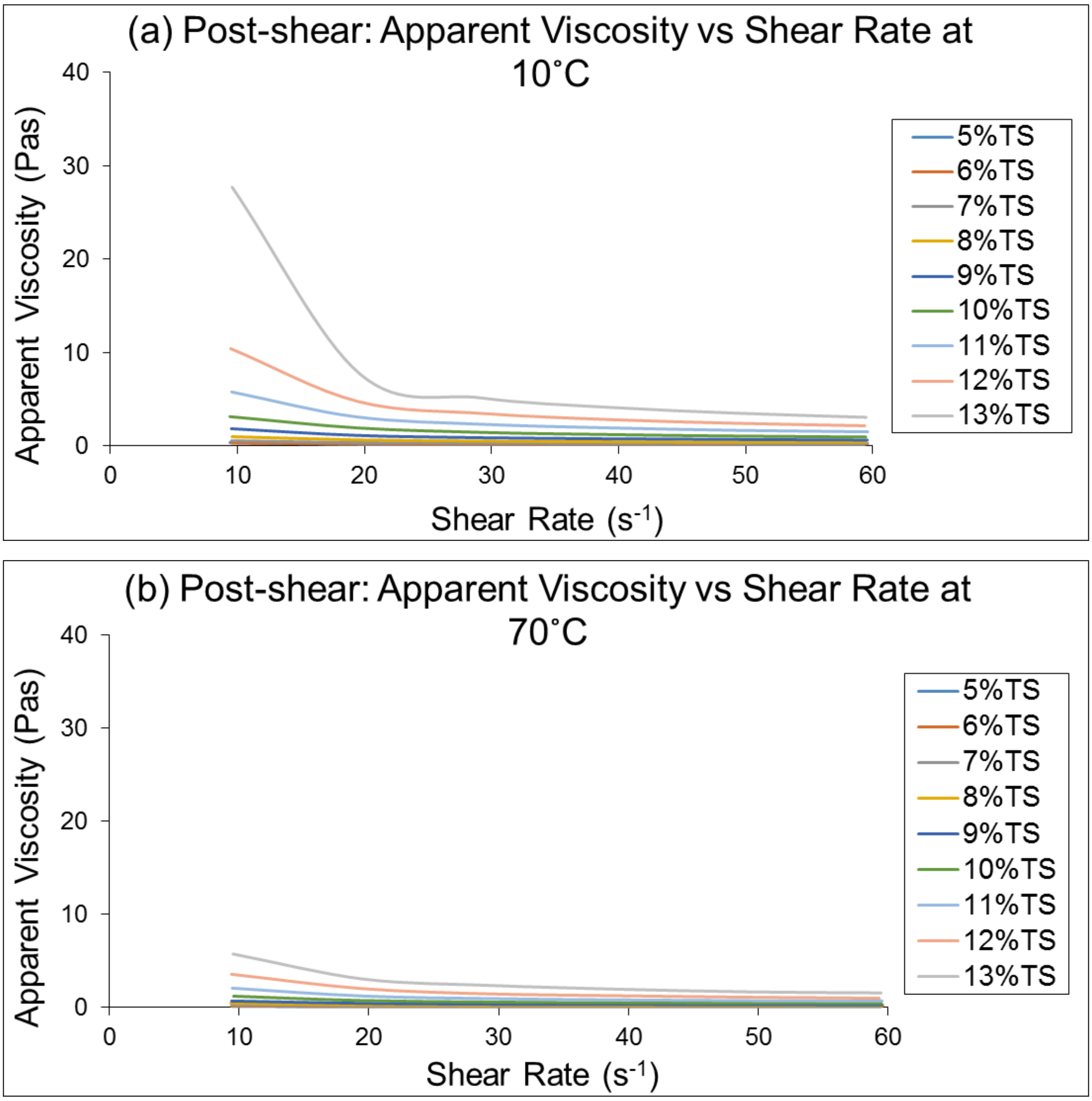


Figure 27 – Comparison of apparent viscosity at extremes of temperature after post-shearing

Other variables had the following effect on the rate of change of shear rate-induced shear stress:

- An increase in %TS increased the linear rates of change above and below 20s^{-1} (Figure 25).

- An increase in conditioning (pre-shearing) had a substantial reducing effect below 20s^{-1} and a minimal effect above (Figure 25).
- Increasing temperature had a reducing effect (Figure 27).

Importantly, the transition shear rate of approximately 20s^{-1} remained constant.

2:3:4:14 Response to Resting

After post-shear conditioning, slurries of 6, 9 and 12%TS recovered their original rheological characteristics after 1 hour of resting (Figure 16). No reference to previous studies in this area could be found. Periods below 1 hour were not tested.

2:3:5 Electrical Resistance Tomography

2:3:5:1 Electrode Positioning Using CMC

CMC modelling was carried out using the CMC analysis detailed in appendix 1. Coloured beads suspended in a range of concentrated CMC solutions (3.5, 4.0 and 4.5 percent) were used to identify the area of the 500ml vessel that took longest to mix when a particular shear rate was applied. On all occasions, the beads took the longest period to reach the upper quarter of the 400ml of fluid in the vessel. Furthermore, the time taken (minutes rather than seconds) suggested that the slight positive buoyancy of the beads was not a factor. Electrodes were therefore placed on opposite sides of the inner wall of the digester 10mm below the surface of the fluid.

2:3:5:2 ERT Analysis

Before introducing CMC to the ERT apparatus, the relationship between electrical resistance in water and the latter’s salinity was identified. The 500ml vessel fitted with 2 electrodes was filled with 400ml of de-ionised water before a known current was passed through the fluid at a fixed voltage. The measured voltage across the electrodes was applied to the current received at the cathode to provide the electrical resistance of the fluid. Sodium chloride (NaCl) measuring 2g (0.5% concentration) was then dissolved in the water and resistance measured before increasing the NaCl concentration with an additional 2g. The procedure was repeated until a level of NaCl saturation was reached that induced no further significant decrease in resistance (approximately 12g (3 percent concentration) per 400ml water). Zero salinity provided the other extreme. The procedure was repeated using a range of CMC concentrations and a common stirrer configuration and the results compared (Figure 28).

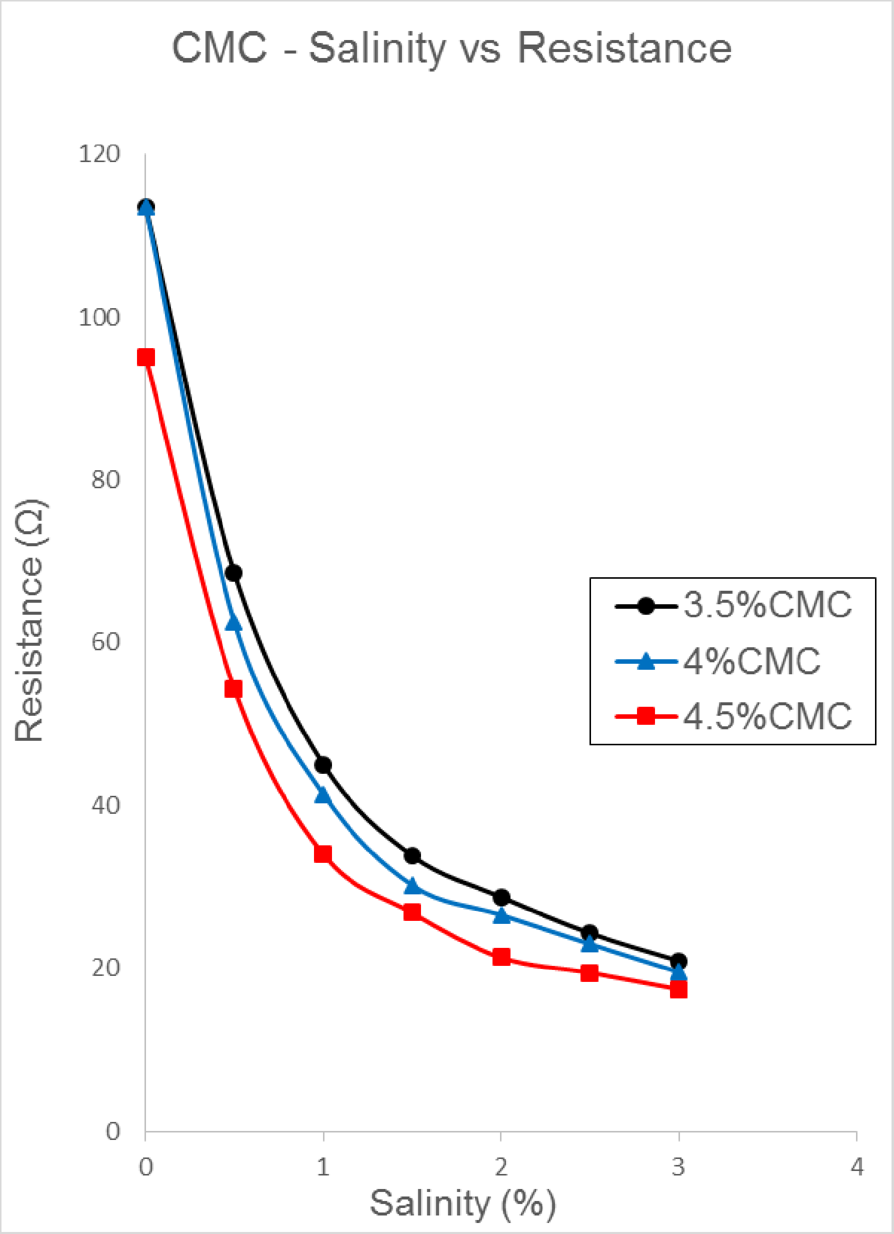


Figure 28 – Salinity verses resistance in CMC solutions of various concentrations

To identify the time taken to mix a stratified CMC fluid, a solution of 3.5% CMC was produced using de-ionised water. Samples of 300ml and 100ml were separated. The larger sample was left untouched whilst 12g of NaCl was dissolved in the smaller to provide a concentrated saline solution. The vessel was carefully charged with a stratified solution: 100ml of plain CMC, followed by 100ml of saline CMC at approximately the stirrer tip height (100-200ml from the base of the vessel). The remaining 200ml of plain CMC solution was then added. Stratification was visually evident and remained until mixing commenced. Mixing was started at each shear rate and resistance was measured at minute intervals. This was carried out for each CMC concentration (3.5, 4.0 and 4.5 percent) to identify the effects of a range of mixing intensities on different CMC concentrations although only 3.5%CMC data was eventually used. Figure 29 shows the relationship between mixing time and resistance using a 3.5%CMC solution.

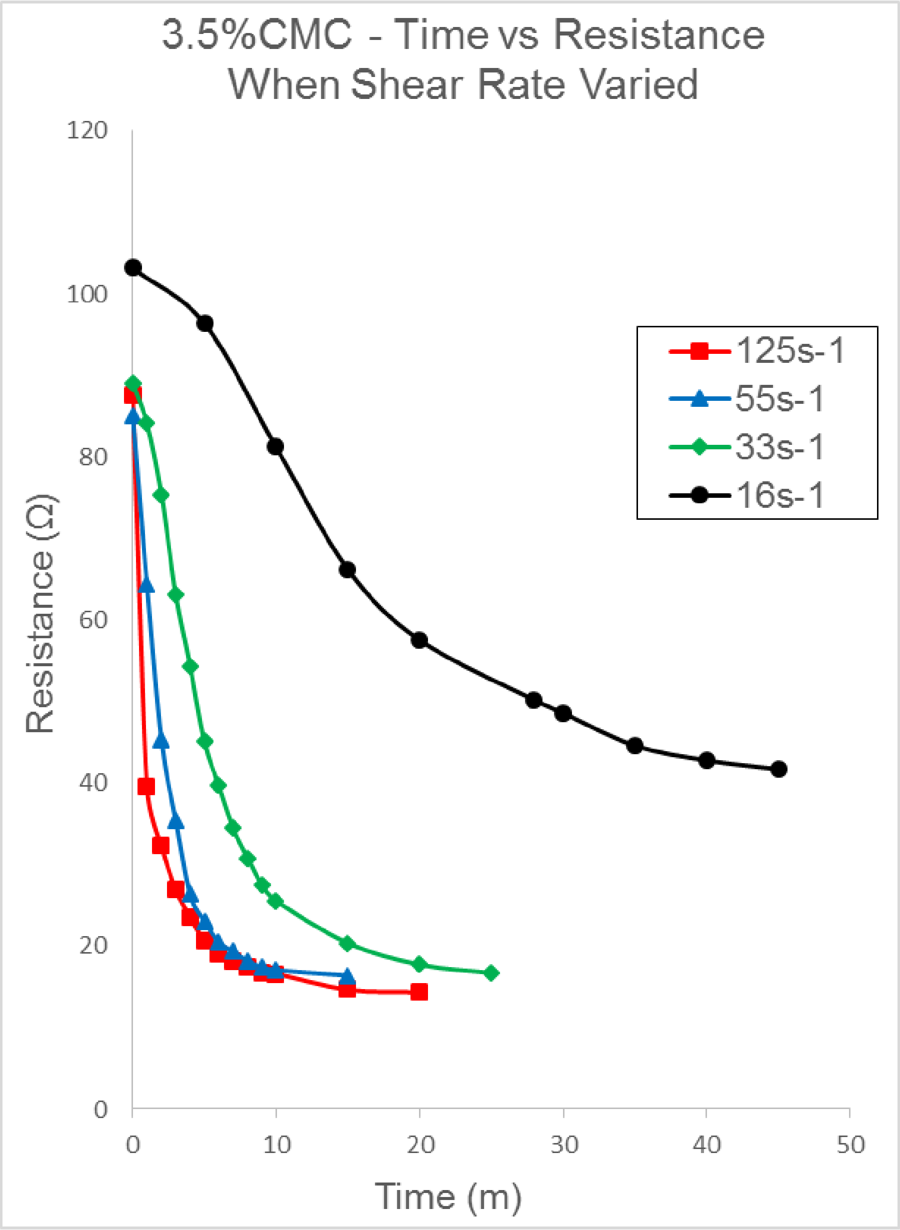


Figure 29 – Time verses resistance for key shear rates using a 3.5%CMC solution

Maximum and minimum values of resistance were compared and 40, 80 and 90 percent of extreme range values measured were calculated to represent similar levels of homogeneity. Times (in decimal minutes) to achieve levels of mixing are listed at Table 5.

	3.5% CMC		
	Degree of Homogeneity		
Shear Rate (s^{-1})	**40%**	**80%**	**90%**
125	0.7	2.7	4.7
55	1.5	3.6	5
33	3.4	8	12
16	10.1	21.6	28

Table 5 – Effects of shear rate on mixing time (in decimal minutes) to achieve various degrees of homogeneity using 3.5%CMC

After considering the importance of effective mixing to the process and on observing the profile of the resistance degradation and the way the profile rapidly levelled out as time progressed, 90 percent homogeneity was selected as a minimum acceptable degree of mixing. Table 6 lists the independent variables used in the batch process experiment. Throughout the ERT modelling AC was found to be more appropriate than DC due to electrolysis occurring when the latter was attempted.

Shear Rate (s^{-1})	16	33	55	125	-
DC Voltage (V)	2.5	4	6	12	
On Period (minutes)	28	12	5	4.7	-
Off Period (hours)	0	1	3	6	12

Table 6 – Intended input parameters used in batch process experiment

2:4 Conclusions

For clarity, conclusions have been separated into 2 distinct groups to differentiate between those that:

- Effect more general practices such as pumping or mixing and hence may have broader scientific implications.
- May specifically affect CH_4 production in the AD process.

As mixing is recognised as having a direct impact on CH_4 production (Stroot et al., 2001) those conclusions associated with mixing/pumping may also have an indirect impact on CH_4 production.

2:4:1 Mixing, Pumping and Broader Scientific Implications

The following conclusions were made:

- Cow slurry is a non-Newtonian fluid that demonstrates shear-thinning thixotropic properties above 5%TS and follows the Herschel-Bulkley model of fluid flow. Apparent viscosity is influenced by %TS, temperature, conditioning and shear rate, properties that can induce a large range of shear stress values (at least 412 Pa) that equipment/components would have to overcome.
- Highest shear stress is experienced when high %TS low temperature samples are initially exposed to high rates of shear force. Induced shear stress can therefore be minimised by:
    - Diluting the slurry with water.
    - Increasing the temperature of the slurry.
    - Conditioning the substrate through practises such as continuous mixing.
    - Minimising shear rate.
- Highest apparent viscosity is experienced when high %TS low temperature samples are initially exposed to low rates of shear force. Induced apparent viscosity can therefore be minimised by:
    - Diluting the slurry with water.
    - Increasing the temperature of the slurry.
    - Conditioning the sample.
    - Maximising shear rate (a measure that conflicts with that taken to reduce shear stress).

- Cow slurry between 6%TS and 12%TS requires an applied shear rate of approximately $1.5s^{-1}$ to yield and begin to flow at temperatures of 10, 25 and 37˚C (55˚C and 70˚C were not measured). Yield stress values at the yield point can range from 45 to 122 Pa at 37˚C and 10˚C, respectively.
- Solids content has the greatest effect on fluid shear stress and apparent viscosity which increases exponentially as %TS increases.
- Temperature is the second most influential factor on shear stress and apparent viscosity.
- Conditioning is the third most influential factor.
- The shear rate of $20s^{-1}$ is key when handling cow slurry at all levels of %TS analysed as this is the point above which the majority of shear thinning has taken place. However, once above $20s^{-1}$ shear rate had the least effect on shear stress and apparent viscosity, particularly when comparing mesophilic and thermophilic conditions with the former experiencing lower shear stress but higher apparent viscosity.
- A rest period of 1 hour allows shear-thinned cow slurry to regain original non-Newtonian characteristics.
- CMC was an appropriate substitution fluid to support the initial stages of the ERT modelling when fluid transparency was required to correctly position the electrodes.

Due to the nature and influence of conditioning, a dimensionless relationship could not be produced to directly compare the effects of individual and combinations of variables on the rheological characteristics of cow slurry.

2:4:2 Potential Effects on CH_4 Production in the AD Process

If shear stress is accepted as having the potential to disrupt the microbial communities that include the methanogens responsible for producing CH_4, a substrate's rheology may effect CH_4 production because:

- The levels of shear stress experienced by dairy farm slurry when pumped/mixed is primarily influenced by the solids content and temperature of the slurry and the rate and length of time that the shear force is applied. Rest periods associated with intermittent mixing also have an effect on the shear stress induced when mixing starts again if recovery from thixotropy is allowed.

- Increasing shear rate is the only variable that has a conflicting effect on shear stress and apparent viscosity which could be particularly relevant when prioritising between substrate homogeneity/heat distribution and minimising microbial shear stress.
- The reduction of shear stress which takes place in slurry as temperature increases may have a positive effect on CH_4 production because:
    - Higher process temperatures reduce the shear stress to which microbial communities are subjected, particularly when the %TS is higher. Hence, thermophilic bacteria could experience up to 30 percent less shear stress than mesophilic.
    - Optimum mesophilic and thermophilic temperatures are at or above the 37˚C cut-off below which the rate of change of shear stress is much higher per degree of temperature change. So, microbial communities could enjoy more stable levels of shear stress during small fluctuations in temperature than those in lower temperature environments. However, such benefits may be relatively insignificant when compared to the potential gains of operating equipment in the less viscous environment experienced when operating at higher temperature.
- Thixotropic effects associated with conditioning could have a substantial effect on the levels of shear stress to which microbial communities are subjected. For example, at mesophilic temperatures shear stress levels post-shear are approximately 24 percent lower than those experienced during pre-shear conditions and 34-53 percent lower than Initial values (higher percentage reduction achieved at lower shear rate). Of course, the latter must be experienced before realising the former, but once achieved may encourage continuous mixing to maximise the benefits of lowering shear stress. Conversely, intermittent mixing could periodically subject microbial communities and mixing components to relatively high levels of shear stress due to increases in the viscosity of the fluid after resting. This could increase CH_4 production as microbial communities would experience lower extremes of stress if the process is continuously, rather

than intermittently, mixed. This could be particularly relevant if an intermittent mixing regime includes long periods of dormancy allowing the fluid‘s viscosity to recover.

2:4:3 Application of Conclusions

Homogenising a fluid effectively whilst inducing minimum shear stress to the microbial communities and minimising parasitic energy to do so requires strict control of the mixing process and subsequently the equipment used. In turn, effective automation of that process will rely on current and accurate parametric data inputs informing control algorithms. Realistic parameter selection and mixer positioning will therefore be reliant on a sound understanding of the rheology of the substrate in question. Apparent viscosity provides a clear indication of the current state of the fluid as a result of %TS, the shear rate the slurry is being subjected to, slurry temperature and any conditioning experienced or period of resting. However, Doran (2013) provides evidence that this is only relevant to the localised point of mixing and not necessarily to the whole digester; indeed, the rate of shear being applied in other areas of the digester will be a factor of the bulk fluid flow inducing it. Depending on the design and capacity of the digester, this may be very different to the shear stress measured at the point of mixing, as will be the resultant apparent viscosity. To avoid areas of ineffective mixing (dead zones) within the digester, sufficient shear rate must be generated at the point(s) of mixing to induce the apparent viscosity required at the slowest point of fluid flow over the whole digester if complete homogeneity is to be realised. Hence, to understand the conditions experienced around the digester the characteristics of the fluid at any particular time and location must be known so that an appropriate degree of mixing/agitation can be applied where needed to achieve and maintain homogeneity to ensure optimisation of the biodegradation process. Hence, knowledge of the range of likely extremes of values that a mixing system will need to address is essential to inform digester design. The practical experimental analysis demonstrated that %TS has the greatest effect on the apparent viscosity of cow slurry and is a reliable indicator of the general non-Newtonian status of the 3-phase substrate at the point of mixing if the temperature and applied shear rate is known. Fortunately, the content and calorific value of dairy farm slurry being fed into the process is generally predictable allowing the consistency or

%TS of the slurry to be more readily estimated. Furthermore, should heavy rainfall over exposed dairy working areas of a farm dilute the slurry, the resultant drop in %TS will cause a reduction in shear stress and apparent viscosity and hence benefit the mixing process.

Mixing Newtonian fluids rather than their non-Newtonian counterparts is accepted as being more predictable and therefore less complex. If we accept that a less than 5 percent change in apparent viscosity over a 10s^{-1} increase in shear rate results in Newtonian fluid flow then slurries can be managed to benefit from those characteristics in the following way:

- Slurries of 5%TS at 25˚C require a shear rate of 30s^{-1} to be applied before being characterised as Newtonian; this does not reduce over time and seems to be the thixotropic limit of the slurry. If process temperature is increased to 37˚C, the necessary shear rate to maintain Newtonian flow reduces to 20s^{-1} (the pre-shear temperature of 37˚C when subjected to a shear rate of 20s^{-1} was just above the Newtonian boundary at 5.11%).
- Slurries of 6%TS at 25˚C also required an applied shear rate of 30s^{-1} before demonstrating Newtonian characteristics, although that reduced post-shear to 20s^{-1}, if heated to 70˚C.
- Slurries of 7%TS at 25˚C demonstrated Newtonian characteristics when subjected to a shear rate of 40s^{-1} after the Initial run which required 50s^{-1} (reducing to 40s^{-1} at 37˚C). The shear rate requirement reduced further post-shear when heated to 55˚C (20s^{-1}).
- 8%TS slurries tended to require shear rates above 60s^{-1} to appear Newtonian although this could be reduced slightly, if heated.
- 9%TS appeared to be the highest %TS fluid that would adopt Newtonian characteristics at shear rates of 60s^{-1} and above, across all conditions. However, Initial conditions would require heating to 55˚C to do so.
- After post-shearing, slurries of 10%TS and 11%TS required heating and a shear rate of 60s^{-1} before flow became Newtonian.

As shear rates below 20s^{-1} will result in high apparent viscosity at all levels of %TS analysed, particularly at lower temperatures, design and operation of the mixing regime in the digester could be influenced to avoid/reduce higher levels of apparent viscosity levels and the effects they incur. Such effects could include higher than necessary parasitic energy demand, increased wear on equipment, a higher maintenance burden and a shortening of equipment life. Although low rates of shear must be transited before reaching higher shear rate conditions, the length of the transit period could be minimised by employing a mixing technique with rapid shear rate acceleration. Conversely, if the %TS of the fluid is known, before mixing commences the fluid could be heated to a temperature region that enjoys Newtonian conditions and then reduced to the process operating temperature, once homogenised. This could be particularly useful at start-up or after a prolonged dormant period caused by non-routine maintenance. Of course, without mixing, the fluid will experience a temperature gradient which could reduce the benefits of pre-heating if the heat source is not located at the point of mixing, such as around the perimeter of the digester wall. An alternative may be dilution with water to reduce %TS to a level easier to manage.

2:5 Next Research Step

Key outcomes of this rheological analysis will now be exploited in an attempt to:

- Quantify the impact of shear rate on methanogen communities and hence CH_4 production when cow slurry is digested under batch AD process conditions.
- Quantify the impact of resting (intermittent mixing) on methanogen communities and hence CH_4 production when cow slurry is digested under batch AD process conditions.
- Model CH_4 production and the parasitic energy demand of a range of mixing regimes used to produce the gas to identify the optimum AD mixing regime for cow slurry using a batch AD process.

CHAPTER 3 – EFFECTS OF MIXING REGIME ON CH_4 PRODUCTION IN A BATCH PROCESS

3:1 Introduction

The application of shear rate is necessary to achieve homogeneity within a fluid. However, too much can influence microbial community diversity (Hoffmann et al., 2008), disrupt microbial community metabolism (McMahon et al., 2001) and waste energy (Deublein & Steinhauser, 2011), thereby reducing the net energy gain of an AD process. Conversely, resting the fluid may give the embedded microbial communities time to recover from the disruption caused by mixing and realise the benefits of product removal. Mixing is also a primary requirement for mass transfer and heat distribution which in turn are intrinsically linked to CH_4 production (Wu, 2012b). Quantifying the effects of different mixing regimes on methanogenesis, parasitic energy use and hence net energy production would provide useful information when optimising AD systems.

3:1:1 Benefits of Batch Processing

The batch process provides a fixed environment in which to observe the effects of specific variables on a single charge of feedstock. Temperature and nutrient input were fixed so that the shear rate intensity and resting element of intermittent mixing could be temporally separated to identify the impact of each on microbial kinetics and CH_4 production. Non-mixed and continuously mixed regimes were also investigated.

3:1:2 Aims

The aims of this chapter are to:

- Quantify the effects of shear rate and resting (intermittency) on methanogenesis and hence the rate of CH_4 production and cumulative yield during a 21-day batch process.
- Compare cumulative CH_4 yield and produce a dimensionless yield factor (YF).
- Compare the parasitic energy demand of each mixing regime and produce a dimensionless power factor (PF).
- Combine YF and PF values for each mixing regime to produce an overall comparative rating on which a net energy gain performance hierarchy can be based.
- Identify any trend in CH_4 production rate that could inform HRT optimisation in terms of CH_4 production.

3:2 Materials and Method

Anaerobically processing cow slurry can be procedurally challenging due to the lack of consistency of the substrate and CH_4 yield. Accurately monitoring and comparing different digestion processes over a set period required digester configurations to be duplicated to provide statistically meaningful values and increase accuracy.

3:2:1 Limitations Associated With Lab-scale AD Research

Fouling was an issue when attempting to process cow slurry as the substrate was not easily accommodated by lab-scale equipment, particularly hoses and components with relatively small internal-diameters. Also, mixing reduces the thermal gradient across a digester, an essential requirement when optimising the AD process. Heated baths are a common solution by which ideal constant temperature conditions can be maintained despite thermal variation in the surrounding environment. Using such apparatus for this research task could mask benefits of mixing such as heat transfer, particularly if attempting to compare the performance of mixed digesters with unmixed.

3:2:2 Data Requirements

Results from chapter 2 demonstrated that shear stress and apparent viscosity are directly dependent on %TS, temperature, shear rate, the length of the mixing period (conditioning) and the time rested. By fixing %TS and temperature, the effects of shear rate intensity, mixing period and resting associated with intermittent mixing were identified and CH_4 production measured. The parasitic energy demand associated with each mixing regime was also monitored to calculate net energy production.

3:2:3 Equipment

Consistency of farm slurry can vary considerably so calorific values (CV) and hence CH_4 potential may vary within each sample. Therefore, mean CH_4 production values were obtained using digesters running in parallel but fed using the same sample. The Automatic Methane Potential Test System (AMPTS II) Bio-processor manufactured by Bioprocess Control Sweden AB provided a means of supporting trials for up to 15 sub-samples per unit (Bioprocess Control Sweden AB, 2012). The system consisted of 15 x 500ml digesters housed in a common heated water bath (unit on left in Figure 30). Each digester used a stirring rod mixing system driven by an independent top-mounted 12V DC motor. Inlet and outlet pipes provided access to the digester headspace for feeding and biogas removal, respectively. Biogas pressure naturally increased in the digester headspace (as biogas formed) forcing the gas through a connecting hose to a dedicated 100ml gas processing vessel containing a sodium hydroxide (NaOH: Sigma-Aldrich 221465) solution that included a pH indicator, Thymolphthalein ($C_{28}H_{30}O_4$: Sigma-Aldrich 114553) (unit in centre of Figure 30). CO_2 was absorbed by the NaOH and the remaining gas, primarily CH_4, passed through a further connecting hose to a water bath containing a hinged flow cell that accommodated 10ml of gas (green chamber in right of Figure 30). When the flow cell was full, buoyancy lifted the cell releasing the CH_4 to atmosphere through the water and gravity reset the cell. A counter recorded the event and time of each release thereby registering CH_4 production, in terms of normalised millilitres (Nml) and flow rate. An assumed CH_4:CO_2 biogas ratio was selected by the operator. Each digester had a separate measuring system that fed data to a process monitoring and control system that presented the data in raw and graphical form. Alternatively, each unit could accommodate up to 6 x 2000ml digesters for analysing larger samples. This research had access to 3 AMPTS II units (45 x 500ml digesters). Most farm AD systems operate at mesophilic temperatures so the process temperature was fixed at 37.5˚C.

Figure 30 – Automatic Methane Potential Test System II
(courtesy of Bioprocess Control Sweden AB)

3:2:4 Equipment Limitations

The potential support that the AMPTS II system offered was initially limited as each unit was subject to a single mixing protocol, resulting in a similar shear rate and mixing regime being applied to all digesters in that unit.

3:2:5 Methods Adopted to Address Limitations

Although 3 units could accommodate 3 shear rates, variations in mixer on and off periods necessary to compare intermittent mixing regimes had to be individually applied to each digester. The dimensions of the stirrer configuration supplied was used to calculate the rpm necessary to generate the required shear rates using formula provided by the manufacturer of the rheometer and confirmed using an adaptation of that used by Clarke & Greenwood (1993), as follows:

$$Shear\ rate\ (ý) = \frac{\omega\ r^i}{r^d - r^i} \qquad \text{Equation 5}$$

The formula was re-arranged as follows:

$$\omega = \frac{ý\ (r^d - r^i)}{r^i} \qquad \text{Equation 6}$$

where ω is the rotational velocity (*rads*$^{-1}$), r^i is the external radius (m) of the circle made by the rotating stirrer tip (at tip depth) and r^d is the internal radius (m) of the digester, again at tip depth. As this equated to stirrer tip velocity divided by the gap between the 2 surfaces at which the shear rate was being measured and the gap remained constant, shear rate was defined by stirrer rotational velocity. This provided the maximum shear rate subjected to the contents of the digester. Calculation of rpm was achieved using:

$$rpm = \frac{\omega \cdot 60}{2\pi} \qquad \text{Equation 7}$$

By selecting a shear rate, the necessary rotational velocity could be calculated and converted to an rpm that was measured and adjusted using a strobe light. Digesters were then grouped using a communal shear rate requirement and motors electronically connected in parallel to provide the necessary stirrer rpm to the variable speed DC motors. Power was provided using individual DC generators for each shear rate group. Further grouping allowed common mixing regimes/rest periods to share common electrical circuits that were timed to switch on and off at specific intervals using programmable logic controllers (PLC).

3:2:6 Variables

Key variables used were:

- Independent (control) variables consisting of shear rate and mixer on and off periods. Shear rate values were selected to straddle the key shear rate of $20s^{-1}$ above which the majority of shear-thinning has taken place (identified in chapter 2). Mixer-on periods were calculated to achieve a specific minimum level of homogeneity and mixer off periods to reflect protocols appropriate to farm AD operations.
- Dependent variables consisting of CH_4 production (Nml), in terms of daily production rate and cumulative yield. As each shear rate was associated with a parasitic energy requirement when the mixer was operating, the voltage and current required to achieve a particular shear rate for each mixing regime was used to estimate power consumption.

The AMPTS II required a CH_4 content of the biogas to be assumed and programmed into the system. In addition, access to gas analysis equipment was not available so biogas composition was not included in the study. VFA analysis and alkalinity testing was also excluded as simple pH monitoring was regarded as adequate to monitor process stability of the simple batch experiment.

3:2:7 Assumptions

The analysis was based on the following assumptions:

- 1ml of sample weighed 1g.
- A common CH_4:CO_2 biogas ratio of 60:40 for all digesters was programmed into the AMPTS II.
- Levels of H_2S produced were insignificant.
- Continuous mixing used the lowest level of mixing intensity to minimise power consumption.

3:2:8 Feedstock

Fresh slurry was secured from the same farm used during the rheology analysis. Inoculum was provided by Langage Farm AD, a municipal solid waste (MSW) plant situated in Devon, UK. MSW inoculum was selected due to the high levels of biomass contained, the reliability of the source and the immediate digester start-up that the inoculum enabled. A 50:50 slurry:inoculum charge of 10%TS was introduced at the start of the experiment using relatively high 15.5%TS slurry (Table 7). A 75:25 ratio was considered but the resultant 12.7%TS was regarded as too high to be representative of the long-term solids content of a dairy farm digester which was estimated as 10%TS. The slurry sample was gently mixed prior to being divided into sub-samples.

Experimental Process	**Slurry %TS (%VS)**	**Inoculum %TS (%VS)**	**50:50 mix %TS (%VS)**	**Biodegraded Feedstock %TS (%VS)**
Batch	15.5 (66.1)	4.4 (68.6)	10.0 (68.0)	3.32 (0)

Table 7 – Planned substrate %TS and %VS values

3:2:9 Digester Procedure and Set-up

Three AMPTS II units consisting of 42 x 500ml digesters were used to quantify the effects of a range of shear rates on methanogenic activity by comparing the levels of CH_4 that each community produced. Each digester was charged with cow slurry and inoculum totalling 400g leaving 20 percent headspace for biogas accumulation. The experiment ran for 21 days.

Each shear rate to be investigated was allocated 3 digesters, 1 control sample charged with 50:50 inoculum and de-ionised water and the remainder with 50:50 inoculum and cow slurry. Each shear rate was matched to a stirrer 'on' period that would achieve the required homogeneity as defined by the ERT modelling detailed in chapter 2 (Table 6). 'Control' digesters would likely achieve higher levels of homogeneity due to their lower %TS. Mixer 'off' periods of 1, 3, 6 and 12 hours were selected to reasonably capture the 12-hour routine associated with a twice-daily milking practice of a typical dairy farm which was regarded as the maximum practical rest period. Digester trios for each shear rate/mixing period configuration were grouped into digesters with similar shear rate requirements (Figure 31). 'Non-mixed' and 'continuously mixed' regimes were also included for completeness. However, if continuous mixing was implemented commercially, mixing would likely be carried out at the lowest shear rate that achieved effective mixing to minimise parasitic energy use so that level of intensity was applied. Shear rates of 33, 55 and 125s^{-1} were selected based on the outcome of trials conducted during the initial stages of the experiment (outlined in the results section). With the exception of the 'non-mixed' digester trio, each AMPTS II unit was allocated a shear rate at which to mix, allowing a single DC power supply to be used. Voltages required to produce the selected shear rates were identified in pre-experiment trials described in the results section. PLCs were configured to provide the necessary on/off periods for each digester trio. Mean CH_4 production values were achieved by taking the average CH_4 output of each pair of slurry/inoculum-fed digesters and subtracting the CH_4 value produced by the control digester associated with that pair.

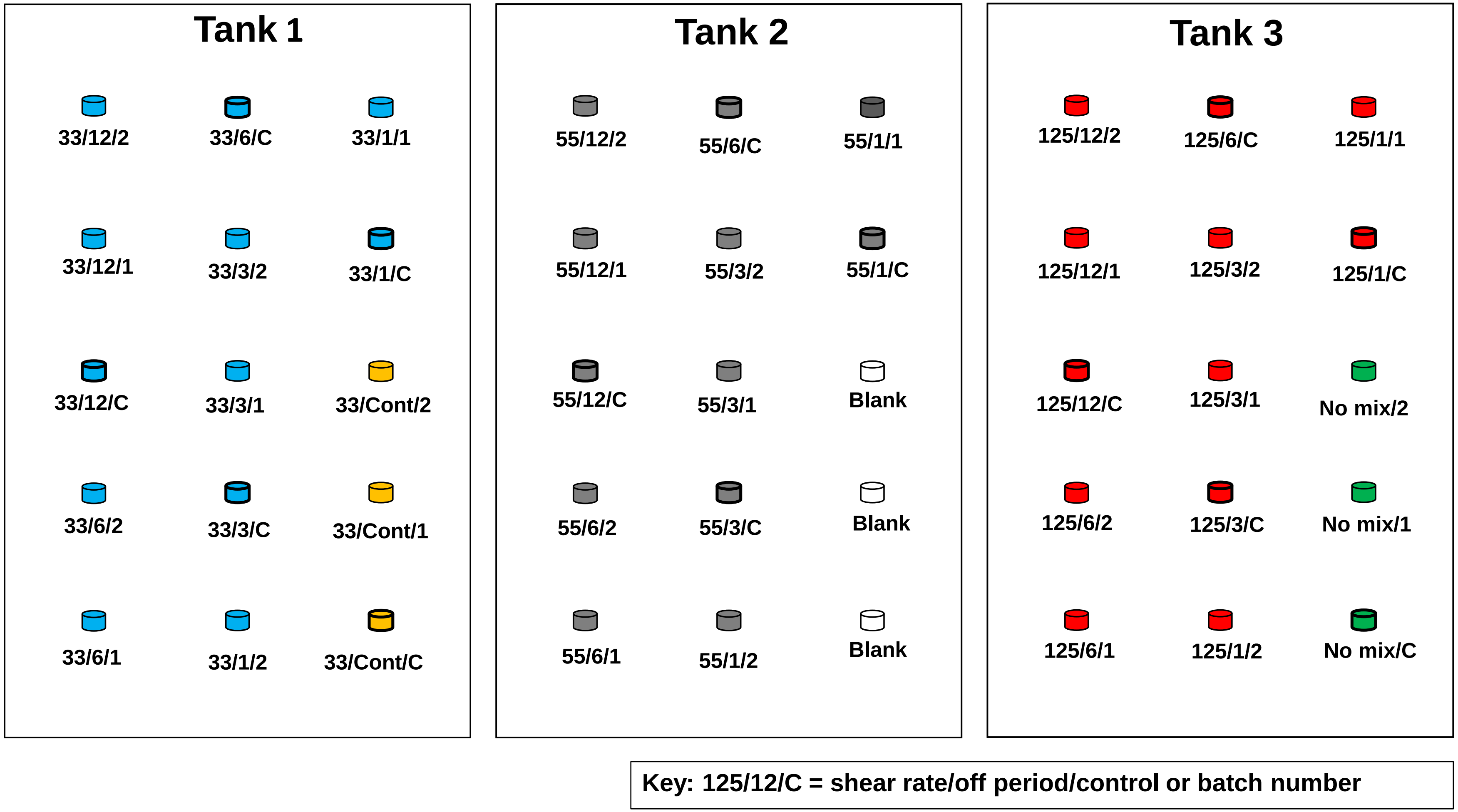


Figure 31 – Digester configuration for batch experiment

3:2:10 Data Comparison

The potential for the mixing regime of a digester to influence CH_4 production rate (flow) and cumulative yield was substantial (Stroot et al. 2001; Kaparaju et al. 2008). However, these key metrics could have opposing implications when designing a system or process. Cumulative CH_4 yield over the length of the batch process quantifies the maximum potential levels of gas generated. However, if the feedstock is a cost-free waste slurry, variations in the rate of CH_4 production over the period required to achieve complete bio-degradation of the VS may have a greater influence on financial viability than ultimate yield. Hence, both metrics were measured. In addition, the specific CH_4 production rate was also calculated to inform digester design. But financial viability of a digester also depends on gas production outweighing costs such as those generated by the parasitic energy demanded by the process. Calculating net energy output by balancing the energy value of the CH_4 output and the mixing energy input was achieved by reducing all energy to be compared to a baseline unit, the kilowatt hour (kWh). To do so required the following assumptions:

- A volume of $1m^3$ of biogas is equivalent to $2.2kWh_e$ of electricity (Andersons Centre, 2010) although some claim $2.4kWh_e$ (Deublein & Steinhauser, 2011). The first figure assumes that a small-scale CHP engine of approximately 30 percent electrical conversion efficiency is used and this figure was used as the default in this analysis.
- Biogas is assumed to consist of 60 percent CH_4 so 1 m^3 of CH_4 is therefore equivalent to approximately $3.67kWh_e$ if used to fuel a CHP engine.

3:2:10:1 Power Factor

Mixing efficiency can be determined by the amount and length of time power is consumed (Ochieng & Onyango, 2008) and is integral to the energy balance of a system (Deublein & Steinhauser, 2011) and therefore net energy output. As the components of mixing regime (mixer on/off periods and shear rate) were key variables the power demanded of each regime was recorded to identify the parasitic mixing energy used by each digester. A dimensionless value (based on the kWh) was devised to allow the parasitic energy value of each mixing regime to be compared. As there were variations between the current demanded and hence electrical efficiency of each of the 42 DC motors when a fixed voltage was applied, mean values were used. Each voltage/mean current pair provided a mean power for the 3 mixer shear rates used. As on/off periods for each mixing regime over the experimental period was known the maximum power demanded by each was calculated. The total power demanded by the most efficient mixing regime was then used as a baseline into which the total power used by each regime was divided to provide a dimensionless PF on which a hierarchy could be based.

3:2:10:2 Yield Factor

Using the kWh as a baseline unit a dimensionless hierarchy was again derived to compare the cumulative CH_4 yields achieved by each mixing regime. The cumulative yield (Nml) of the highest producing regime was divided into the cumulative yield of the others to provide a rating, termed the YF from which a common hierarchy could be produced.

3:2:10:3 Overall Comparison Using Power Factor and Yield Factor

The units of measurement used to quantify parasitic energy was the kWh whereas CH_4 yield was measured in Nml. To allow PF and YF to be combined to provide an overall comparative rating a baseline relationship was identified. As $1m^3$ of CH_4 is equivalent to 3.67kWh of electrical output a direct comparison was possible by correcting the YF to account for the conversion of CH_4 to kWhs of electricity. YF was corrected by dividing the YF value by 3.67. The overall comparison rating was a factor of PF and corrected YF.

3:2:10:4 Specific CH_4 Production Rate

Bensmann et al. (2013) regarded temporal distribution as an important factor in digester design whereby the digester is large enough to support maximum gas yield. However, the author also suggested that selecting a HRT that supports only the period of maximum achievable specific CH_4 production rate allows digester capacity to be optimised for CH_4 production at minimal investment. In short, a lower HRT requires a smaller digester and is therefore economically favourable (Keshtkar et al., 2003). Specific CH_4 production rate (SPR) is given as:

$$SPR = \frac{maximum\ \mathrm{CH4}\ production\ rate}{digester\ volume} \qquad \text{Equation 8}$$

3:2:10:5 Overall Comparison Using Specific Production Rate and Power Factor

This was not appropriate for reasons described alongside the results to which they refer.

3:3 Results and Discussion

3:3:1 Evolution of Experimental Technique

The rheological analysis in chapter 2 demonstrated that the major extent of shear thinning of dairy slurries above 5%TS occurred before a rising shear rate had reached $20s^{-1}$ at all temperatures investigated (Figure 32). Above this key level, apparent viscosity levelled out to become relatively constant until $60s^{-1}$ was reached (the limitation of the AR2000) and limit viscosity was achieved in lower %TS slurries. Similar research found the trend continued at shear rates well above $60s^{-1}$ (El-Mashad et al., 2005).

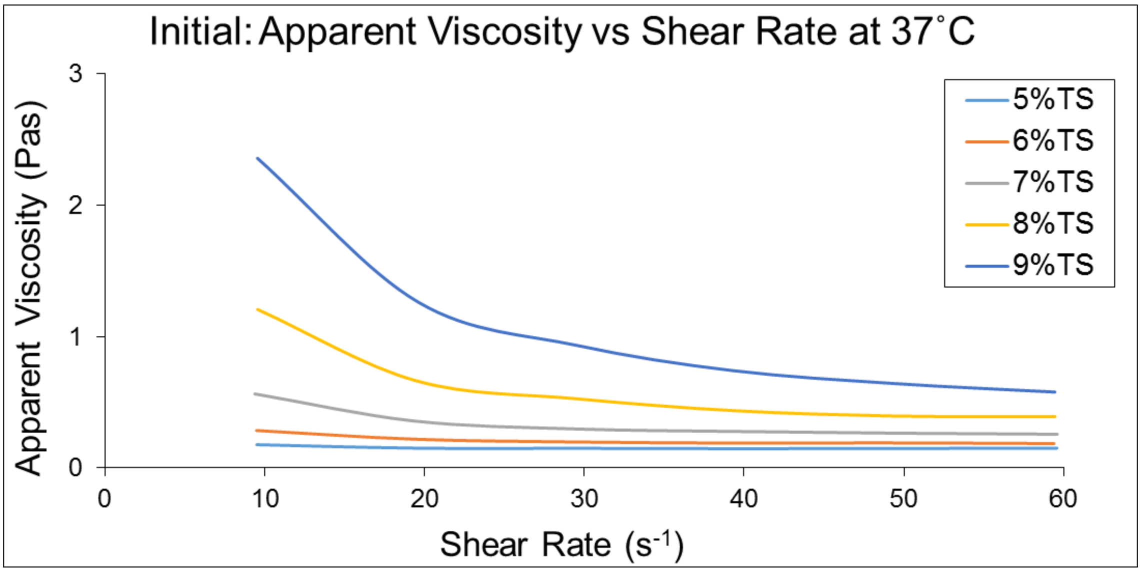


Figure 32 – Effect of shear rate on apparent viscosity of cow slurry

To quantify the effect of shear rate on CH_4 production either side of the key shear rate of 20s^{-1} initial experiments were designed to capture shear rates of 16, 33, 55 and 125s^{-1}. However, over prolonged periods, voltages applied to the stirring motors to achieve shear rates less than 25s^{-1} were often insufficient to overcome the yield stress of the substrate and rotate the stirrer mechanism used by the AMPTS II bio-processor. This was particularly evident when re-initiating stirring after the substrate had been subjected to long periods of rest so may have been due to post-thixotropic fluid recovery observed in sewage sludge (Eshtiaghi et al., 2012). Settling of particulates at stirrer tip depth may also have been a factor (Hashimoto & Chen, 1976). To guarantee the movement of fluid in all digesters when demanded by the procedure, different shear rates were tested and 33s^{-1} was observed as the minimum shear rate that would guarantee stirrer rotation across the range of viscosity values predicted during the batch process. Shear rates of 55 and 125s^{-1} were selected to provide CH_4 production data across the remaining range of shear rates to include a value close to the maximum investigated using the AR2000 rheometer (60s^{-1}) and a value approximately 4 times the lowest shear rate monitored (132s^{-1}). A limit of 125s^{-1} was imposed as that was the maximum achievable using the 12V DC motor and 3.5%CMC.

The task of ensuring 42 digesters performed as required proved challenging. Initial issues included leaking valves in gas lines, unreliable and erratic DC voltage generators and incorrectly programmed PLCs. However, a trial period resolved all issues and all digesters performed to the required standard for the duration of the experiment. The requirement to programme the AMPTS II with a common assumed CH_4 content of all biogas produced also attracted concern as the practice could mask effects that mixing regime may have had on biogas quality, primarily CH_4 and CO_2 content. By assuming a level of CH_4 content and not measuring biogas yield, the volume of CO_2 removed during gas purification was not quantified. Hence, the efficacy of the research could have been improved by individually measuring the biogas produced and the CH_4 content of all gaseous products and using the data to calculate biogas quality. Process stability was adequately monitored using pH.

3:3:2 Cumulative CH_4 Yield

Daily rates of CH_4 production for each mixing configuration indicated the extent of gas produced during particular periods within the batch process. Meanwhile, cumulative CH_4 yield over the duration of the process quantified what could be achieved if the process period was altered. Indeed, both metrics were used to compare digester success. However, the specific daily production rate may have more influence when sizing a digester to optimise volume for net energy gain. Figure 33 provides a comparison of cumulative CH_4 yields achieved by all configurations. At first glance, an obvious high-to-low hierarchy was observed with high shear rate mixing producing more CH_4 than intermediate mixing and low shear rates producing the least as suggested by Sindall et al. (2013). A shear rate of $125s^{-1}$, rested for 1 hour, produced 3000Nml which equated to $110.6Nml_{CH4}g^{-1}{}_{VS}$ in 21 days. Meanwhile, mixing at $33s^{-1}$ rested for 12 hours produced the least CH_4 (2636Nml) that equated to $97.2Nml_{CH4}g^{-1}{}_{VS}$. These extremes differed by 12.2 percent. On all counts, the gradient of the profile tended to begin to ease at approximately day 7 indicating that the majority of the CH_4 produced over the experimental period occurred in the first 7 days as reported by the Andersons Centre (2010). However, although the lowest shear rate within each rest grouping produced the lowest CH_4, lowest shear rates did not necessarily produce the lowest yields when rest groups were compared so a more detailed analysis was required.

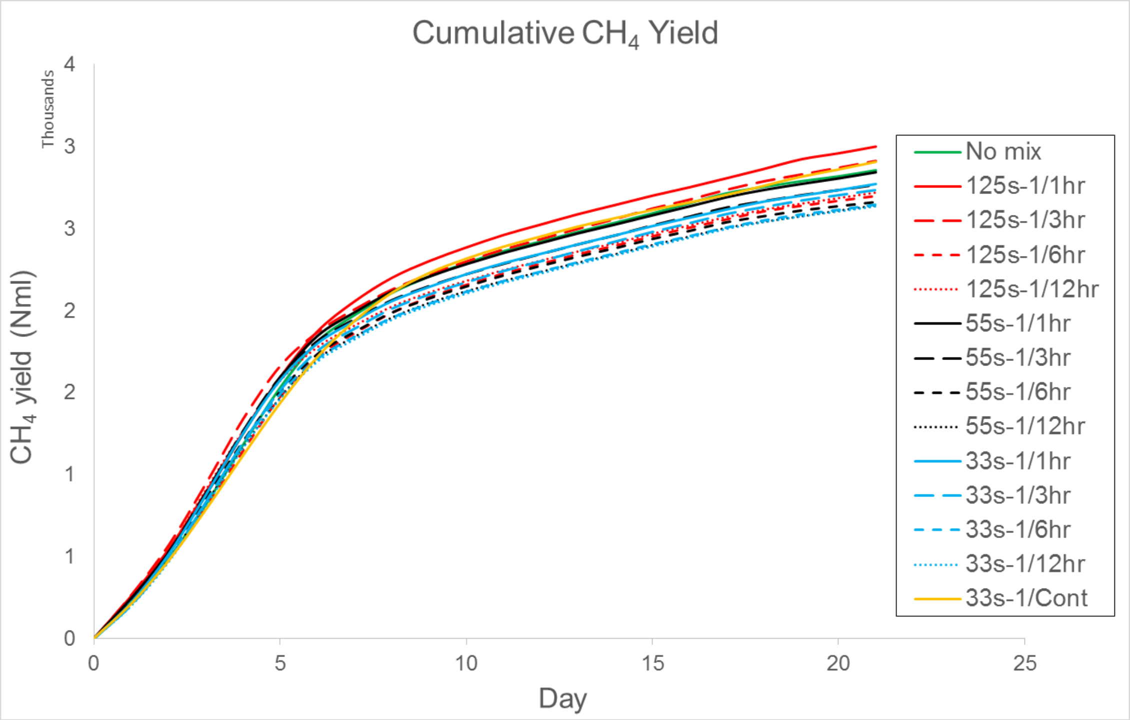


Figure 33 – Cumulative CH_4 yield achieved by all mixing regimes

3:3:2:1 Effect of Shear Rate on Cumulative CH_4 Yield

Stafford (1982) found that increasing shear rate when mixing sewage sludge resulted in no improvement in biogas production when mixing with impeller speeds of 140-1000rpm. The highest mixing level associated with this study was 140rpm using a shear rate of $125s^{-1}$. On detailed analysis, the common high to low hierarchy of cumulative CH_4 yield observed within rest period groupings indicated a maximum variation of 7.6 percent within a shear rate regime adopting a similar rest period of 1 hour (Figure 34). The minimum variation was achieved when a digester was rested for 6 hours (1.9 percent). Variations within the 3 and 12-hour regimes were 6.2 and 3.1 percent, respectively. However, the CH_4 yield hierarchy observed when comparing mixed digesters were different for each rest period which confirmed conflicting results previously reported when digesting other wastes (Tian et al., 2013; Ghanimeh et al., 2012). This may be due to microbial communities responding to shear rate in different ways at particular stages of the process (Stroot et al., 2001). Moreover, although shear rates above $20s^{-1}$ (and hence Newtonian fluid flow) were achieved at the point of mixing this would not have been so across the whole digester meaning microbial communities within the digester were not subjected to a uniform degree of mechanical stress and may have metabolised at different rates.

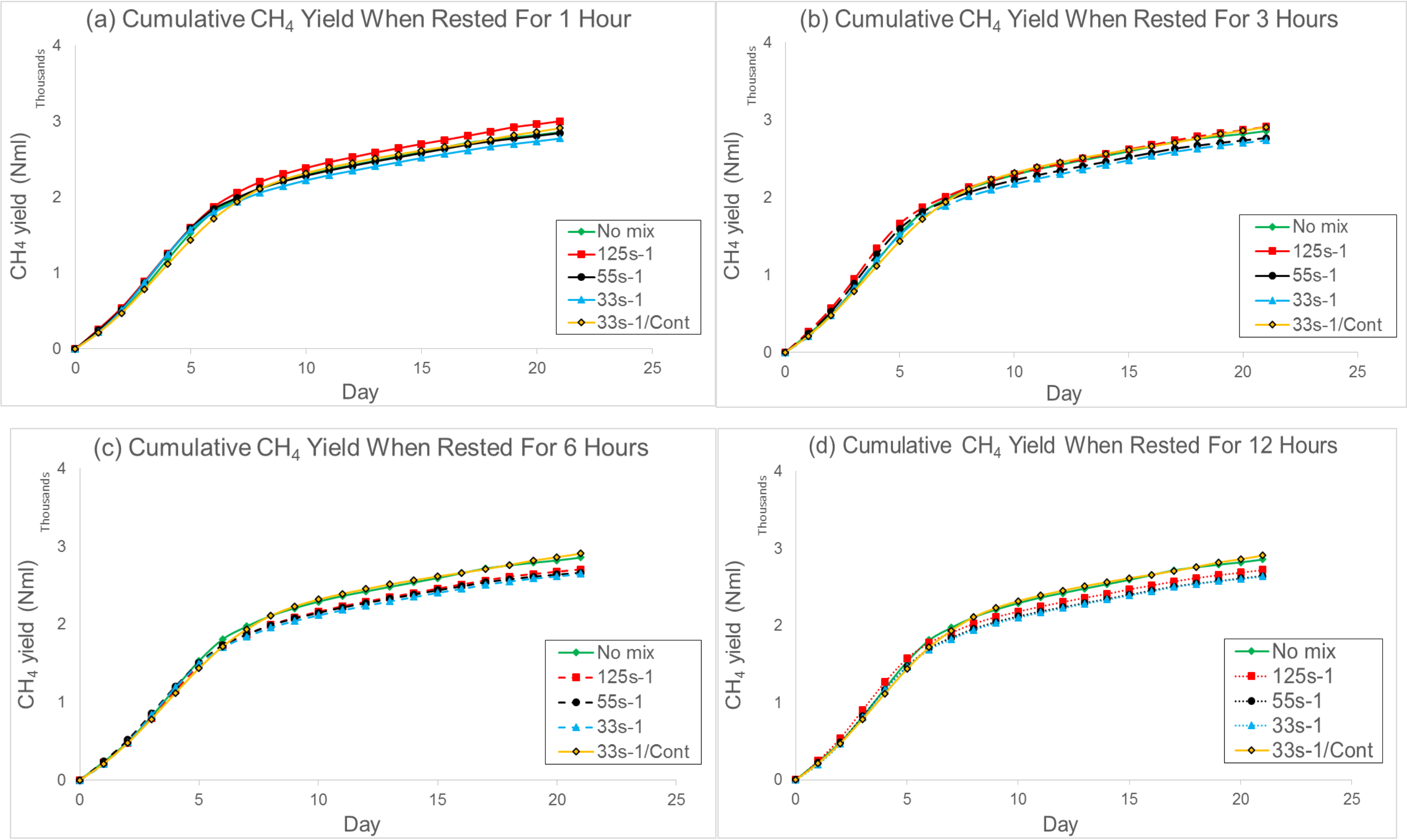
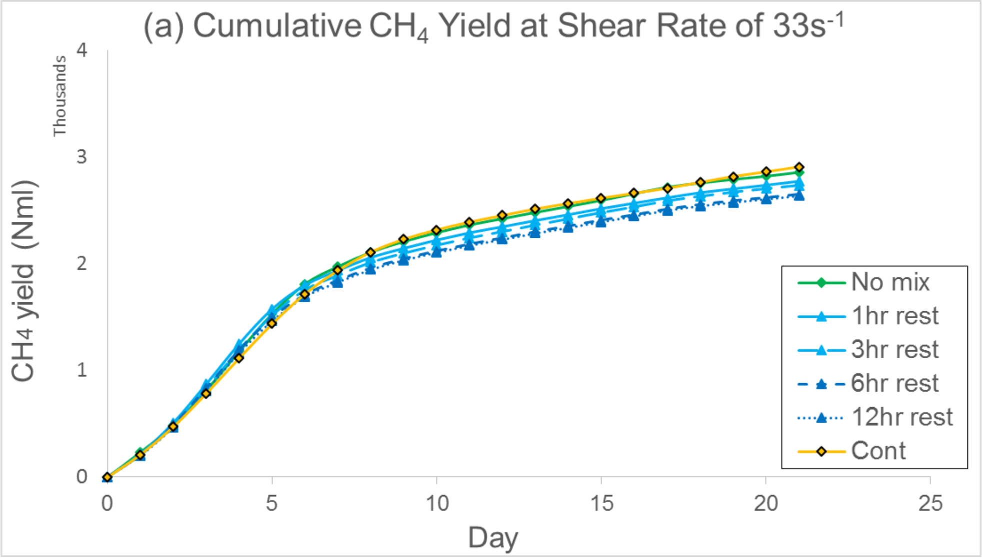
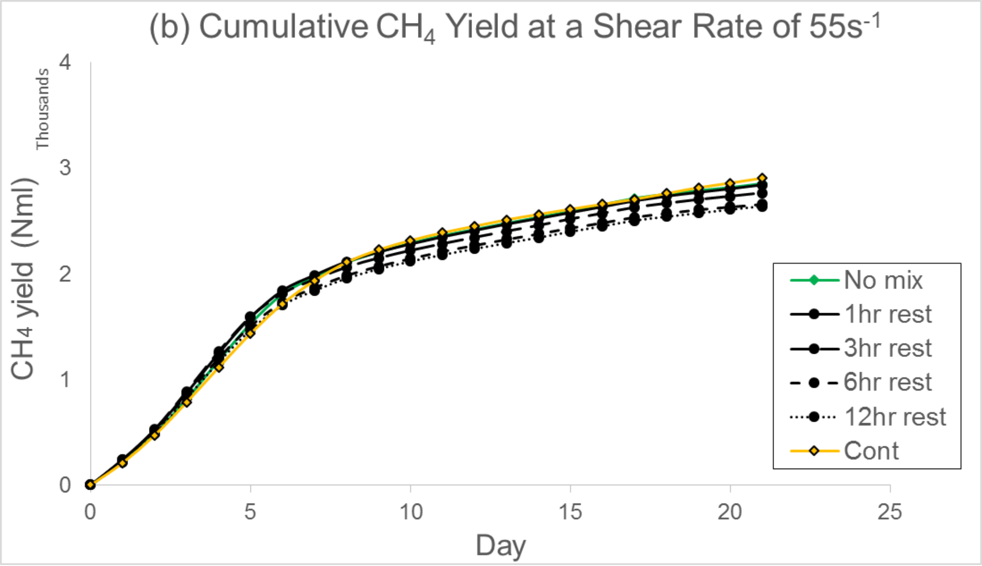


Figure 34 – Effect of changing shear rate on CH_4 yield when rested for (a) 1, (b) 3, (c) 6 and (d) 12 hours

3:3:2:2 Effect of Resting on Cumulative CH_4 Yield

When the effect of resting was considered within a particular shear rate a common hierarchy was evident with shorter rest periods always producing more CH_4 (Figure 35). As the temperature gradient was likely to be minimal in all digesters (para 3:3:4) this was likely to be due to an increase in mixing events facilitating gas removal, product distribution and microbial access to VS. Continuous mixing at $33s^{-1}$ is included for reference. No other research into the effects of rest period on CH_4 production could be found with which to compare results. Detailed analysis indicates a maximum variation of 9.3 percent using the highest shear rate of $125s^{-1}$ followed by 7.1 percent at $55s^{-1}$ and 4.9 percent at the lowest shear rate. Interestingly, continuously mixed and unmixed digesters produced higher yields than all other digesters except those mixed at $125s^{-1}$ and rested for 1 and 3 hours. The results achieved when a digester was subjected to continuous mixing with a low shear rate were understandable as mixing supported continuous microbial access to available nutrients (para 1:5:3); however, achieving similar values to the unmixed process presented a contradiction and potential causes were considered (para 3:3:4).


(a) Cumulative CH_4 Yield at Shear Rate of $33s^{-1}$


(b) Cumulative CH_4 Yield at a Shear Rate of $55s^{-1}$

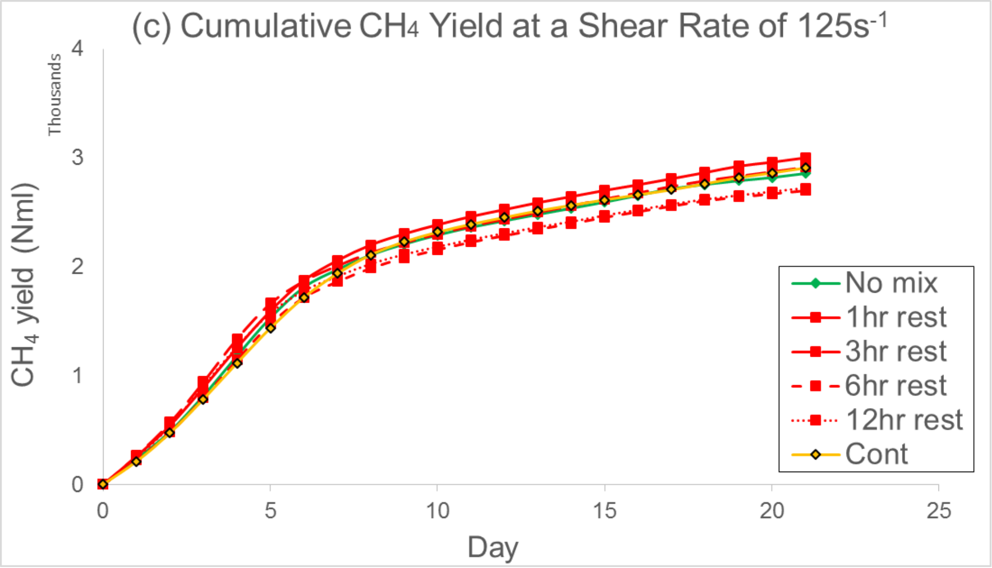

(c) Cumulative CH_4 Yield at a Shear Rate of $125s^{-1}$

Figure 35 – Effect of changing rest period on CH_4 yield when shear rate was (a) $33s^{-1}$, (b) $55s^{-1}$ and (c) $125s^{-1}$

3:3:2:3 Cumulative CH_4 Yield Using Inoculum Only

Most CH_4 was produced from isolated inoculum in the first 5 days at which time the gradient of the cumulative yield profile began to ease (Figure 36). This period was shorter than that typically observed when processing fresh cow slurry (Khanal, 2008). A shear rate of $55s^{-1}$ rested for 3 hours produced the most CH_4 (355.7Nml), closely followed by the unmixed digester. Profiles tended to be grouped by shear rate rather than rest period. A shear rate of $33s^{-1}$ rested for 3 hours was the worst performing regime producing 238.4Nml, 37 percent less than the highest performer. Sindall et al. (2013) also observed that gas production was directly related to substrate velocity induced when mixing at different speeds. Again, the effects of resting were not considered.

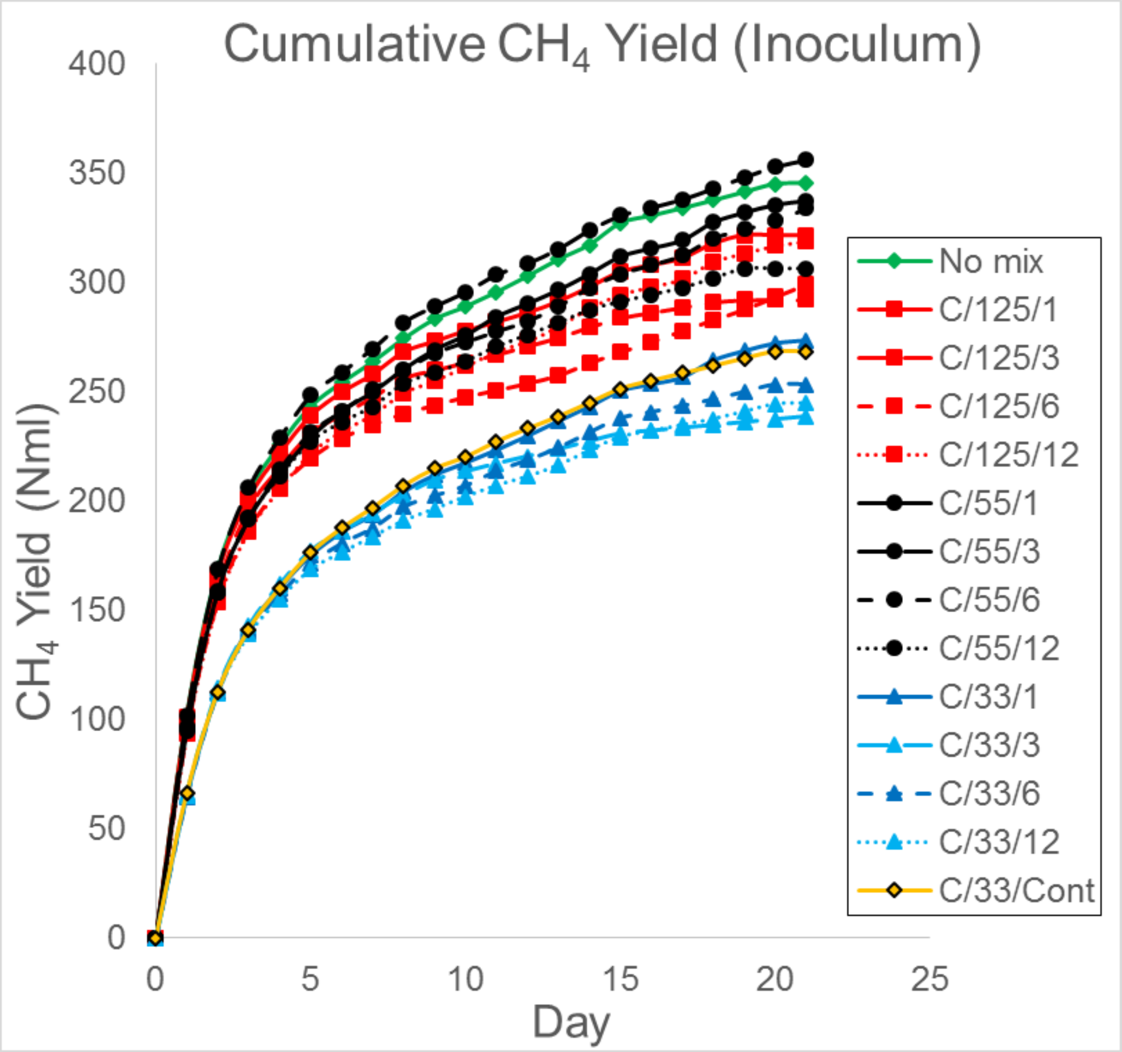


Figure 36 – Cumulative CH_4 yield achieved using inoculum only

3:3:3 CH_4 Production Rate

In a stable AD process, the rate of anaerobic bio-degradation of a substrate tends to be higher during the early stages of a fixed substrate retention period (Deublein & Steinhauser, 2011; Khanal, 2008; Andersons Centre, 2010). Indeed, peak CH_4 production rates were achieved between days 3 and 7. These were similar to predictions made by Keshtkar et al. (2001) using mathematical modelling and to observations made by Liao et al. (1984) when comparing CH_4 production from screened manure with unscreened. Approximately 70 and 80 percent of the total CH_4 yield achieved in the 21 day experiment occurred in the first 7 and 10 days, respectively (Figure 37) confirming previous observations. A rapid increase from the outset demonstrated that inoculation was effective, with peak production occurring on day 4. In some cases an 88 percent decline in production followed peak rates before levelling out on day 10. This was followed by a gradual reduction of a further 12 percent over the remaining period. A general profile similarity was observed for all mixing configurations. Minimum and maximum values at the height of CH_4 production (peak rate) varied by 16.3 percent (13.7 percent with continuous mixing removed). The highest rate realised was $395.1Nml_{CH4}d^{-1}$ using a shear rate of $125s^{-1}$ with a 3 hour rest. This equated to $14.6Nml_{CH4}g^{-1}{}_{VS}d^{-1}$ which in turn would equate to approximately $1.65m^3{}_{biogas}t^{-1}{}_{slurry}d^{-1}$. Continuous mixing realised the lowest peak rate of production. However, if continuous mixing results were removed, the lowest rate achieved was $12.6Nml_{CH4}g^{-1}{}_{VS}d^{-1}$ using a shear rate of $55s^{-1}$ rested for 12 hours. The unmixed digester produced peak values slightly higher than mid-range. To better understand the effects of shear rate and resting on the rate of production the variables were considered independently.

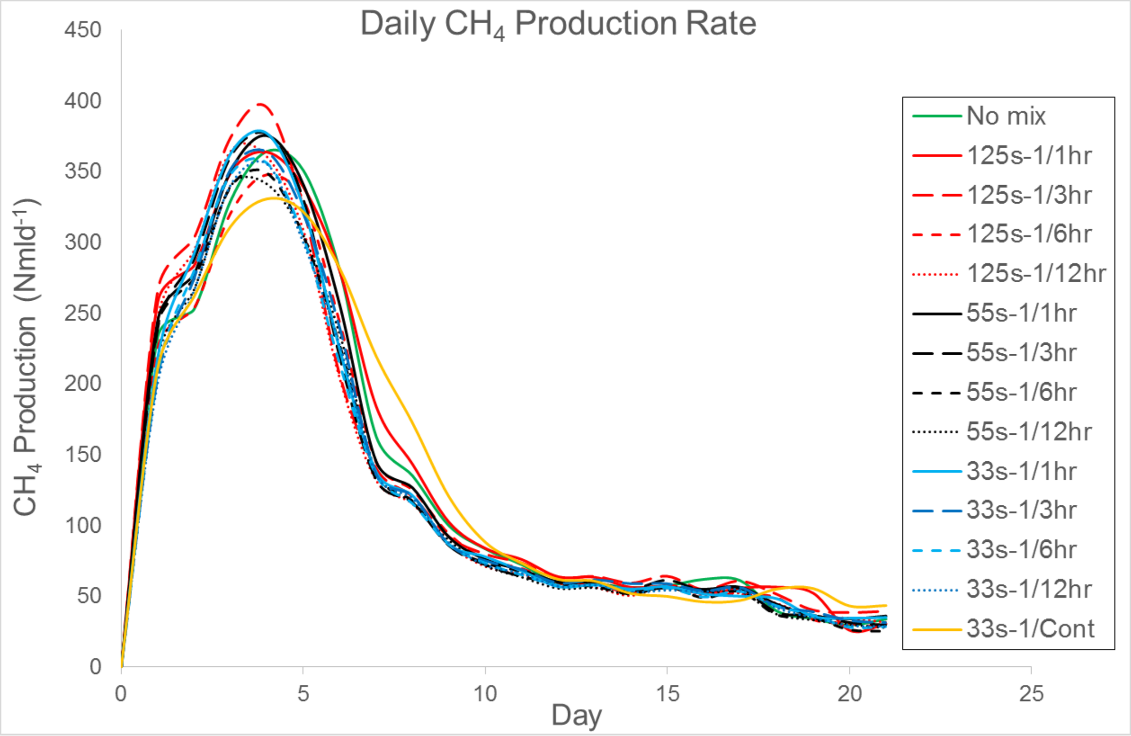


Figure 37 – Daily CH_4 production/flow rate of all mixing regimes

3:3:3:1 Effect of Shear Rate on Daily CH_4 Production Rate

Trends in daily production rate profiles were grouped by rest period to try and identify a common hierarchy in response to a changing shear rate. Unmixed values are included for reference only. When rested for 1 hour a shear rate of $33s^{-1}$ produced the highest peak rate of production closely followed by 55 and $125s^{-1}$ with a maximum difference of 3.5 percent being observed (Figure 38a). Resting for 3 hours resulted in a shear rate of $125s^{-1}$ producing the highest rate followed by 55 then $33s^{-1}$, an 8 percent difference (Figure 38b). Six hour resting returned $33s^{-1}$ as the best performer with 55 and $125s^{-1}$ producing similar values (Figure 38c). An overall difference of 2.3 percent was observed. 12 hour resting resulted in a shear rate of $125s^{-1}$ realising the highest production rate followed by 33 and then $55s^{-1}$ (6.4 percent) (Figure 38d). Continuous mixing at $33s^{-1}$ achieved the lowest peak rate. No common performance hierarchy for daily CH_4 peak production rate was apparent when shear rates were compared in fixed rest periods. When mean values of outcomes were calculated, $125s^{-1}$ was observed to be the most favourable shear rate producing a mean production rate of

367.6$Nml_{CH4}d^{-1}$ across the rest periods considered. However, the difference between best and worst performing shear rate (55s^{-1}) was only 1.3 percent. Such detailed research in this area had not been carried out before and demonstrated that varying shear rate had a minimal effect on the rate of CH_4 production over the length of a batch process using cow slurry.

3:3:3:2 Effect of Resting on Daily CH_4 Production Rate

When daily CH_4 production rates at specific shear rates but different rest periods were compared in detail, the hierarchy observed for each applied shear rate varied slightly depending on mixing regime (Figure 39). Continuously mixed values are included for reference. At a shear rate of 33s^{-1} the peak daily rate of production decreased from the most productive case (1 hour resting) to the least (12 hours), with a 5.7 percent difference of extreme values (Figure 39a). When 55s^{-1} was applied a similar hierarchy was observed although in this case 1 and 3 hour resting realised similarly high daily rates of production (12.3 percent difference overall) (Figure 39b). However, in the 125s^{-1} shear rate grouping, 3 hour resting achieved the highest daily rate of production followed by 12, 1 and finally 6 hours (Figure 39c). The overall difference was significantly higher at 22 percent. When mean values were calculated, 3 hour resting was observed to be the most favourable producing a mean production rate of 378.4$Nml_{CH4}d^{-1}$ across the shear rates considered. The difference between the best and worst performing rest period (6 hours) was significant at 7.4 percent. Again, this was new research demonstrating that varying rest period had a minimal effect on the rate of CH_4 production over the length of a batch process using cow slurry.

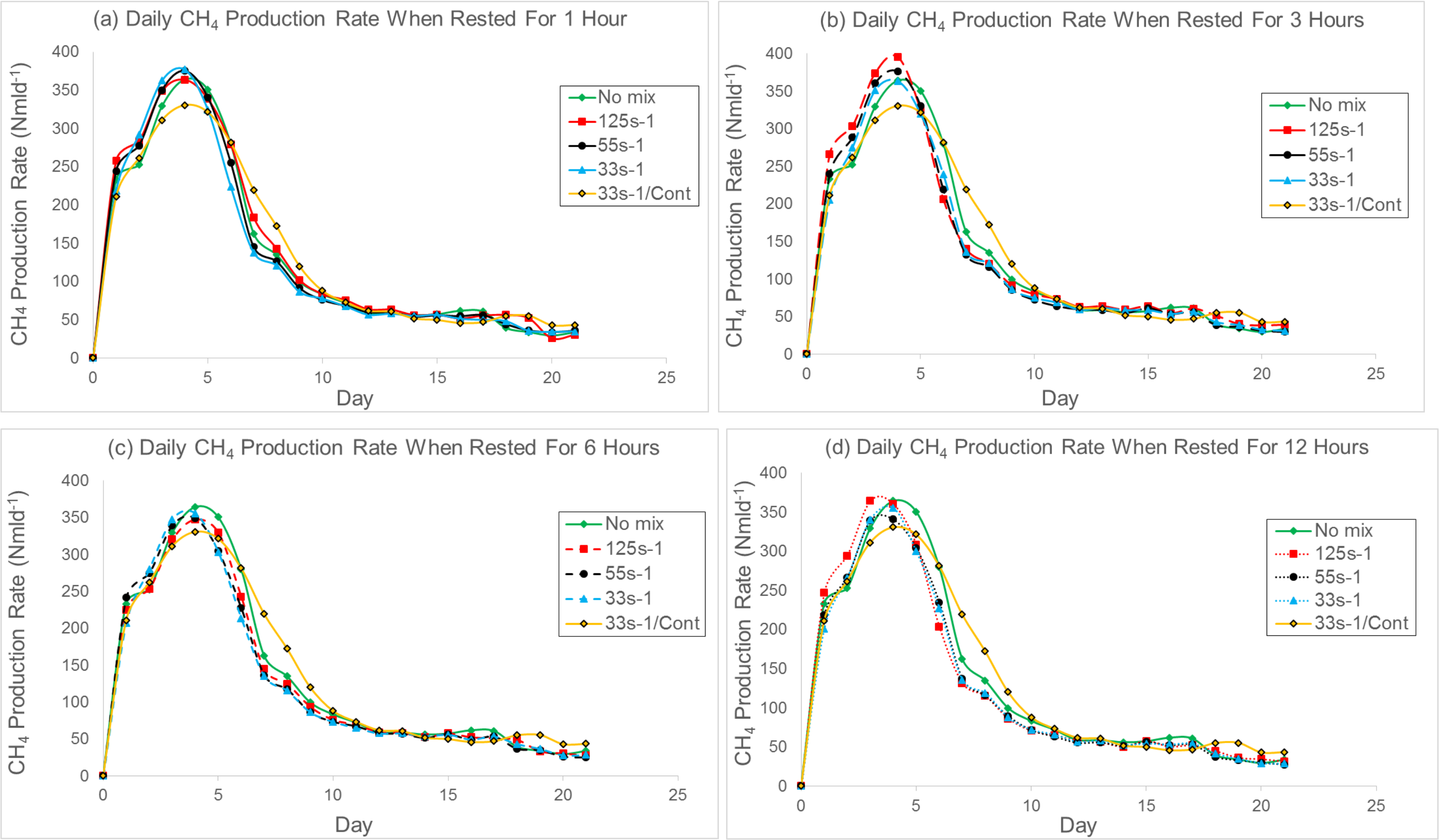
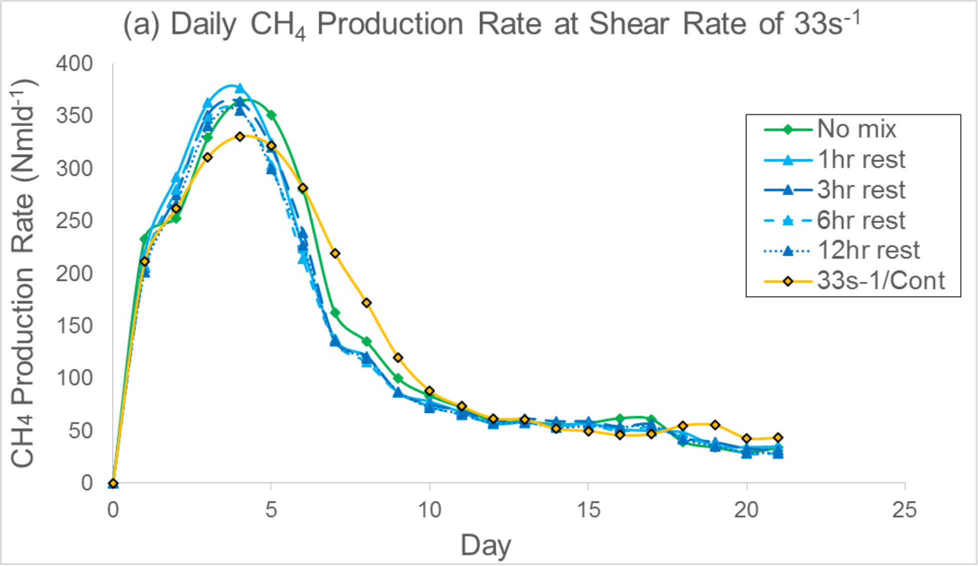
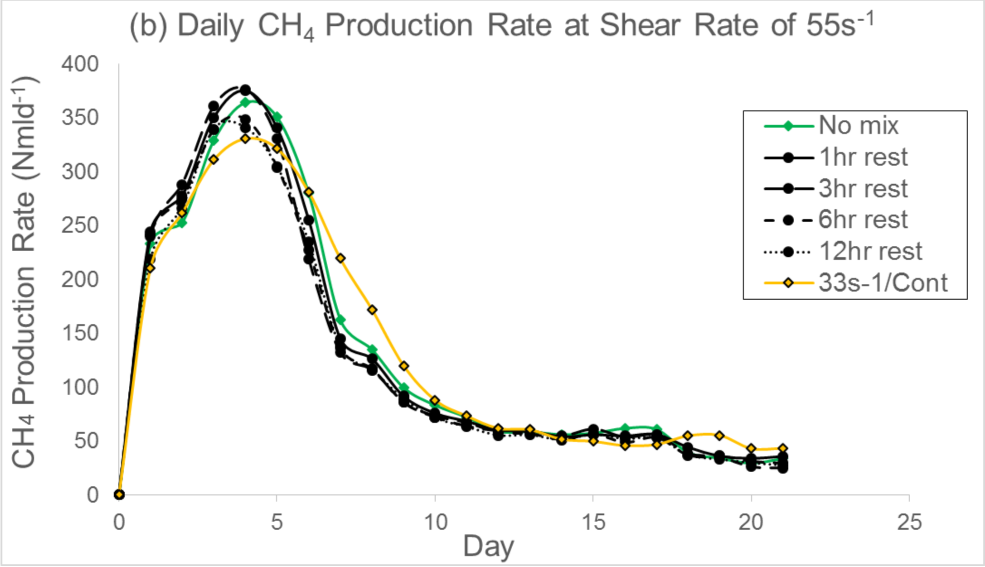


Figure 38 – Effect of changing shear rate on CH$_4$ yield when rested for (a) 1, (b) 3, (c) 6 and (d) 12 hours





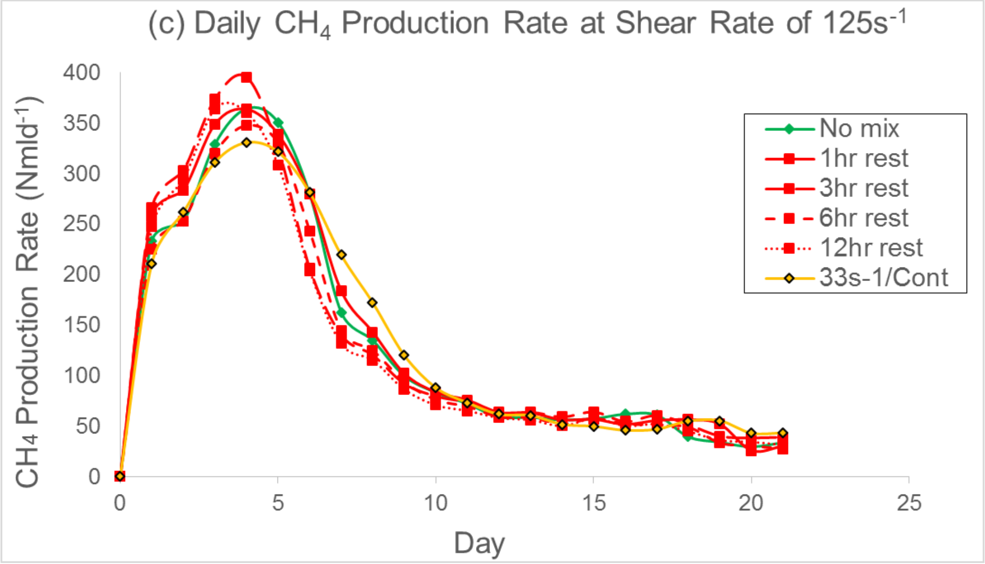


Figure 39 – Effects of resting on daily CH_4 production rate at shear rates of (a) $33s^{-1}$, (b) $55s^{-1}$ and (c) $125s^{-1}$

3:3:3:3 CH_4 Production Rate of Inoculum Only

The rate of CH_4 production in the digesters charged only with inoculum and de-ionised water displayed a similar profile to that of inoculum and slurry but over a shorter period of intensity of 5 days (Figure 40). This period was shorter than that quoted for fresh cow slurry (Andersons Centre, 2010; Khanal, 2008). The rapid rise from start-up reached a peak value of 101.9$Nml_{CH4}d^{-1}$ on day 2 and declined rapidly by 91 percent by day 6 followed by a further 5.6 percent over the following 16 days. No clear pattern was evident when the effect of resting within a particular shear rate was considered which is best portrayed by the cumulative yield profiles (Figure 36). However, the effect of shear rate itself on the rate of production was significant with shear rates of 125 and 55s^{-1} producing similar results that outperformed a shear rate of 33s^{-1} by 29 percent. Continuous mixing produced similar rates of CH_4 production to 33s^{-1} rested for 1 hour. Interestingly, the unmixed digester outperformed all but the highest CH_4 production rate observed (55s^{-1} rested for 3 hours). Such detailed analysis of the effects of resting on CH_4 production rate when batch processing high biomass/low nutrient rich inoculum could not be found in previously published research although Sindall's suggestion (2013) that substrate velocity may influence biogas production may have some merit even when processing low nutrient feedstock.

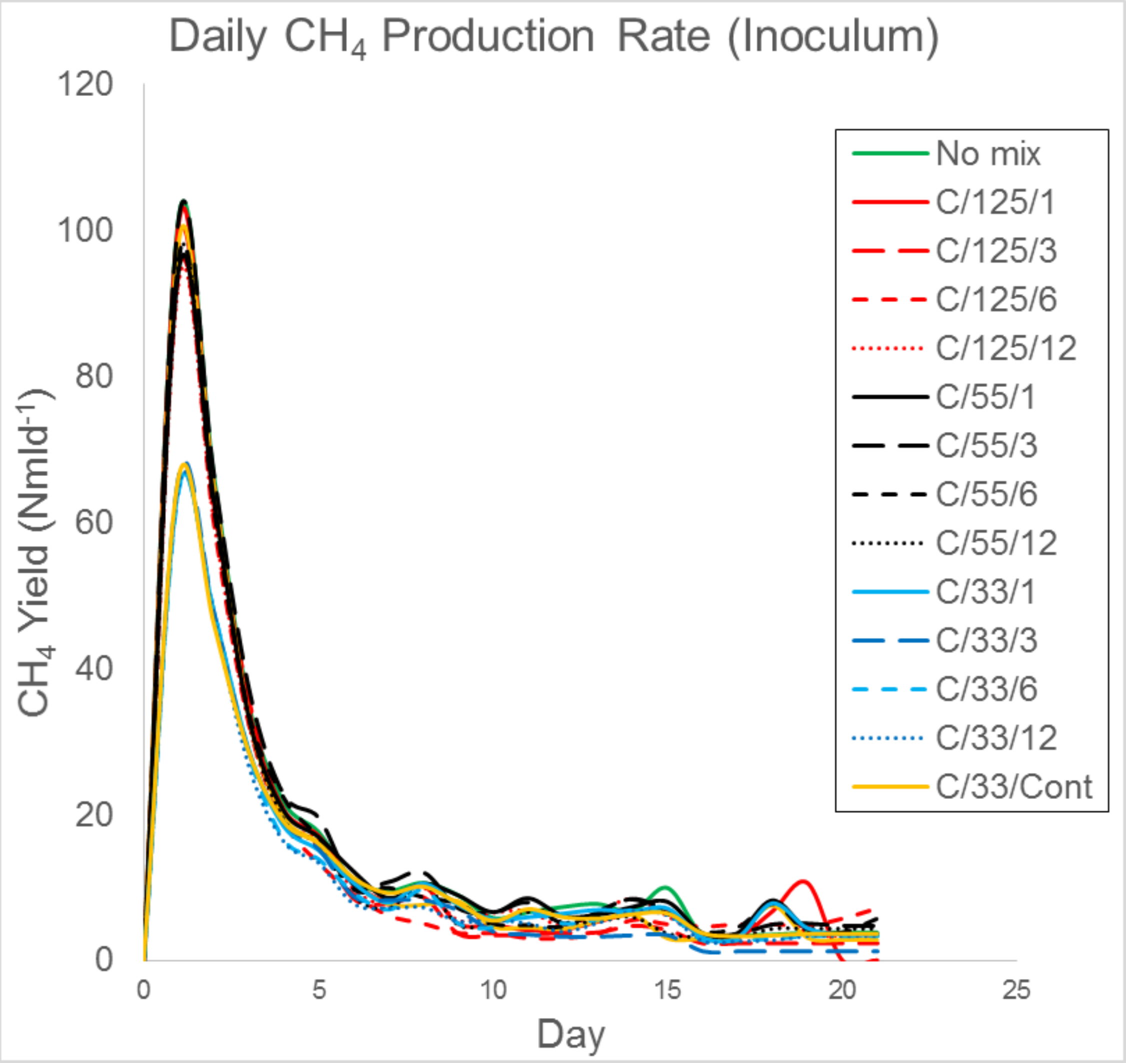


Figure 40 – Daily CH_4 production rate using inoculum only

3:3:3:4 Considerations When Comparing Values

Differences in rate of CH_4 production values were found to be quite obvious in some instances (different rest periods at $55s^{-1}$) yet hardly discernible in others (6 hour resting across a range of shear rates). However, caution should be applied when making comparisons as:

- CH_4 values achieved were relatively low when the volume of the measuring device, the relatively high rate of flow and the rigid 24 hour measuring period were considered. At peak production, the time taken to accumulate the 10ml of CH_4 necessary to activate the gas counter ranged from 37 to 42 minutes, depending on the shear rate applied, which could equate to as much as 3 percent of the production rate for that day.

- CH_4 content of the off-gas was assumed rather than measured.
- Shear rates were compared using common rest periods but the mixing periods varied to achieve the required homogeneity using a particular shear rate, so stirrer activation times gradually digressed as the experiment progressed. This may have not only affected the rate at which CH_4 was produced but also when the gas was released from the fluid into the gas headspace.
- Only single inoculum samples were processed at each shear rate/rest interval so mean values were not available.

Comparing CH_4 production over shorter periods was considered but regarded as having limited value due to the above constraints. A longer periodic measuring unit was also considered but a daily rate was more compatible with the short 5-day duration of the most active production period of the batch process.

3:3:4 CH_4 Production Without Mixing

CH_4 production without mixing followed similar cumulative yield and production rate profiles to mixed digesters; yield was generally higher than the mid-range of what was achieved across all digesters (Figure 33 and Figure 37) and outperformed all but the highest achievers. This was also the case in the inoculum-only control digesters and supports previous suggestions that mixing has minimal effect on biogas production (Stafford, 1982; Hoffmann et al., 2008; Tian et al., 2013). However, as all digesters were immersed in a heated bath and contained a relatively small volume of substrate held at a constant temperature without feeding, benefits accredited to mixing such as heat distribution to avoid thermal gradients may have been masked by the equipment. Moreover, as CH_4 yields were generally mid-range or better, the microbes must have had access to the feedstock despite the lack of conscious physical mixing. This may have been achieved by the rising of the biogas in the relatively small digester. Karim et al. (2005) also observed higher CH_4 yields being achieved in an unmixed digester when comparing gas-induced draft tube mixing of 5%TS substrates. They suggested that the natural fluid movement induced by biogas rising provided sufficient process mixing [at lab-scale], a suggestion that could question the validity of this experiment. However, chapter 2 indicated that 5%TS slurries demonstrate Newtonian characteristics so such observations may have been influenced by the rheological nature of the substrate which may not be the case for the non-Newtonian slurry used in this work. Indeed, amongst actively mixed digesters this experiment demonstrated a common cumulative yield hierarchy in response to shear rate, even at this scale. Furthermore, this phenomenon may not be a factor on scale-up when mixing is necessary for heat transfer and to transport new nutrients across a large digester being intermittently fed. However, the potential for inadvertently introducing an additional variable does demonstrate the caution that should be applied when researching at lab-scale.

3:3:5 Optimisation Based on Cumulative Yield

Identifying the different cumulative CH_4 yields achieved by each mixing regime was informative (Figure 42) but in practical terms meant little unless compared with the parasitic mixing energy required to produce them and a net energy gain quantified. The energy balance of each regime was therefore calculated to produce a net CH_4 productivity hierarchy and identify an optimum mixing regime.

3:3:5:1 Parasitic Energy Use and Power Factor

By measuring the current demanded by each motor at the known fixed voltages of 4.19V, 6.16V and 12V respective mean currents of 0.064A, 0.069A and 0.080A were calculated. Known on/off periods for each mixing regime over the experimental period were used to calculate total power used. Generally, mixing regimes with longer rest periods used less power despite the longer mixing periods required by lower shear rate configurations. A shear rate of $55s^{-1}$ rested for 12 hours used significantly less power than all other regimes. The power demanded by each mixing regime was divided into this baseline figure (PF = 1) to provide individual PFs from which a hierarchy was derived based on the kWh, as detailed in Table 8 with the baseline PF highlighted (red). Shear rate/rest regimes of $33s^{-1}$/12hrs and $55s^{-1}$/6hrs were rated second and third with PFs of

0.66 and 0.50, respectively. Mixing using a shear rate of $33s^{-1}$ and resting for 12 hours used 46 percent more power than the most economic regime. The continuously mixed digester had the lowest rating (PF = 0.01) and used 9 times the power of that rated highest confirming the concerns raised in para 1:5:10. Figure 41 illustrates the PF relationship of the mixing regimes that required parasitic energy to function. The ratio that the PF provided can be applied to any period within the length of the experiment. The unmixed digester was excluded as no power was used. This data should not be used when comparing systems when scaling up due to previously highlighted issues associated with the non-linear increase required in mixing power to achieve the same degree of mixing when digester volume is increased linearly.

Total seconds in 1 hr:	3,600
Total seconds in 3 hrs:	10,800
Total seconds in 6 hrs:	21,600
Total seconds in 12 hrs:	43,200
Total seconds in analysis period:	1,814,400
Electricity unit cost (p/kWh):	11.5

Mean Values from motor comparison:	
Mixing Location	Power (W)
Tank 1 (12V)	0.960
Tank 2 (6V)	0.426
Tank 3 (4V)	0.269

Mixing Regime (ý/rest)	**Timing**							**Parasitic Power Use**			**Power Factor**	kWh conversion (1/2.2)
	On (s)	**Off (s)**	**Cycle (s)**	**Total Cycles**	**Rounded down**	**Total on (s)**	**Total off (s)**	**Power (W)**	**Power (kW)**	**Power (kWh)**		
No mix	Not applicable											
125/1	280	3,600	3,880	467.63	467.00	130,760	1,683,640	125,574	125.57	**0.035**	**0.04**	0.019
125/3	280	10,800	11,080	163.75	163.00	45,640	1,768,760	43,830	43.83	**0.012**	**0.12**	0.054
125/6	280	21,600	21,880	82.93	82.00	22,960	1,791,440	22,049	22.05	**0.006**	**0.24**	0.108
125/12	280	43,200	43,480	41.73	41.00	11,480	1,802,920	11,025	11.02	**0.003**	**0.48**	0.216
55/1	300	3,600	3,900	465.23	465.00	139,500	1,674,900	59,481	59.48	**0.017**	**0.09**	0.040
55/3	300	10,800	11,100	163.46	163.00	48,900	1,765,500	20,850	20.85	**0.006**	**0.25**	0.114
55/6	300	21,600	21,900	82.85	82.00	24,600	1,789,800	10,489	10.49	**0.003**	**0.50**	0.227
55/12	300	43,200	43,500	41.71	41.00	12,300	1,802,100	5,245	5.24	**0.001**	**1.00**	0.455
33/1	720	3,600	4,320	420.00	420.00	302,400	1,512,000	81,373	81.37	**0.023**	**0.06**	0.029
33/3	720	10,800	11,520	157.50	157.00	113,040	1,701,360	30,418	30.42	**0.008**	**0.17**	0.078
33/6	720	21,600	22,320	81.29	81.00	58,320	1,756,080	15,693	15.69	**0.004**	**0.33**	0.152
33/12	720	43,200	43,920	41.31	41.00	29,520	1,784,880	7,944	7.94	**0.002**	**0.66**	0.300
Cont	1,814,400			1,814,400	1,814,400		0	488,239	488.24	**0.136**	**0.01**	0.005

Table 8 – Power factors for each mixing regime

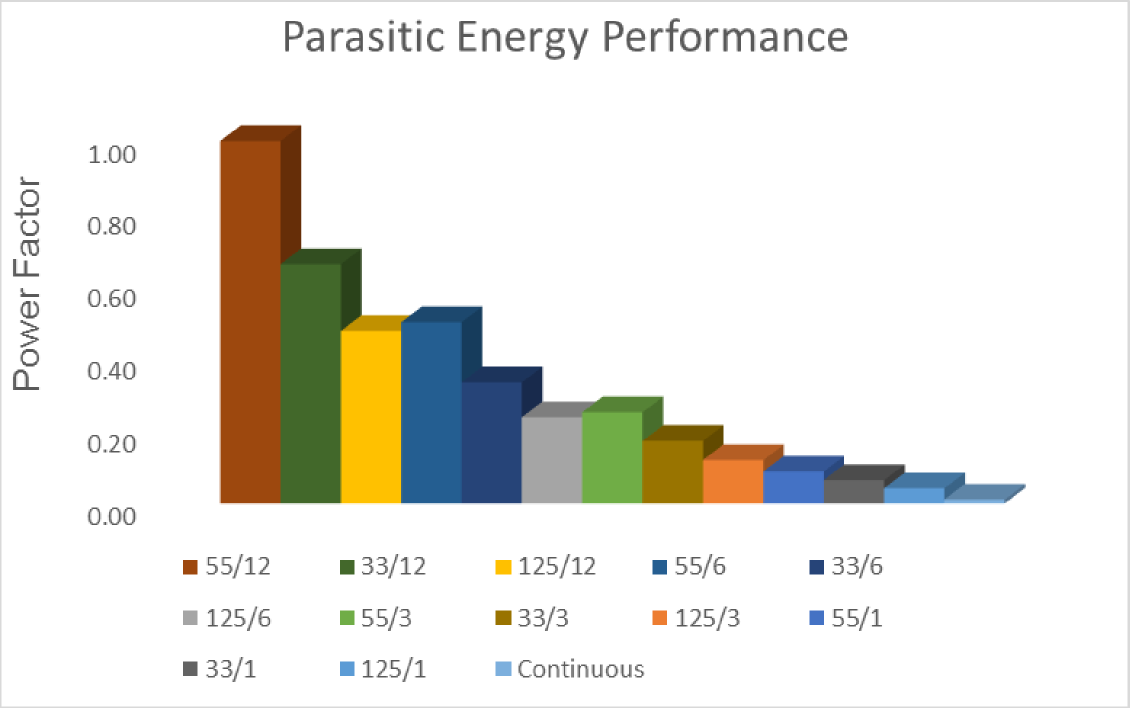


Figure 41 – Comparison of parasitic energy performance using power factor

3:3:5:2 CH_4 Yield and Yield Factor

The highest cumulative yield was achieved by mixing with a shear rate of 125s^{-1} and resting for 1 hour (YF = 1). Dividing that baseline yield into all other cumulative yield measurements produced dimensionless YF values (Table 9). The baseline YF is again highlighted in red. Mixing regimes were compared based on CH_4 yield. A shear rate of 125s^{-1} rested for 3 hours and the continuously mixed regime were joint second best performers (YF = 0.97) followed by the digester using a shear rate of 55s^{-1} rested for 1 hour and the unmixed digester in joint third place (YF = 0.95). The shear rate/rest period regimes of 55s^{-1}/12hrs, 33s^{-1}/6hrs and 33s^{-1}/12hrs were the worst performers (YF = 0.88). Figure 42 provides a graphical representation of YFs.

Mixing regime (ý/Rest (hr))	Cumulative CH4 Yield (Nml)	Yield Factor (YF)
No mix	2855.5	0.95
125/1	2999.85	1.00
125/3	2912.55	0.97
125/6	2700.00	0.90
125/12	2719.75	0.91
55/1	2843.35	0.95
55/3	2765.25	0.92
55/6	2661.45	0.89
55/12	2640.60	0.88
33/1	2771.70	0.92
33/3	2732.90	0.91
33/6	2647.95	0.88
33/12	2635.45	0.88
Cont	2906.95	0.97

Table 9 – Yield factors for all mixing regimes

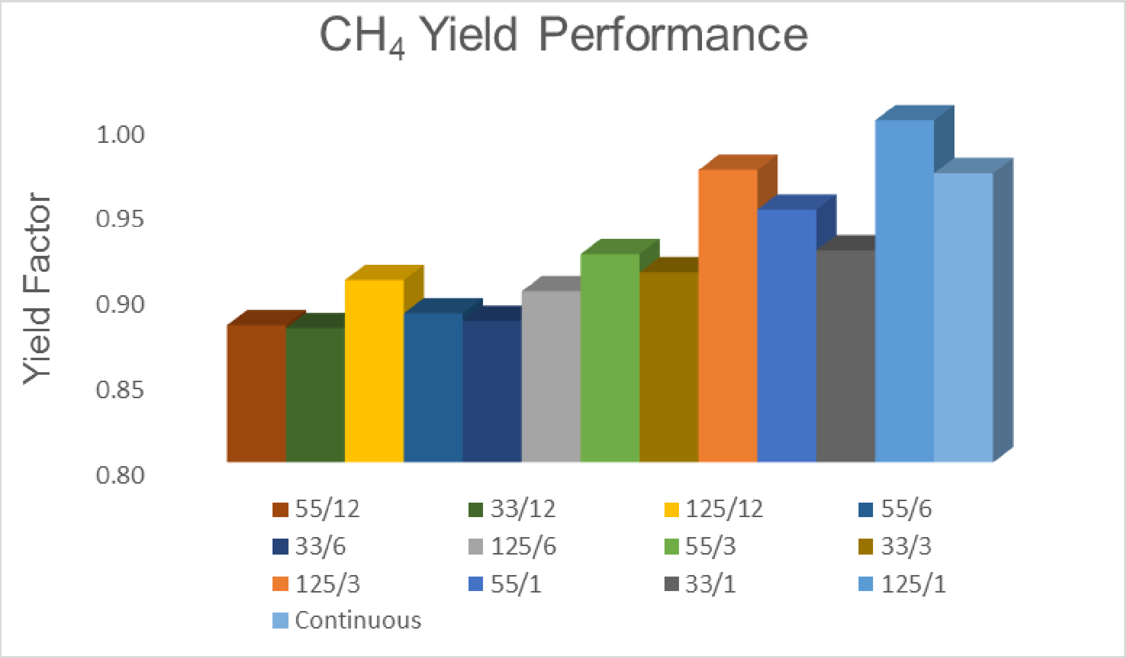


Figure 42 – Comparison of CH4 yield performance using yield factor

3:3:5:3 Balancing CH_4 Yield and Parasitic Energy

Once YF values had been corrected to the baseline kWh unit of measurement the product of PF and YF provided an overall comparative rating (Table 10) with the top 3 performers highlighted in red. A graphical comparison (Figure 43) indicates that the overall best performing mixing regime of 55s^{-1}/12hrs was followed by 33s^{-1}/12hrs which trailed by a significant margin (34 percent). The 55s^{-1}/6hrs regime came third, trailing the second place digester by 23 percent. Such large differences are significant and were mainly influenced by the parasitic energy demanded by different regimes. The continuously mixed digester was the worst performer throughout the experiment despite being the second highest producer of gas.

Mixing regime (ý/rest (hr))	Power Factor (PF)	Yield Factor (YF)	Corrected Yield Factor (weighted)	PF x YF	Overall Rating
No mix		0.95	0.26		
125/1	0.04	1.00	0.27	0.011	**12**
125/3	0.12	0.97	0.26	0.032	**9**
125/6	0.24	0.90	0.25	0.058	**7**
125/12	0.48	0.91	0.25	0.118	**4**
55/1	0.09	0.95	0.26	0.023	**10**
55/3	0.25	0.92	0.25	0.063	**6**
55/6	0.50	0.89	0.24	0.121	**3**
55/12	1.00	0.88	0.24	0.240	**1**
33/1	0.06	0.92	0.25	0.016	**11**
33/3	0.17	0.91	0.25	0.043	**8**
33/6	0.33	0.88	0.24	0.080	**5**
33/12	0.66	0.88	0.24	0.158	**2**
Cont	0.01	0.97	0.26	0.003	**13**

Table 10 – Overall performance rating for all digesters

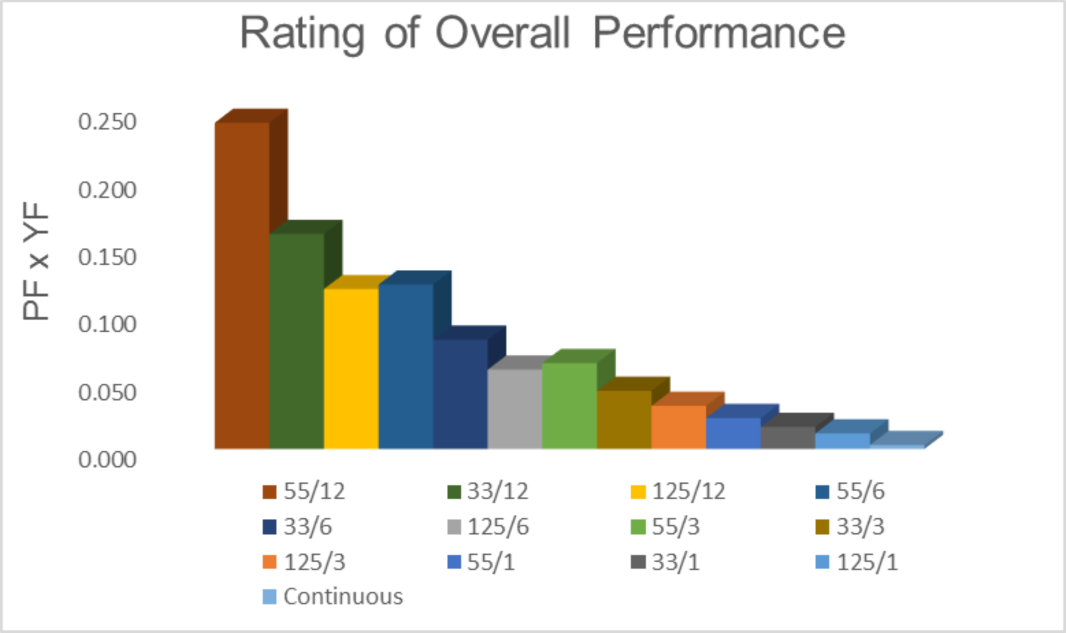


Figure 43 – Comparison of net energy production of all mixing regimes

3:3:6 Optimisation Based on Production Rate

Identifying process optimisation based on production rate required a more general technique although the results were more definitive. This was because, unlike cumulative yield, any maximum net energy value based on the rate of production had to account for the dynamic daily changes of production rate. A daily production rate/parasitic energy balance was calculated to compare net energy gain (in kWh) for each mixing regime.

3:3:6:1 Specific CH_4 Production Rate

At first sight, the overwhelming similarities in the daily CH_4 production profiles using batch data supported the approach suggested by Bensmann et al. (2013). Using the SPR formula, extremes of specific CH_4 production rates of 0.988 (125s^{-1}/3hrs) and 0.852 $Nml_{CH4}ml^{-1}{}_{substrate}d^{-1}$ (55s^{-1}/12hrs) were achieved using maximum CH_4 production values realised by each mixing regime on the day of best performance (which for all but 125s^{-1}/12hrs was on day 4). A full list of CH_4 production values is presented in Table 11 (maximum and minimum values in red).

ý	Rest Period (hrs)					
(s-1)	**1**	**3**	**6**	**12**	**Mean**	**Δ%**
33	0.942	0.909	0.889	0.888	0.907	1.31%
55	0.938	0.941	0.872	0.852	0.901	
125	0.909	0.988	0.869	0.910	0.919	
Mean	0.930	0.946	0.876	0.884		
Δ%	7.35%					

Table 11 – Comparison of maximum specific CH4 production rates achieved by each mixing regime

Plotting the maximum SPRs achieved by all mixing regimes indicated no obvious pattern on which to select a preferred method (Figure 44). However, as all but one of the maximum values was achieved on day 4 of the process and production trends were similar for all regimes (Figure 37), calculating SPRs for each day using the mean daily CH_4 production rate of all regimes offered an alternative representation of the data.

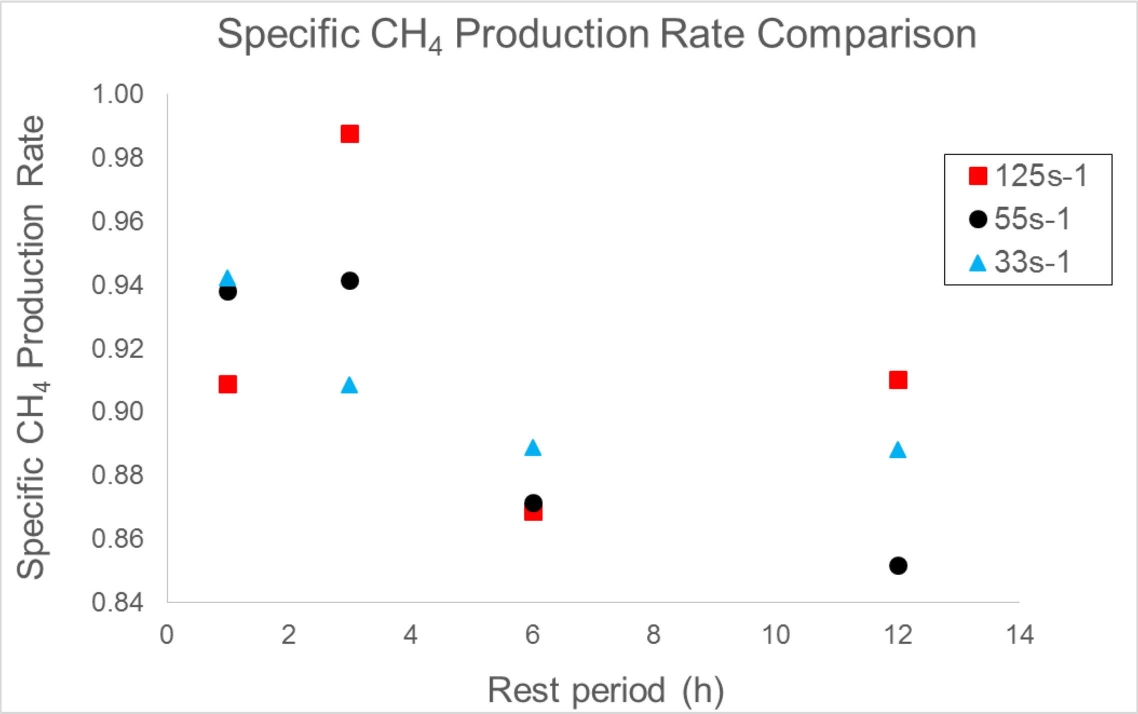


Figure 44 – Comparison of maximum specific CH4 production rates

SPR values using this alternative method (Table 12) provided an appreciation of the day-to-day benefits that may be realised by basing a digester design on production rate rather than cumulative yield. The highest production rate achieved is indicated using dark blue (SPR in red) with the shade getting lighter as production rate decreased. When presented in graphical form (Figure 45) the first 7 days of the substrate bio-degradation process was easily identified as the most active CH_4 generation period of the 21 days observed as reported by Khanal (2008). However, a substantial rate of CH_4 production continued for another 3 days before reducing to relatively low levels of production.

Day	**Mean Daily CH4 Production (Nml)**	**Specific Production Rate(SPR)**
0	0.0	0.00
1	229.7	0.57
2	276.2	0.69
3	345.6	0.86
4	361.0	0.90
5	321.4	0.80
6	238.1	0.60
7	148.4	0.37
8	125.8	0.31
9	92.4	0.23
10	76.5	0.19
11	68.5	0.17
12	59.1	0.15
13	59.0	0.15
14	54.1	0.14
15	57.0	0.14
16	52.4	0.13
17	54.2	0.14
18	44.8	0.11
19	38.4	0.10
20	31.9	0.08
21	31.9	0.08
Highest value	360.95	0.90

Table 12 – Specific production rate calculated using mean CH_4 values for all digesters each day

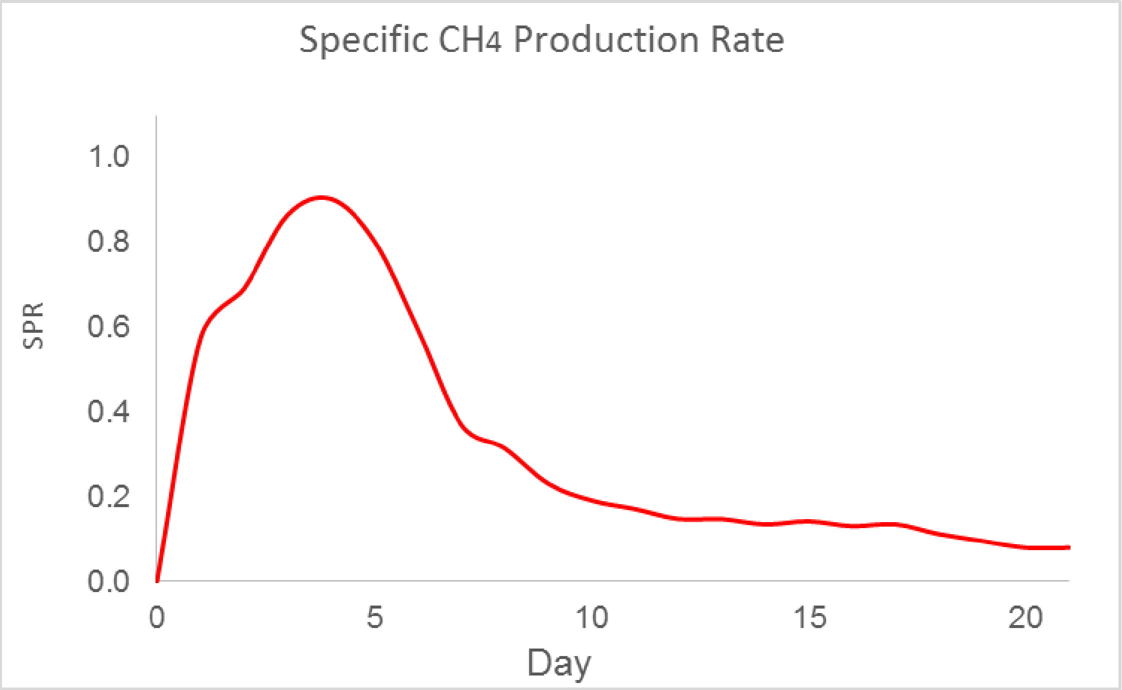


Figure 45 – Specific CH_4 production rate profile using mean digester regime CH_4 production values for each day

To better inform digester sizing based on CH_4 production rate, the areas under the curve for the key periods of days 0-7, 7-10 and 10-21 were calculated using Simpson’s rule. These areas effectively represented combined totals of SPR over each period. This apportionment indicated that using a smaller digester accommodating a batch period of 7 days when CH_4 production is most active may be more cost-effective in terms of potential CH_4 production than a larger solution when the reduced cost of the smaller digester and subsequent CAPEX is considered (Figure 46). However, the feasibility and benefits of such a strategy (when intermittently feeding) would have to be investigated to identify any potential increase of the possibility of process inhibition due to reduced alkalinity and buffering offered by lower volumes of slurry when the OLR is relatively high.

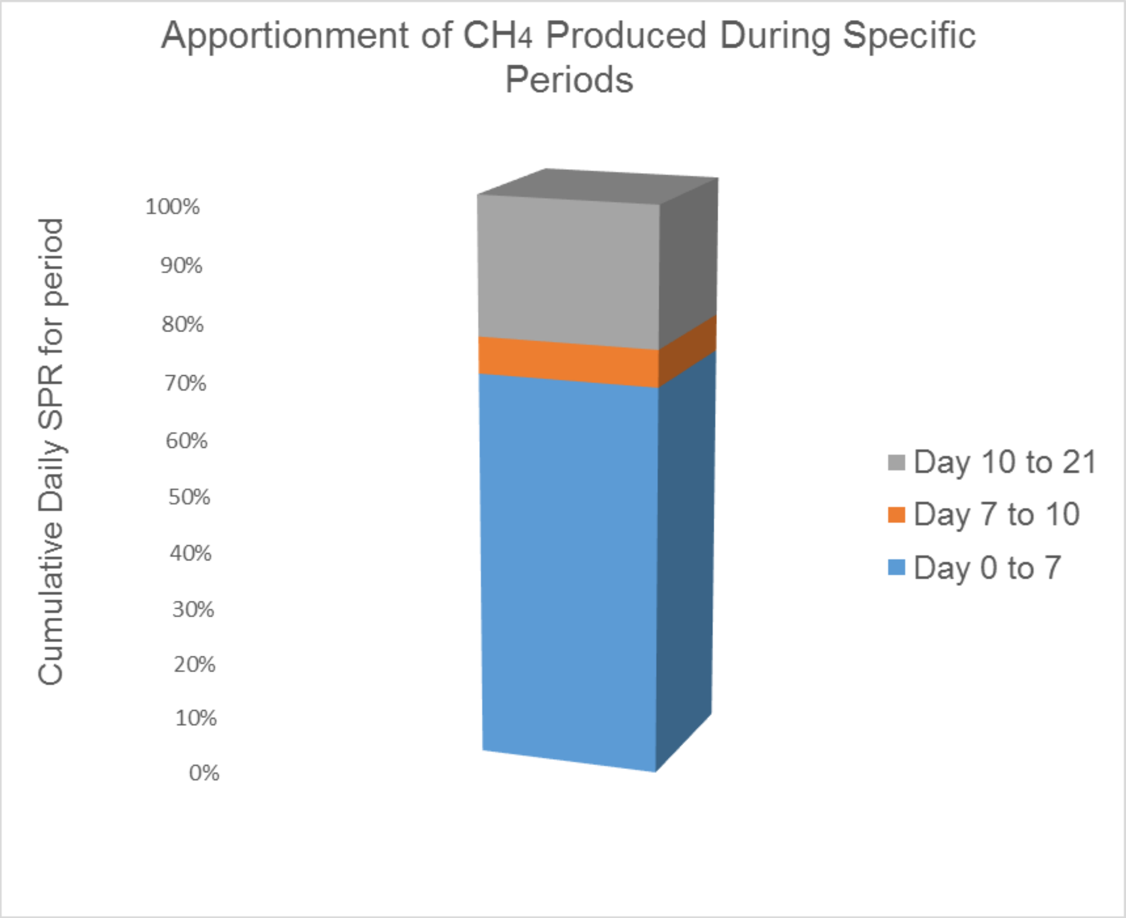


Figure 46 – Apportionment of CH_4 produced over 21 days

3:3:6:2 Balancing CH_4 Production Rate and Parasitic Energy

Dividing the experiment length into periods having similar benefits/drawbacks in terms of CH_4 production rate effectively provided a ratio of process performance over time. But PF is a ratio between the different mixing regimes so could not be directly applied to the accumulated daily SRP apportionment in Figure 46 which was based on mean CH_4 production rate values across the complete range of mixing regimes on a specific day. However, a shorter batch period would use less energy. Indeed, by dividing the parasitic energy used over a 21 day batch period into 7, 10 and 21 days energy use would be 33, 48 and 100 percent of the total used, respectively.

3:4 Conclusions

The analysis confirmed observations of previous authors in a number of areas but also presented new findings achieved by separating the effects on CH_4 production caused by the individual metrics such as the rest period associated with intermittent mixing techniques. The analysis supported the following conclusions:

- The use of an effective inoculum can realise rapid AD from the outset.
- Shear rates of 33, 55 and $125s^{-1}$ were appropriate to compare the effects of shear rate on overall CH_4 yield and production rate using the mixing technique adopted.
- Rest periods of 1, 3, 6 and 12 hours were appropriate to compare the effects of shear rate on CH_4 production rate and yield. Rest periods higher than 12 hours were not regarded as operationally appropriate as long periods without mixing may cause unacceptable settling/stratification of the slurry.
- Maximum CH_4 yields were observed when intermittent, high stress, short duration mixing was applied. Indeed, most CH_4 was produced when mixing hourly at a shear rate of $125s^{-1}$ for 4.7 minutes. However, CH_4 production using that shear rate alone but different rest periods identified that CH_4 production is also proportional to the number of mixing events that occur within a set period. When the parasitic energy used to produce the CH_4 was considered to provide net kWh gain, medium to low shear rates of 55 and $33s^{-1}$ and long rest periods (12 hours) produced the best results overall. Therefore, lower mixing intensities mixed and rested for longer periods may be a more cost-effective mixing regime although less CH_4 is produced.
- Unmixed and continuously mixed digesters produced relatively similar and competitive CH_4 yields. However, not mixing is unlikely to be appropriate for intermittently-fed farm systems for reasons described earlier and continuous mixing resulted in much higher than necessary parasitic energy use. Therefore, these regimes are not considered appropriate for dairy farm AD.
- Maximum daily CH_4 production rates were achieved between day 3 and 7. Logically, a digester design based on a 7-day HRT would support a high substrate throughput strategy rather than waiting for AD process completion,

particularly for low energy-potential feedstock such as cow slurry. This would substantially reduce digester volume requirements and hence CAPEX, system footprint and heating demand. Furthermore, the parasitic energy demand would substantially reduce OPEX to improve efficiency even further.

- Alternatively, as over 80 percent of the CH_4 realised in the 21-day process was produced in the first 10 days, a compromise strategy embracing a 10-day HRT could be adopted. Such a system design would again support high throughput rather than process completion and may be appropriate when processing low-cost feedstock such as slurry. Again, this could reduce CAPEX as smaller digesters would be required with associated reductions in parasitic energy demand (OPEX). However, the ability of low HRT regimes to accept the increase in OLR would have to be explored.
- Low-nutrient feedstock, such as inoculum, preferred medium to high intensity mixing (shear rates of 55 and $125s^{-1}$) to optimise nutrient/microbe interaction, as demonstrated in the inoculum-only analysis. The majority of bio-degradation was achieved in 5 days. This may support a digester configuration in series if a different mixing regime was required although this would increase CAPEX and OPEX. However, as demonstrated when PF was applied to YF in the primary digestion process, a shear rate of $55s^{-1}$ rested for 12 hours may be a sensible default to provide maximum net gain. However, further modelling would be required to quantify the impact of applying higher levels of parasitic energy when the available CH_4 generating potential of the substrate is less than that of the primary digester.

The optimum mixing configuration for financial viability using this particular stirrer technique and mechanism used a shear rate of $55s^{-1}$ rested for 12 hours. This compromise between shear rate/rest period and CH_4 yield achieved the most favourable net energy balance. Adopting such an analysis technique when designing a digester could reduce OPEX substantially. Furthermore, as the energy source for mixing is generally electricity, this could release surplus energy for other farm applications, thereby reducing reliance on importing electricity at a cost. Conversely, energy could be exported to attract revenue, though the expectation would be that substitution for grid-supplied power would be more economic than selling through the wholesale market.

The differences in the effects of different mixing regimes on CH_4 production are distinctive. However, actual biogas yield was not measured and CH_4 produced by each mixing regime was assumed as 60 percent rather than measured. Therefore, a true representation of the effects of mixing regime on CH_4 production and hence biogas quality and quantity were not fully captured in the analysis.

3:5 Next Research Step

Although batch processing may not be appropriate for most dairy farm AD operations the experiment provided fundamental data to inform process length and digester design that could be used to improve the financial viability of intermittently fed systems. The outcomes of this chapter will now be applied to a fed-batch process and the method refined to identify:

- The effects of shear rate and resting on methanogenesis and CH_4 production using a HRT of 30 days to produce a YF relationship.
- Parasitic energy demanded by each mixing regime to produce a PF relationship.
- A net energy hierarchy and therefore optimum mixing regime for the mixing system used.

CHAPTER 4 – EFFECTS OF MIXING ON A FED-BATCH PROCESS USING A 30-DAY HRT

4:1 Introduction

Although the outcomes of the batch experimentation were useful to compare the effects of mixing regime on net energy production, dairy farm operations generate a continuous feedstock of cow slurry of reasonably predictable content that has to be managed on a daily basis, as outlined in chapter 1. This continuous access to a sustainable feedstock fixes the OLR for an AD system fed on slurry alone, particularly if cattle are housed throughout the year. With large volumes of new feedstock being introduced daily, a fed-batch process is more appropriate. The importance of mixing the digester contents therefore increases as new nutrients need to be distributed throughout the digester and thermal gradients within the substrate minimised (Benbelkacem et al. 2013; Ghanimeh et al. 2012). Furthermore, as demonstrated in chapter 3, selecting a mixing regime that minimises parasitic energy demand could significantly influence net energy production.

4:1:1 Aims

The aims of this chapter are to:

- Quantify the effects of shear rate and resting (intermittency) on methanogenesis and hence the rate of CH_4 production and cumulative yield in an intermittently fed digester using a 30-day HRT.
- Assess process biodegradation performance for each mixing regime.
- Compare the parasitic energy demanded by each mixing regime and produce a dimensionless power factor.
- Compare cumulative CH_4 yields produced by each mixing regime and produce a dimensionless yield factor.
- Combine power factor and yield factor values for each mixing regime to produce an overall comparative rating on which a performance hierarchy can be based.

- Identify any trend in CH_4 production rate that could enable the adjustment of the HRT to optimise CH_4 production.

4:2 Materials and Method

The fundamental materials and methods used were similar to those applied in the batch experiment (chapter 3). Any differences to the methods are highlighted at the appropriate point to provide a clear comparison.

4:2:1 Data Requirements

Shear rate intensity, mixing time and resting associated with intermittent mixing were the control variables applied to identify their effect on CH_4 production rate, yield and the parasitic energy associated with each mixing regime (as per chapter 3). Results were used to calculate a net energy balance for each experimental configuration.

4:2:2 Equipment

The AMPTS II Bio-processor configured with 2000ml digesters was used to investigate the intermittent feeding with cow slurry in an AD process. Results of the batch analysis informed the configuration of 2 fed-batch experiments each using 6 digesters housed in a single AMPTS II unit (Figure 47).

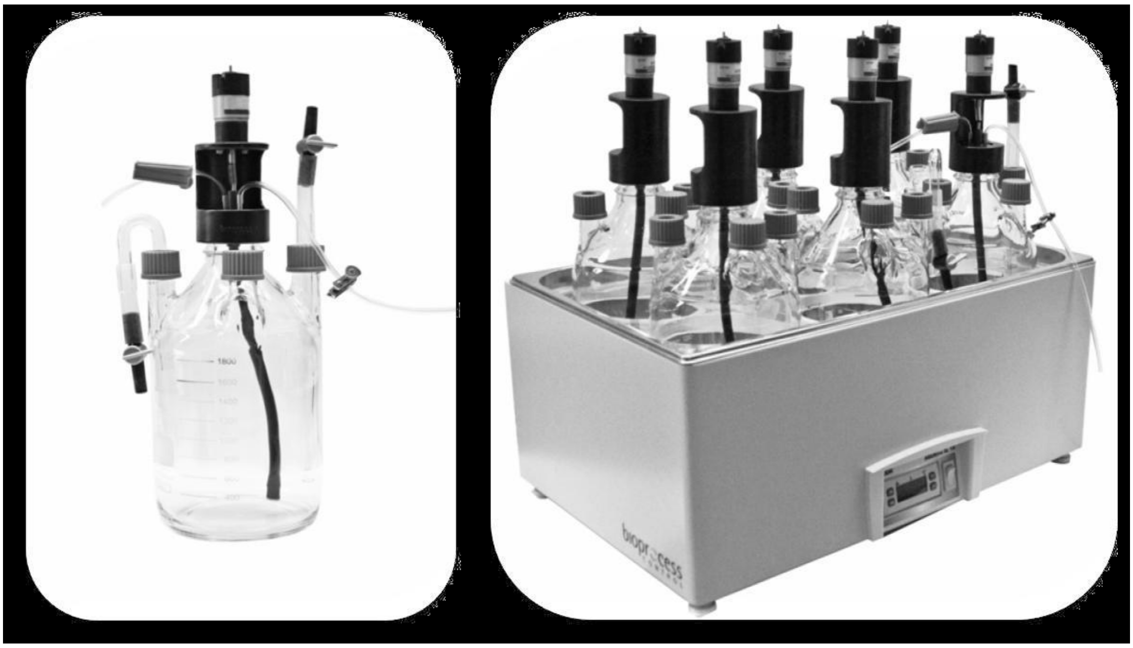


Figure 47 – The AMPTS II 2000ml digester and hot water bath unit housing 6 digesters
(Courtesy of Bioprocess Control Sweden AB)

4:2:3 Equipment Limitations

The application of the equipment was initially limited as follows:

- As explained in chapter 3, the mixers used in the AMPTS II system could not accommodate different mixing intensities and on/off periods for individual digesters.
- The requirement to obtain more than one measurement per digester configuration to address substrate inconsistency by obtaining mean values reduced the number of mixing configurations that could be monitored.
- Digesters had to be transferred to a fume cabinet to be fed.
- A common CH_4 content of the biogas for all digesters had to be assumed and programmed into the AMPTS II bioprocessor.

4:2:4 Methods Adopted to Address Limitations

Equipment limitations were addressed as follows:

- The wiring configuration and PLC programmes used to mix the batch process digesters were adapted to provide the required mixing regimes.
- Data from the batch experiment was used to parse the extensive selection of mixing regimes used in chapter 3 to an achievable number that still captured key extremes of variables in duplicate.
- An operating procedure was devised to disconnect digesters from the gas monitoring system and isolate the motors electrically before transferring the digesters from the heated water bath to the fume cabinet. This increased the opportunity for procedural error and the risk of digester integrity being breached but allowed feeding to take place inside the laboratory.
- A common biogas quality of 60 percent CH_4 and the subsequent limiting effects on the research were accepted.

4:2:5 Assumptions

The analysis adopted similar assumptions to those used in the batch experiment.

4:2:6 Feedstock

Fresh cow slurry was sourced from the same farm as previously used. A 30-day HRT resulted in an average feed rate of 67g of slurry per digester per day, equating to an initial OLR of $2.53g_{VS}l^{-1}d^{-1}$ based on a feedstock of 11%TS. A similar amount of digestate was simultaneously removed. A breakdown of slurry content for both experiments is summarised at Table 13.

Experiment Number	**Start-up**		**Subsequent Feedstock**		
	%TS	**%VS**	**%TS**	**%VS**	**OLR (g VSl^{-1}d^{-1})**
1	8.0	68.3	11.0	68.9	2.53
2	8.5	65.8	10.6	67.8	2.40

Table 13 – Characteristics of substrate

4:2:7 Quantifying Homogeneity

The results of the batch analysis suggested that similar shear rates should be captured (33, 55 and 125s^{-1}) during intermittent feeding. The outcomes of the ERT modelling using a larger digester vessel and a 3.5%CMC concentration was applied to simulate rheological conditions experienced and hence the time required to homogenise cow slurry when mixed using different shear rates after scaling up.

4:2:8 Improving AMPTS II Bio-processor Safety

Prior to the start of the analysis, a trial attempt at running 6 digesters fed daily on cow slurry resulted in an over-pressurisation of 3 digesters (including one explosion) when biogas outlets became fouled with substrate. This may have been the result of gas bubble activity at the surface causing substrate to foul the narrow gas outlet. However, on dismantling the digesters in question, substrate was also found to have migrated up the stirring rod, the top of which was adjacent to the gas outlet. This apparent weakness in the mixing technique used by the equipment when mixing cow slurry was accepted. However, the apparatus was re-designed using the third outlet of the Duran flask to introduce a secondary gas outlet and pressure relief valve (PRV) distanced from the active area of the gas headspace and the stirrer mechanism (Figure 48).

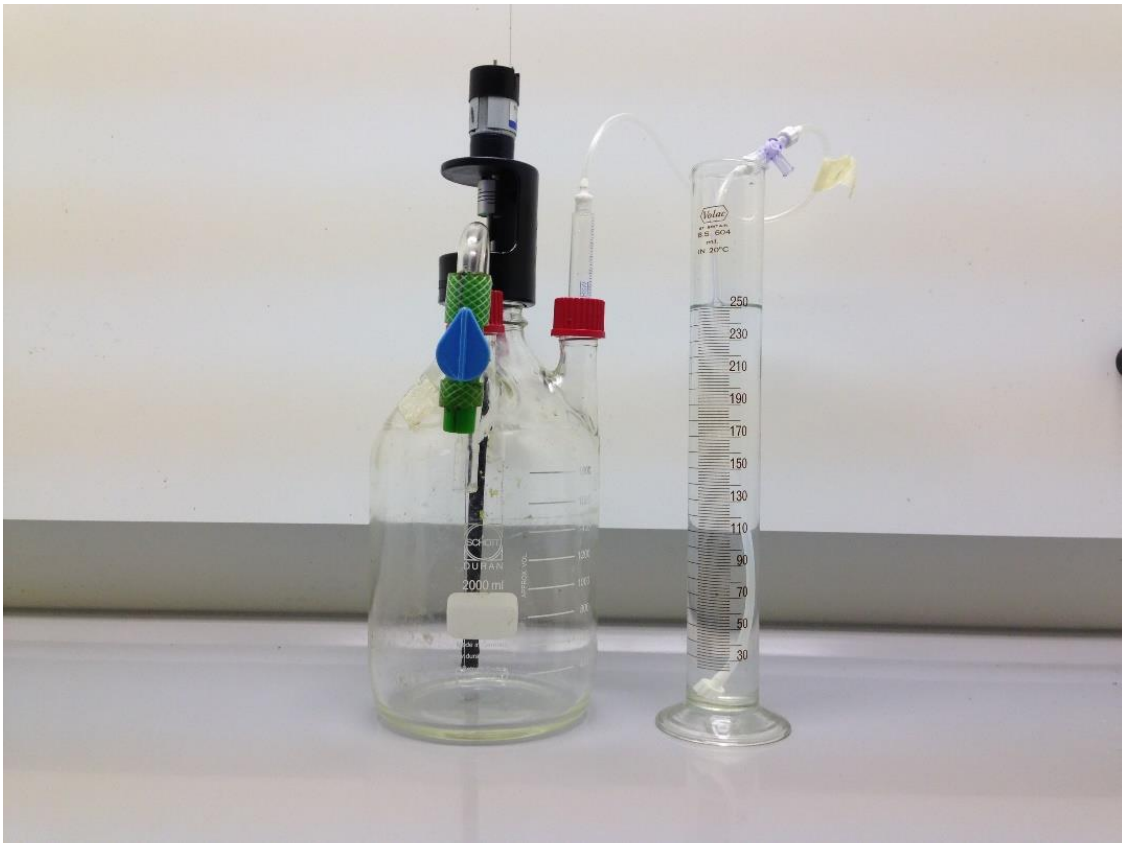


Figure 48 – Pressure relief valve system

A length of gas hose with a connecting valve at the top and weighted at the bottom was immersed in a column of 25 centimetres of water to provide 25 millibars (mb) of overpressure at the hose outlet. As the CH_4 tippers activated at 5mb this provided an overpressure safety factor of 5, ensuring that the tipper would activate before the PRV. Should pressure exceed 25mb due to fouling of the primary gas outlet hose, biogas would be released through the PRV into the water column. A valve was introduced to allow isolation of the apparatus during feeding. Figure 49 outlines the 6-digester configuration. A blast tray, cover and weighted lid was included in case of PRV failure.

Figure 49 – Adapted Duran flask and AMPTS II with safety features installed

4:2:9 Digester Procedure and Set-up

The reduction of digester numbers from 42 (used in the batch experiment) to 6 required the experimental set-up to be adjusted without compromising the range of key control variables to be captured. Shear rates were similar to those used in the batch experiment but rest periods were restricted to 1, 6 and 12 hours. The larger digesters required lower stirrer rpm and hence lower voltages to be calculated before mixing times could be identified using the same ERT technique detailed in chapter 2. The updated rpm settings were tested on slurry samples to ensure rotation was achievable. Table 14 captures the key input variables used in the various mixing configurations. Mixing periods were higher than those used in the batch experiment. Unfortunately, the extremes of non-mixing and continuous mixing had to be excluded although a non-mixed regime was introduced later. Separate experiments were designed to provide temporal separation of shear rate and resting so an independent assessment of their impact could be made. Within each experiment digesters where paired to provide mean CH_4 output values. A mesophilic temperature of 37.5˚C was used throughout the experiment.

Shear Rate (s^{-1})	33	55	125
Stirrer speed (rpm)	17.3	28.8	65.6
DC Voltage (V)	3.24	4.45	7.74
On Period (min/sec)	23m59s	19m33s	7m21s
Off Period (hour)	1, 6 and 12		

Table 14 – Input parameters used when intermittently feeding

4:2:9:1 Experiment 1: Variable Rest Period and Fixed Shear Rate ($55s^{-1}$)

The 6 digesters were inoculated with 1800ml of substrate from the terminated pre- experiment trial. During the 4 months since last used the substrate had been stored at 4˚C with no obvious signs of AD taking place such as biogas accumulation in the storage vessel. The experiment was initiated at 37.5˚C. An additional 200g of cow slurry was added 2 days after start-up without removing any digestate, resulting in 2000ml of digester content leaving approximately 10 percent gas headspace. Digesters were then acclimatised by feeding every 3-days and intermittently mixed using the shear rate regime of $55s^{-1}$ rested for 6 hours (outlined in Table 14). CH_4 production was similar to that gained before the previous experiment terminated so the process was regarded as stable and the substrate suitable. An enforced 12-day period of no feeding then occurred. On returning, a 5 percent difference was observed in cumulative biogas values across the digesters so all were dismantled and the substrate communally mixed before being re-distributed. Biogas outputs were monitored for 48 hours with a reduction in discrepancies noted. The digesters were paired according to output with worst and best performers forming the first pair, second best/worst the second and the 2 remaining digesters the third. This ensured that the digesters providing the widest discrepancies were used to provide mean values and avoid biasing the results. Experiment 1 then commenced consisting of 3 paired 2000ml digesters subjected to a similar feeding regime and mixed at a similar shear rate of $55s^{-1}$. Each digester pair was electrically connected in parallel and a PLC used to switch each pair on for the same duration. However, each pair was programmed with individual rest periods as outlined in Figure 50. A 30-day HRT was applied to simulate a common mesophilic farm AD system. The experiment ran for 35 days (1.17 x HRT) to ensure a full HRT cycle was captured. An experimental run time of 3 x HRT would have been preferred to confirm long-term process stability and provide mean results over 3 complete retention cycles but access to equipment and time was limited. As the substrate would already be acclimatised the need for long-term monitoring of the process was reduced and the shorter experimental length accepted.

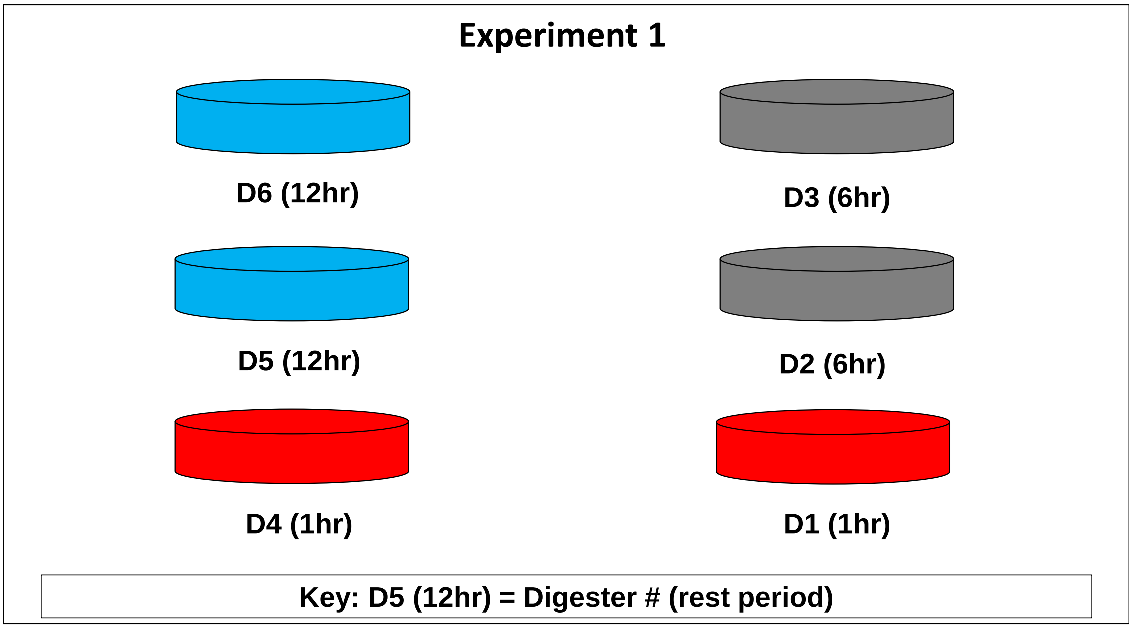


Figure 50 – AMPTS II configuration using a 30-day HRT, variable rest period and fixed shear rate ($55s^{-1}$)

4:2:9:2 Experiment 2: Variable Shear Rate and Fixed Rest Period (6hrs)

On completion of experiment 1 the digesters were dismantled, cleaned and serviced prior to re-assembly. Once again the substrate was communally mixed and re-distributed charging each digester with 1800g. Digesters were then fed with 200g of cow slurry and left to stabilise for 3 days. CH_4 production was checked with little discrepancy observed between CH_4 yields. Digester pairing was carried out using the same method as before and the experiment commenced. The rest period was fixed at 6 hours and the paired digesters initially programmed to mix at shear rates of 33, 55 and $125s^{-1}$. However, during the first

4 days of the experiment the stirrer in digester 1 proved unreliable unless the voltage was increased considerably to overcome friction within the substrate. Replacing the motor had no effect. This issue could not be resolved without increasing the voltage to a level almost equal to that used to induce a shear rate of 55s^{-1}, a variable already being monitored. Digester 1 was therefore changed to a non-mixed configuration and the system reset. Although this resulted in only a single digester being mixed at a shear rate of 33s^{-1} the failure provided the opportunity to include a non-mixed digester (Figure 51) but at the expense of achieving mean values for those regimes. The experiment ran for 38 days (1.27 x HRT).

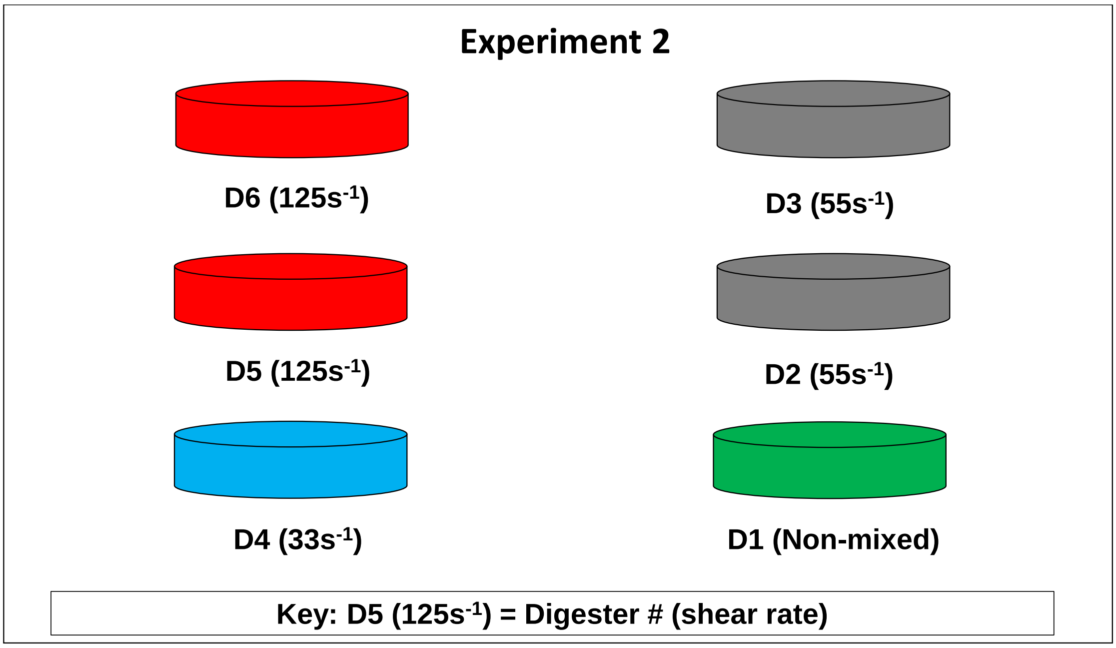


Figure 51 – AMPTS II configuration using a 30-day HRT, variable shear rate and fixed rest period (6hrs)

4:2:10 Feeding

To quantify potential sample losses during the feeding process, slurry and digestate residues on equipment such as funnels, syringes and plungers were weighed after feeding. This occurred during the pre-experimental trials. Average values of losses are presented in Table 15. The resultant percentage of residual ‘waste’ per feed was regarded as unacceptably high (up to 3 percent) when digesters were fed daily, so the feeding period was adjusted until an acceptable residual waste figure of 1 percent was achieved. Although daily feeding would have been more appropriate to simulate typical farm operations, feeding every 3 days was necessary to minimise losses. Losses were eventually reduced further prior to starting experiment 1 by adjusting the procedure to feed each digester with 203g of slurry whilst removing only 199g of digestate.

Feeding Period	**Addition**			**Removal**		
	Feed	**Residue**	**Error**	**Digestate**	**Residue**	**Error**
	(g)	**(g)**	**(%)**	**(g)**	**(g)**	**(%)**
Daily	67	2	3.0	67	1	1.5
Once every 3 days	201	2	1.0	201	1	0.5

Table 15 – Breakdown of potential losses during the feeding procedure

4:2:11 Feeding Procedure

Failing to achieve the same percentage of homogeneity in all digesters prior to effluent removal can affect the SRT of each digester (Lindmark et al. 2014). However, as the mixing times for each digester configuration varied this was impractical without varying the feed time (and complicating the feeding routine) to ensure that digesters were always mixed before removing digestate, a practice that itself would compromise the experiment by potentially over-mixing. Moreover, stratification is directly influenced by the length of the rest period so should be captured in such analysis. As a compromise, digestate was only removed between mixing periods and never allowed to interfere with a mixing protocol. Feeding was achieved using the following procedure:

- Visual check of apparatus and data to ensure experiment was functioning as expected.
- Time the procedure to avoid interrupting mixing periods.
- Remove apparatus weighted lid and safety cover.
- Select a digester and close the taps connecting the biogas outlets to the gas processing vessel and PRV chamber.
- Disconnect biogas hoses at the taps.
- Electrically disconnect digester motor.
- Remove digester from the AMPTS II and transfer to a fume cabinet.
- Attach funnel to feed inlet and place digester on scales and reset scales to zero.
- Charge the funnel with 203g of slurry.
- Remove digester from scales.
- Place suitable receptacle on scales and reset to zero.
- Attach a 100mm syringe with an enlarged nozzle (adapted to accommodate slurry) to the digestate outlet valve of the digester using a 100mm length of ½ inch braided hose.
- Open inlet/outlet valves and extract 199g of digestate before closing the valve.
- Return any surplus digestate to the digester through feed inlet.
- Close all valves and return digester to the AMPTS II heated bath.

- Reconnect hoses and wiring.
- Check valves are open.
- Repeat procedure for remaining digesters.

Although this routine was time-consuming, the procedure was required to allow experimentation using the AMPTS II to continue. Extracted digestate samples were stored at 4˚C in case needed. The bio-degradation process was monitored and process efficiency estimated by comparing original and final %TS and %VS values. However, such calculations were complicated by the occasional but necessary addition of equal quantities of de-ionised water to each digester to address evaporation losses, probably as part of the biogas. Such losses could lower substrate levels in the digester so had to be avoided. As the OLR and the volume of digestate removed were fixed, a relatively stable bio-degradation process was predicted, particularly as the HRT remained unchanged throughout.

4:2:12 Monitoring

Periodic pH measurements of removed digestate were taken to confirm that environmental conditions within the digester were acceptable and stable. CH_4 production was measured hourly as an indicator of microbial community health (particularly methanogens), growth and process stability.

4:2:13 Data Comparison

Techniques were similar to those adopted in chapter 3 to simplify any comparison between outcomes of the batch and fed-batch processes. Hence, process optimisation was assessed using relative CH_4 production rate, cumulative CH_4 yield and the parasitic energy demanded of the mixing regimes. YF and PF values were produced to identify CH_4 yield and net energy production hierarchies.

4:2:14 Process Efficiency

Basic efficiency of an AD process was calculated using a traditional method of comparing the mass of the undigested VS (w/w) remaining in the digester at the end of the process with the total VS (w/w) introduced to the process. However, VS considered as processed (not left in the digester) could take 2 forms: that which was biodegraded and that which was washed out when digestate was removed during fed-batch operations. Only when all VS was accounted for could a reliable mass balance be performed and actual process efficiency be accurately calculated that accounted for VS displaced as efficiency changed over the experimental period. However, differentiating between VS biodegraded and VS washed out required VS analysis of the digestate removed at every feed which was not carried out.

4:2:15 Estimating VS Washout

Total VS introduced to the process, VS remaining at the close of the experiment and cumulative CH_4 produced throughout were measured. As each AD experiment was considered in isolation the VS was initially divided into that which was digested and that which was not. Alternative methods of estimating VS washed out during digestate removal were then applied:

<u>Method A</u>: Using CH_4 yield (ml), total VS introduced (g) and VS remaining (g) values, a ratio was calculated to estimate VS process apportionment based on the assumption that the CH_4 potential would be the same whatever pathway the VS should take. In this analysis 1 gram of VS from a dairy cow in the temperate climate of Western Europe was accepted as having the potential to produce 240ml CH_4 (Zeeman & Gerbens, 1996), research that informed the IPCC Guidelines for National Greenhouse Gas Inventories (IPCC, 2006). CH_4 yield (ml) was converted into the mass required (g) to produce the gas and added to the known mass of the VS that remained in the digester at the end of the experiment. Total VS washed out was then estimated using Equation 9:

$$VS_{(w)} = VS_{(i)} - (VS_{(d)} + VS_{(r)}) \qquad \text{Equation 9}$$

Where $VS_{(w)}$ equals VS washed out, $VS_{(i)}$ is total VS introduced, $VS_{(d)}$ represents VS digested and $VS_{(r)}$ is VS remaining in the digester. A basic ratio was produced and applied to estimate VS apportionment and hence overall washout. This method was limited in the following manner:

- An actual VS/CH_4 conversion factor specific to the research was not identifiable.
- Actual VS washout was likely to vary throughout the experiment as VS removed with digestate at each feed would depend on when during the experiment the digestate was removed and whether the digester contents had been mixed prior to digestate removal. The latter could be significant if the digester had not been mixed for 12 hours and settling had occurred. However, as the primary aim of the research was to identify the effects of different mixing regimes on CH_4 production, mixing was not interrupted and hence compromised for the sake of homogenising digester contents to accurately predict washout at each feed. Instead, washout for the whole experiment was estimated at the end using complete mass balance values.
- No account was taken of any improvement in VS biodegradation over time as methanogens adapted to their environment and metabolism increased (adaptation).

Method B: Although method A provided a means of estimating VS washout and a ratio of VS apportionment the technique relied on generic CH_4 yield data rather than actual yields achieved during the experiment. However, if the process was assumed to be in a steady state and a digester well-mixed when digestate was removed, the %VS of the digestate periodically removed would equal the final %VS value of the digester contents. VS washed out was estimated using the same measured values of CH_4 yield (ml), total VS introduced (g) and VS remaining (g) values. VS digested was then calculated as follows:

$$VS_{(d)} = VS_{(i)} - (VS_{(w)} + VS_{(r)}) \qquad \text{Equation 10}$$

This method allowed actual CH_4 conversion rates to be calculated but was limited as:

- Digesters may have been at different states of homogeneity when digestate was removed.
- The process may not always be at a steady state, particularly after a change in OLR.
- Methanogen adaptation and a subsequent increase in biodegradation performance was not accounted for.

Although both methods have benefits and drawbacks, together they provide an indication of CH_4 production per g of slurry and a more informed appreciation of the extent of potential VS washout and therefore VS available for biodegradation.

4:2:16 Biodegradation Efficiency

With VS introduced and VS remaining measured and VS digested and washed out estimated, the efficiency of the biodegradation process was calculated as follows:

$$\text{Biodegradation Efficiency } (\eta) = VS_{(d)} / VS_{(i)} \qquad \text{Equation 11}$$

This method of calculating biodegradation efficiency included the CH_4 potential of substrate that had yet to be converted (or washed out). Hence, the value represented the efficiency of the biodegradation process at the time of measurement and did not account for any dynamic changes in the balance between future biodegradation and washout if steady state process conditions varied or microbial adaptation during the experiment. Hence, process biodegradation efficiency would likely change should the experiment be extended.

4:2:17 Power/Yield Factors

Calculating PF and YF and the overall comparison factor used the same methods as those described in chapter 3.

4:3 Results and Discussion

4:3:1 Effectiveness of Experimental Technique

Feeding the 6 x 2000ml digesters in a clean laboratory environment proved challenging when using the AMPTS II system fed with cow slurry. Incidents of gas leaks and fouling were common at the outset but were resolved by the end of the settling/acclimatisation phase. The procedure for transferring digesters to and from the fume cabinet proved manageable. As feeding each digester took approximately 20 minutes any drop in digester temperature due to removal from the heating source was minimal and common to all digesters. Feedstock was not heated prior to insertion. To reduce opportunities for error and minimise process disruption, digesters were fed in pairs. As highlighted in chapter 3, measuring actual biogas yield and the CH_4 content of the gaseous products of all mixing regimes would have more accurately quantified the effects of mixing regime on biogas quality. Research efficacy could have been improved further by measuring the VS content of digestate when removed. For clarity, the results of each experiment are presented separately. Only mean values of paired digesters are presented.

4:3:2 CH_4 Production Using a 30-Day HRT and Fixed Shear Rate ($55s^{-1}$)

4:3:2:1 Effects of Resting on Cumulative CH_4 Yield

After 35 days of mixing using different rest periods with a common shear rate of $55s^{-1}$ the 1 hour resting regime produced the most CH_4 (34,500Nml) followed by the digesters rested for 6 hours (33,000Nml) (Figure 52). The 12 hour regime produced the lowest yield (32,500Nml). The 6 hour regime was 4.4 percent lower than the 1 hour with the 12 hour trailing by a further 1.5 percent. Variation in feed cycle timings were reflected in the parallel undulating nature of the profiles. The levelling off of the profile at the end was because the experiment ran on a day without additional feeding. The maximum value achieved equated to a biogas yield of $24.68m^3t^{-1}_{slurry}$ during a 30-day period. Biogas yield was calculated based on a CH_4 content of 60 percent. This equates favourably to the 15-25m^3 predicted in literature (Andersons Centre, 2010) and was 3 percent higher than the maximum achieved when the rest period was fixed and the shear rate varied. As reported in chapter 3, the effects of resting period on CH_4 production had not been previously researched yet demonstrated that resting periods adopted during intermittent mixing could affect CH_4 yield. Moreover, as the rheological characteristics of cow slurry recover within 1 hour of resting (demonstrated in chapter 2), thixotropic recovery is unlikely to be the reason as the condition was common to all. As the same shear rate was used for all rest periods the more likely reason is the increase in microbial access to nutrients and biogas removal opportunities provided by additional mixing events.

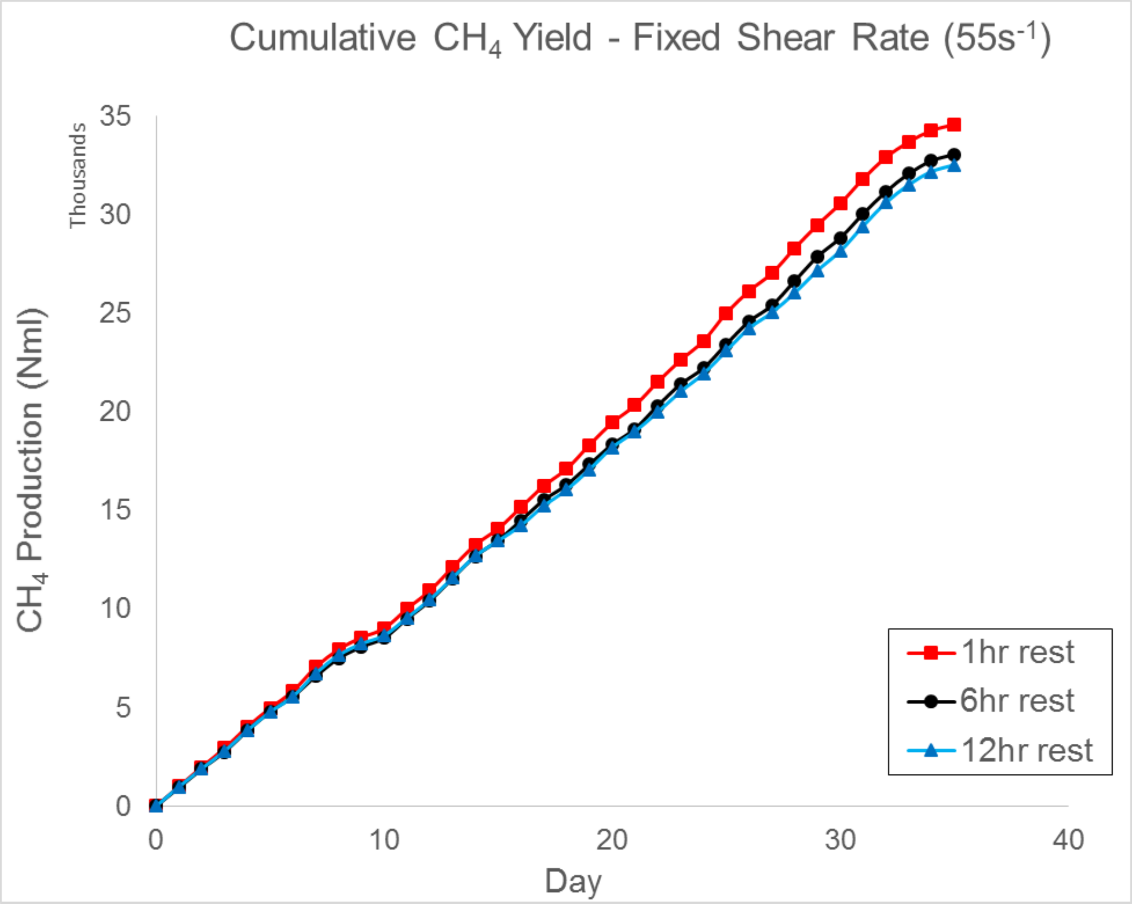


Figure 52 – Cumulative CH_4 yield achieved using a 30-day HRT, variable rest period and fixed shear rate ($55s^{-1}$)

4:3:2:2 Effect of Rest Period on CH_4 Production Rate

Generally, CH_4 production trends were similar for each feeding cycle with the rate of CH_4 production increasing shortly after new feedstock was introduced and then gradually declining as nutrients were consumed making temporal changes in the 3-day feeding regime obvious (Figure 53). A detailed analysis/comparison of CH_4 production rate cycles in response to mixing regime could not be found in literature increasing the value of the results. There were distinct differences between peak levels of CH_4 production for each resting regime at particular times throughout the experiment. The highest hourly CH_4 production of 73Nmlh^{-1} was achieved during hour 594 using a 1 hour rest period (shown in red). The second highest produced 18 percent less (60.7Nmlh^{-1} during hour 743) using a 12 hour rest period (black). Individual values varied between profiles but could not be directly compared as the mixing periods diverged as the experiment progressed due to variations in rest periods.

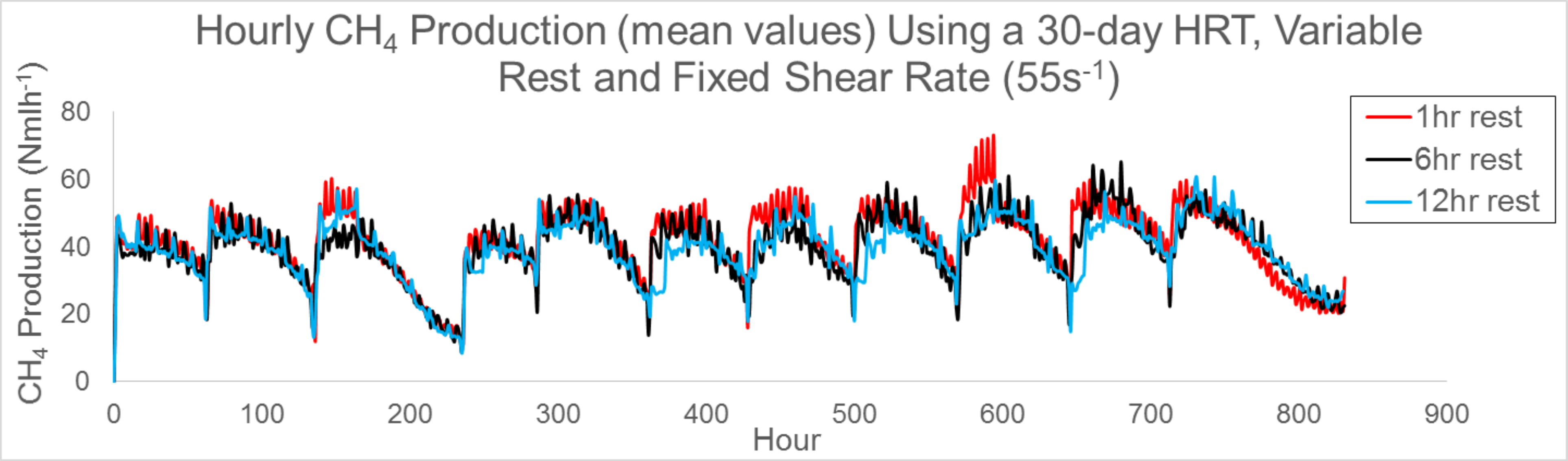


Figure 53 – CH_4 production using a 30-day HRT, variable rest period and fixed shear rate ($55s^{-1}$)

The relatively low CH_4 production rate observed on the 6-hour rest curve (blue) between hours 135 and 165 was caused by the failure of one of the paired digesters to mix after feeding which highlighted the benefits of mixing observed by Ghanimeh et al. (2012b). Investigation uncovered a loose motor grub screw inhibiting stirrer rotation which was corrected and mixing resumed. Other reductions in CH_4 production rate were also observed on the 12-hour rest curve (black) at hours 362, 428, 500 and 646 which coincided with the beginning of a feed cycle. Feed cycle 6 (hrs 362 to 428) is expanded for clarity (Figure 54) with the hours adjusted to describe the cycle in isolation. The reduction in CH_4 production rates common to the beginning of all these feed cycles coincided with feeding being in anti-phase with the mixing period. This could be up to 6 hours in the case of digesters rested for 12 hours; hence the digesters rested for 12 hours (black) were more affected than those rested for 6 (blue). Digesters rested for 1 hour (red) were not affected demonstrating the benefits of shorter rest periods when CH_4 production was considered in isolation. Digesters that experienced relatively lower CH_4 production at the beginning of a feed cycle generally recovered the shortfall before the next feed. The CH_4 production profile for the 1 hour rest cycle tended to be sinusoidal and register increases every 4 hours rather than coinciding with the hourly mixing cycle. The 6 and 12-hour rest cycle digesters registered significant increases that coincided with the mixing intervals.

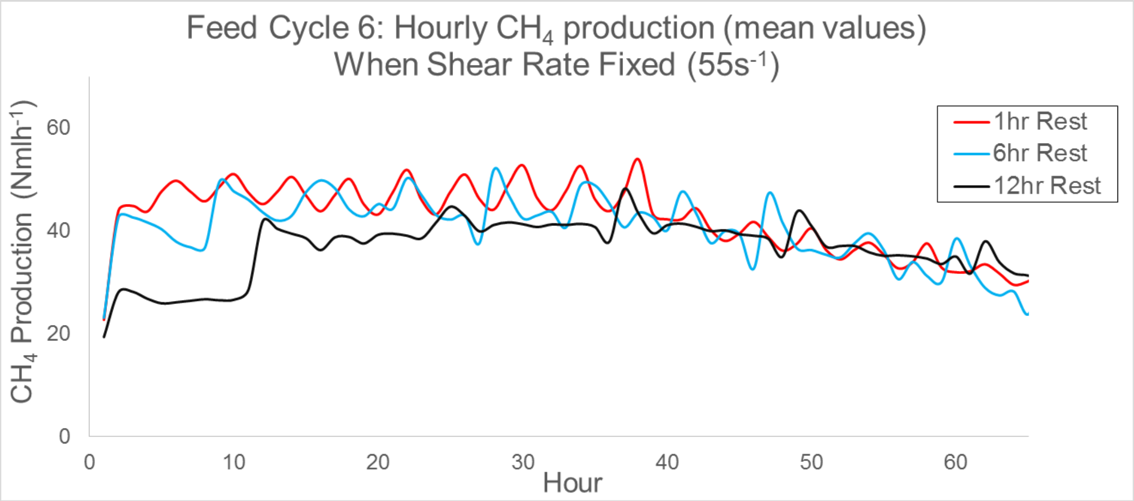


Figure 54 – Hourly CH_4 production using a 30-day HRT, variable rest period and fixed shear rate ($55s^{-1}$) during feed cycle 6

4:3:2:3 Specific CH_4 Production Rate

A histogram of specific CH_4 production rates for all mixing regimes produced distribution curves generally based around a median of approximately $0.02Nml_{CH4}h^{-1}ml^{-1}_{substrate}$. Specific CH_4 production rates were generally similar for all rest periods when a fixed shear rate was applied (Figure 55). CH_4 production rate had been highlighted as important by Bensmann et al. (2013) although detailed analysis similar to that carried out in this study could not be found in literature. In this experiment rest period was demonstrated to have minimal impact on CH_4 production rate when a 30-day HRT was applied in a fed-batch process but may have more relevance when HRT is reduced (chapter 5).

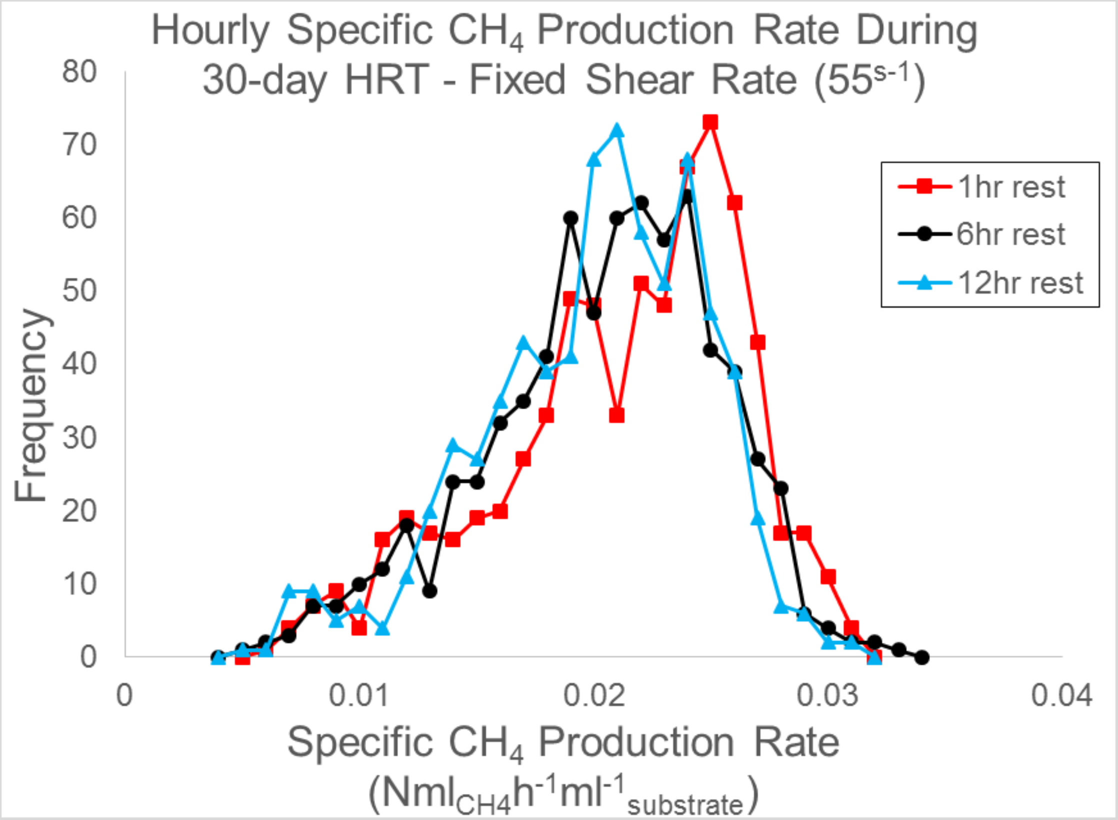


Figure 55 – Specific CH_4 production rate using a 30-day HRT, variable rest period and fixed shear rate ($55s^{-1}$)

4:3:2:4 Changes in Substrate Characteristics

The %TS and VS of the substrate at the start was the same for all digesters (8.0%TS of which 68.3 percent was volatile). The digesters were fed an average of 5.1$g_{VS}d^{-1}$. After 35 days digester contents were measured separately but differed by less than 1 percent (circa 111.5g). Over the length of the experiment the substrate VS reduced by 1.9 percent in all digesters (Table 16) whereas the CH_4 produced from a common substrate varied by as much as 6.6 percent, depending on rest period (Table 19) and (Table 20). The reduction in VS would likely reduce the overall solids content of the substrate making the fluid more Newtonian thereby making rheological responses to mixing more predictable. This would improve the handling characteristics of the digester contents as demonstrated in chapter 2.

Digester	**Rest Period**	**Volume**	**Substrate at Start**			**Substrate at End**			**∆ VS**
			TS	**VS**	**VS**	**TS**	**VS**	**VS**	
(#)	**(hr)**	**(g)**	**(%)**	**(%)**	**(g)**	**(%)**	**(%)**	**(g)**	**(g)**
2&3	**1**	1,800	8.0%	68.3%	113.4	8.5%	65.8%	111.5	-1.9
1&4	**6**	1,800	8.0%	68.3%	113.4	8.5%	65.8%	111.5	-1.9
5&6	**12**	1,800	8.0%	68.3%	113.4	8.5%	65.8%	111.5	-1.9

Slurry fed to each digester over 33 days	Total	TS	VS	Total VS	VSd^{-1}
	(g)	(%)	(%)	(g)	(g)
	2,233	11.0%	68.9%	168.9	5.1

Table 16 – Changes in substrate solids content of digesters over 35 days using a 30-day HRT, variable rest period and fixed shear rate ($55s^{-1}$)

4:3:2:5 Substrate Alkalinity

Alkalinity was monitored by periodically measuring the pH of the removed digestate. A consistent pH value of approximately 8 was maintained throughout suggesting a stable digestion process.

4:3:2:6 Process Efficiency Based on Volatile Solids Biodegradation

As the %TS and VS measurements at the start and finish were similar for all digesters a common basic process efficiency of 61 percent was achieved using method A (Table 19) and method B (Table 20). A similar outcome was expected as the measured data and technique used was common to both methods. However, neither method took account of VS washed out which was not measured when digestate was removed. By estimating VS washout using an accepted value of CH_4 conversion potential derived from source material (method A) (Zeeman & Gerbens, 1996) and applied to all VS pathways (VS converted to CH_4, VS remaining in the digester and VS washed out in digestate) a ratio of VS pathways was produced (Table 17) and the subsequent biodegradation efficiency estimated at between 46-49 percent for all digesters (Table 19).

Alternatively, if digesters were homogenised prior to digestate removal the %VS of the digestate removed should be similar to that of the substrate retained in the digester which was measured (method B), When using this method the VS apportionment was significantly different with more VS being washed out and less digested (Table 18) significantly reducing biodegradation efficiency to 21 percent (Table 20). Both methods indicated that the digester rested for 1 hour digested more VS and experienced less VS washout than those rested for 6 and 12 hours. A mean CH_4 conversion factor of $559ml_{CH4}g^{-1}{}_{VS}$ was achieved using method B which was more than double that cited in key reference literature (Zeeman & Gerbens, 1996) and assumed in the method A calculations and previously published by the Andersons Centre (2010). Any changes in VS washed out can have operational consequences as the rheology of a fluid can change substantially because solids content has an exponential effect on shear stress and apparent viscosity (chapter 2). Quantifying VS washout is therefore not only important for understanding the efficiency of the biodegradation process but essential for predicting the rheological impact on substrate and digestate to ensure mixing effectiveness and hence optimising OPEX.

Whatever the method adopted, the resultant biodegradation efficiencies were regarded as low when digester conditions were ideal for acclimatised mesophilic operations and carried out in a controlled laboratory environment. However, excessive VS and biomass washout is a recognised weakness of single stage CSTR digesters (Deublein & Steinhauser, 2011) which was the configuration that the apparatus represented.

Estimated CH_4 Production Ratio based on $240ml_{CH4}g^{-1}{}_{VS}$			
Rest Period	**Digested**	**Remaining**	**Washed Out**
1	49.4	39.5	11.1
6	47.0	39.5	13.5
12	46.1	39.5	14.4

Table 17 – Estimated ratio of the different VS pathways over 35 days using method A, a 30-day HRT, variable rest period and fixed shear rate ($55s^{-1}$)

Estimated CH_4 Production Ratio			
Rest Period	**Digested**	**Remaining**	**Washed Out**
1	21.2	39.5	39.3
6	20.4	39.9	39.7
12	20.1	40.1	39.9

Table 18 – Estimated ratio of the different VS pathways over 35 days using method B, a 30-day HRT, variable rest period and fixed shear rate ($55s^{-1}$)

The importance of the lack of measured VS data in this experiment must not be underestimated and could not be fully addressed by the estimation methods adopted. By using a common slurry/CH_4 conversion factor, method A may have provided a more accurate estimate of apportionment of total VS introduced to the system whereas method B allowed an actual slurry/CH_4 conversion factor unique to this experiment to be estimated. However, the latter did assume a steady state process throughout the experiment and complete homogeneity at the time of digestate removal which may not have been achieved, particularly if the digester had been rested for some time and subject to settling. Uncertainty was increased further by the assumption that the biogas produced by all mixing regimes had a common 60 percent CH_4 content. Any variation from the assumed figure would affect ultimate biogas yield data.

4:3:2:7 Optimisation Based on Cumulative CH_4 Yield

Cumulative CH_4 yields and the parasitic energy required to produce them were converted to YF and PF values so that regimes could be compared and a performance hierarchy identified. Table 21 provides a summary of the measurements and calculations on which the comparison was based. No comparable literature could be found on the impact of mixing regime (using a common mixing technique) on net energy production.

Rest Period	Total VS Fed (measured)	VS Remaining (measured)	VS Washed Out (estimated)	Theoretical CH_4 Equivalent based on $240ml_{CH4}g^{-1}_{VS}$				Process η	Degradation η
				VS Digested/CH_4 Produced		Remaining	Washed Out		
(hr)	(g)	(g)	(g)	(g)	(ml)	(ml)	(ml)	(%)	(%)
1	282.3	111.5	31.3	139.5	33,469	26,759	7,520	60.5%	49.4%
6	282.3	111.5	38.2	132.6	31,816	26,759	9,172	60.5%	47.0%
12	282.3	111.5	40.6	130.2	31,256	26,759	9,733	60.5%	46.1%

Slurry Conversion to CH_4	0.24 $m^3kg^{-1}_{VS}$ 240,000 $mlkg^{-1}_{VS}$ 240 mlg^{-1}_{VS}	Remarks: Extracted from support research to IPCC Guidelines for National GHG Emissions, 2006

Table 19 – Biodegradation process efficiency of digesters over 35 days using method A, a 30-day HRT, variable rest period and fixed shear rate ($55s^{-1}$)

Rest Period	Total VS Fed (measured)	VS Remaining (measured)	VS Washed Out (estimated)	CH_4 Equivalent				Process η	Degradation η
				VS Digested/CH_4 Produced		Remaining	Washed Out		
(hr)	(g)	(g)	(g)	(g)	(ml)	(ml)	(ml)	(%)	(%)
1	282.3	111.5	110.9	59.8	33,469	62,352	62,040	60.5%	21.2%
6	282.3	111.5	110.9	59.8	31,816	62,352	62,040	60.5%	21.2%
12	282.3	111.5	110.9	59.8	31,256	62,352	62,040	60.5%	21.2%

Mean Slurry Conversion to CH_4	0.56 $m^3kg^{-1}_{VS}$ 559,231 $mlkg^{-1}_{VS}$ 559 mlg^{-1}_{VS}	Remarks: VS washout estimation assumes steady state well-mixed digester content when digestate extracted during feeding process.

Table 20 – Biodegradation process efficiency of digesters over 35 days using method B, a 30-day HRT, variable rest period and fixed shear rate ($55s^{-1}$)

Rest Period (hr)	CH$_4$-derived (m^3)	Equivalent (kWh)	Parasitic (kWh)	Net Power (kWh)	Parasitic (%)	PF	YF	YF (corrected)	PF*YF$_c$	Net Rating
1	0.0346	0.1268	0.0547	0.072	43.10%	0.11	1	0.27	0.03	3
6	0.0330	0.1212	0.0115	0.110	9.50%	0.52	0.96	0.26	0.13	2
12	0.0325	0.1193	0.0059	0.113	4.99%	1	0.94	0.26	0.26	1

Table 21 – Energy output of digesters over 35 days using a 30-day HRT, variable rest period and fixed shear rate (55s^{-1})

4:3:2:8 Parasitic Energy Use and Power Factor

Although the shear rate and associated mixing times were fixed, the differences in rest periods were significant when calculating the long-term parasitic energy demanded of each regime. Shorter rest periods resulted in a higher numbers of mixing cycles. Techniques similar to those used in chapter 3 were applied to identify energy use. As PF is a power demand relationship between mixing regimes based on the best performer, the lowest power consumer was allocated a PF of 1. The digester rested for 1 hour (PF = 0.11) consumed approximately 9 times more power than the digester rested for 12 hours, whereas the digester rested for 6 hours used approximately 5 times (PF = 0.52) the power consumed by the digester rested for 12 hours (Table 21). The percentage of energy derived that was used to satisfy the parasitic demand of the mixed regimes ranged from 5 percent for the 12-hour regime to 43 percent for the digester rested for only 1 hour. Figure 56 illustrates the PF relationship of the mixing regimes.

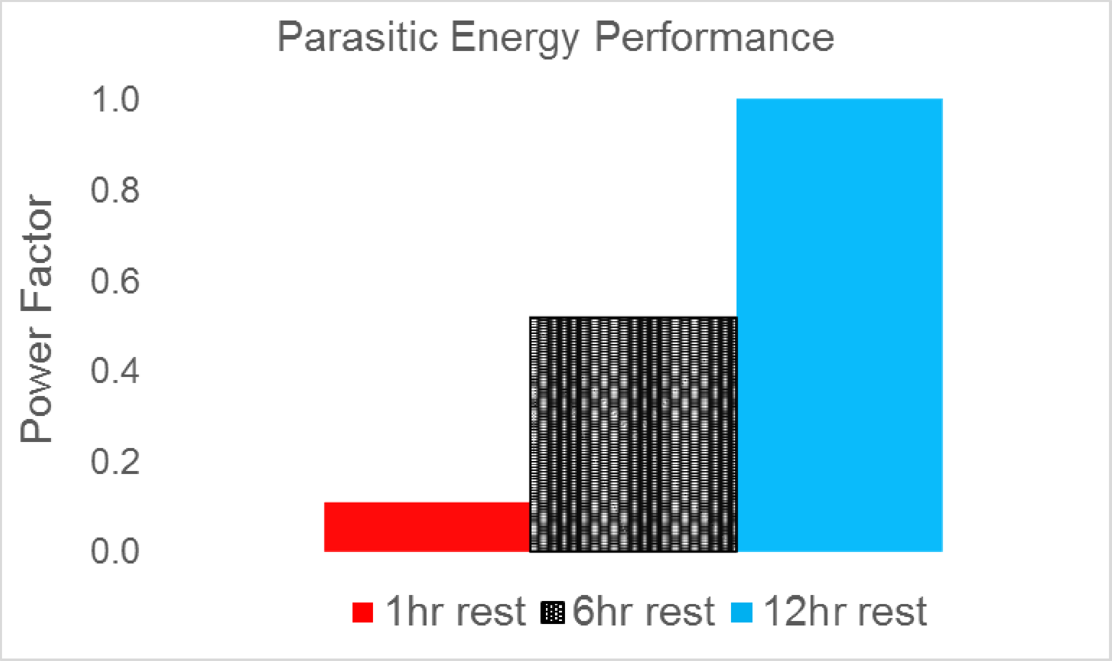


Figure 56 – Comparison of parasitic energy performance using power factor when HRT 30 days, rest period varied and shear rate fixed (55s^{-1})

4:3:2:9 CH_4 Yield and Yield Factor

The comparison of CH_4 yield indicated a small but obvious difference between mixing regimes. However, when converted to baseline kWh values, the YF indicated very little difference with a YF of 0.27 identifying the best performer (highest yield) (Figure 57).

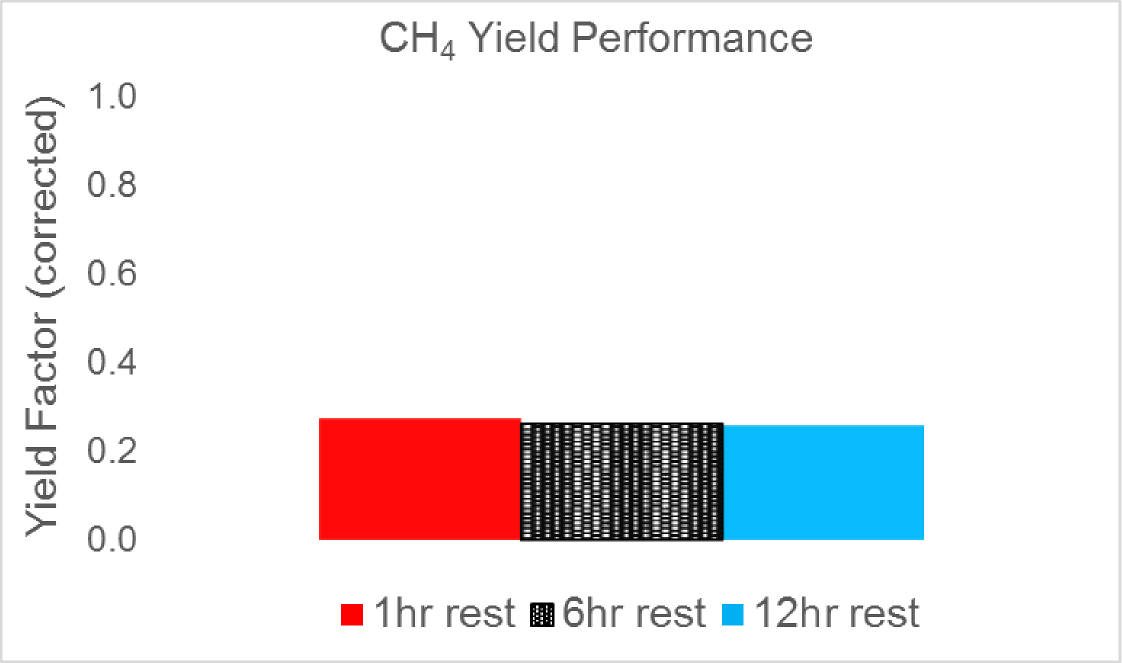


Figure 57 – Comparison on CH_4 yield performance using yield factor when HRT 30 days, rest period varied and shear rate fixed ($55s^{-1}$)

4:3:2:10 Balancing CH_4 Yield and Parasitic Energy

The wide range of PF values compared to the minimal difference in the YF (once corrected to kWh-equivalent values) demonstrated that net energy output was influenced far more by parasitic energy demand than CH_4 production confirming the results of the batch experiment. Despite producing the lowest CH_4 yield, resting for 12 hours produced the highest net yield, followed by the digester rested for 6 hours. The latter produced 53 percent of the net energy produced by the 12 hour resting regime. Resting for 1 hour produced the lowest net energy gain which equated to less than 12 percent of the net energy produced by the digester rested for 12 hours (Figure 58). The full PF/YF range has again been displayed.

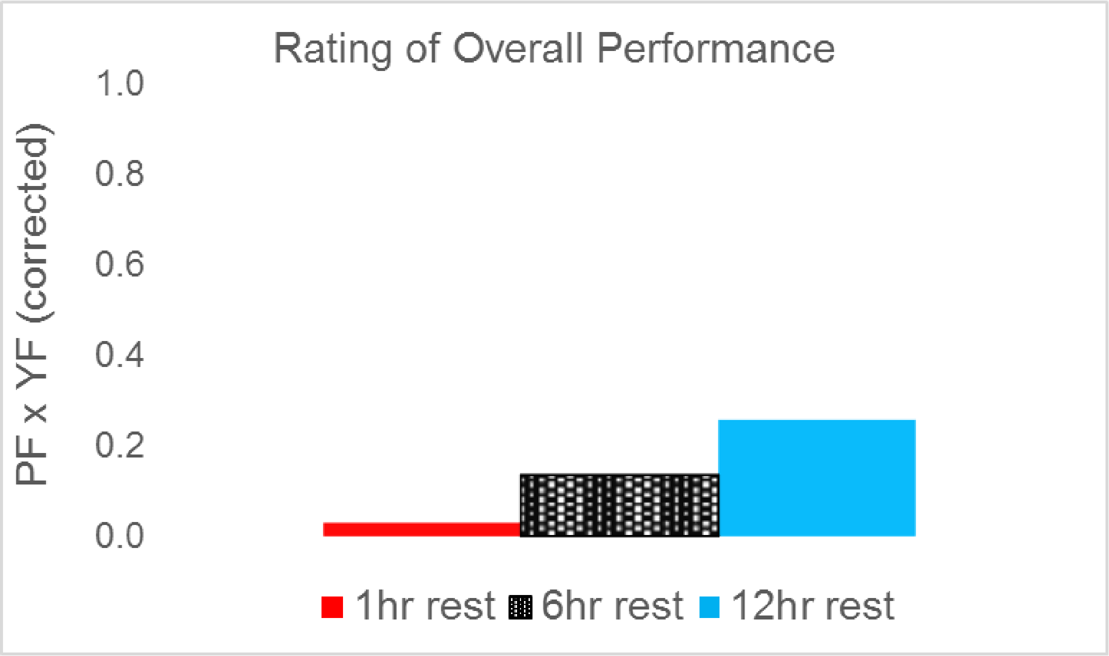


Figure 58 – Comparison of net energy production when HRT 30 days, rest period varied and shear rate fixed ($55s^{-1}$)

4:3:2:11 Optimisation Based on Production Rate

Specific CH_4 production rate profiles were not used as a basis for optimising the rate of CH_4 production to maximise net energy output in this chapter as the main influence of the metric is directly related to HRT which is considered in detail in chapters 5 and 6.

4:3:3 CH_4 Production Using a 30-Day HRT and Fixed Rest Period (6hrs)

4:3:3:1 Effect of Shear Rate on Cumulative CH_4 Yield

Variations in CH_4 yield after 38 days of mixing using different shear rates was less than 1 percent indicating that shear rate had minimal effect on CH_4

production (Figure 59). Again, no comparable literature could be found. The undulating nature of the curve was again probably the result of the 3-day feed cycle. The maximum value achieved was 36,400Nml using a shear rate of 55s^{-1} which equates to a biogas yield of 23.94m^{3}t^{-1}$_{slurry}$ during a 30-day HRT period similar to that reported by the Andersons Centre (2010).

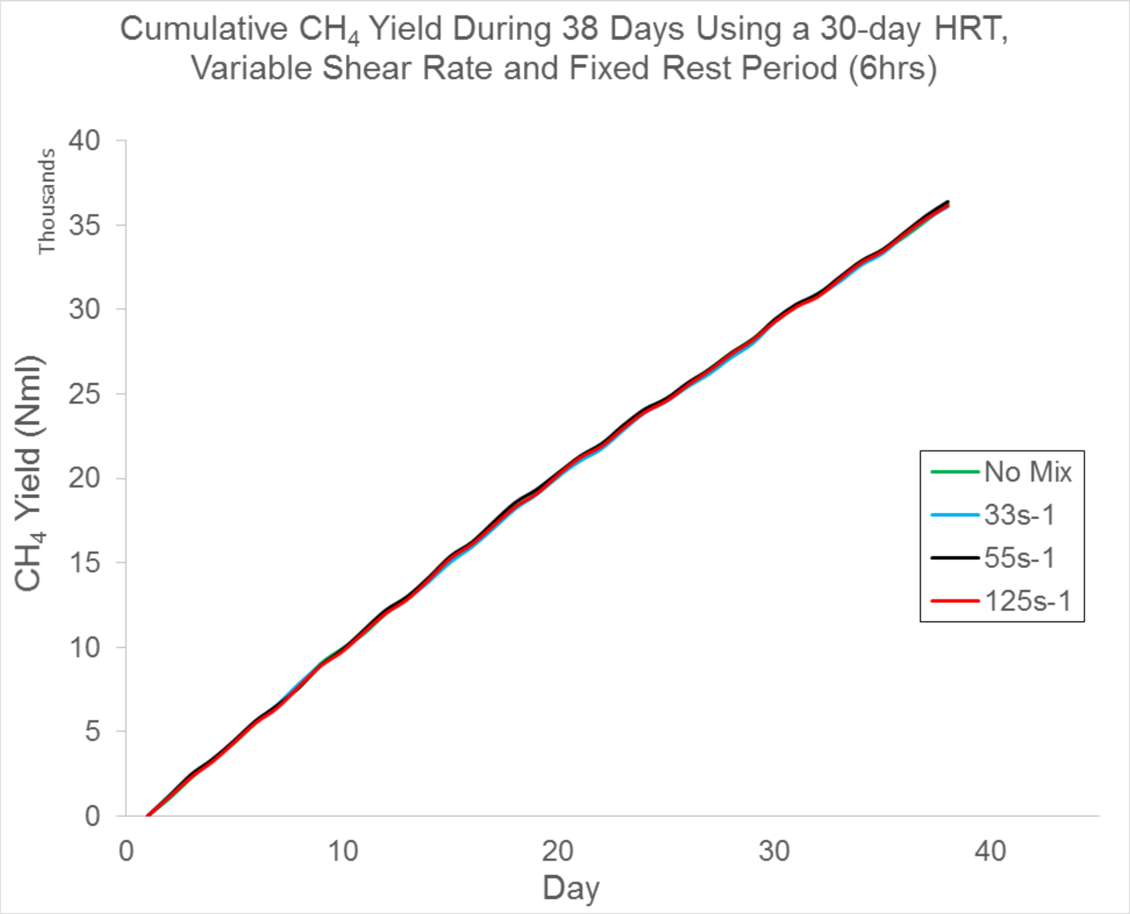


Figure 59 – Cumulative CH_4 yield using a 30-day HRT, variable shear rate and fixed rest period (6hrs)

4:3:3:2 Effect of Shear Rate on CH_4 Production Rate

The rate of CH_4 production increased shortly after new feedstock was introduced and then gradually declined as nutrients were consumed (Figure 60). Hence, the feeding cycle was obvious when observed graphically. Feed rate for cycles 9 and 10 (hours 576-665) had to be reduced to every other day. The routine was recovered later in the experiment by extending a later cycle to 4-days. A peak

CH_4 production rate of 70.8$Nml_{CH4}h^{-1}$ was achieved using a shear rate of 55s^{-1}. Values varied between profiles although overall trends were similar.

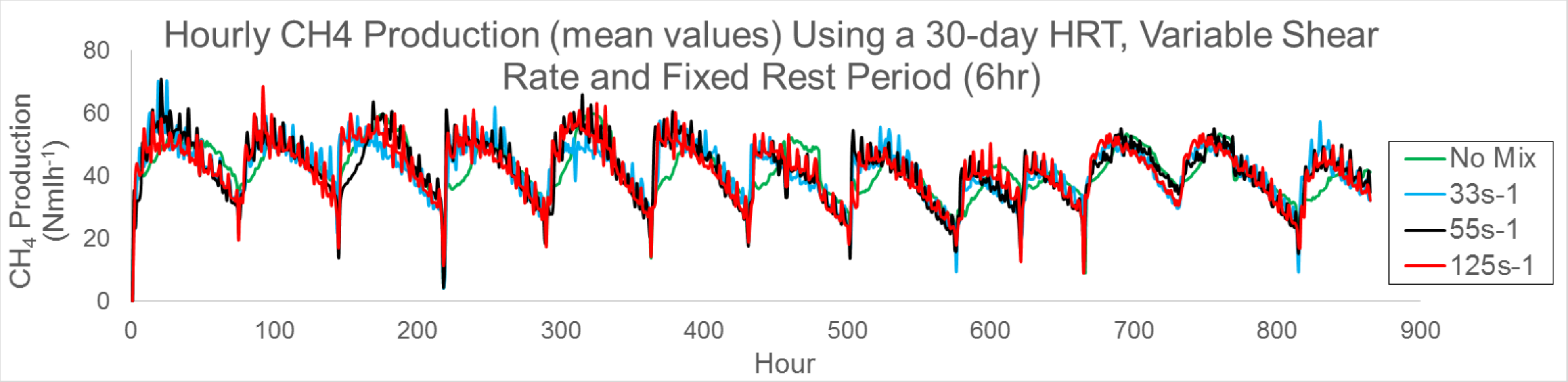


Figure 60 – CH_4 production using a 30-day HRT, variable shear rate and fixed rest period (6hrs)

For clarity, 3 typical 3-day cycles (post-feed 4) are presented (Figure 61). Profiles for the mixed digesters are similar but not synchronised due to different shear rates requiring different lengths of mixing period. However, the unmixed digester (shown in green) had a consistently lower rate of production during the first third of the cycle (hours 218-245) which then coincided with that of the mixed digesters for the next third of the cycle before outperforming them during the final third, resulting in approximately the same CH_4 yield overall. This ability to recover and achieve similar CH_4 yields as mixed digesters during a 3-day feed cycle is important as reducing the cycle period could reduce the potential for CH_4 production recovery thereby reducing biodegradation potential and hence overall yield. A build-up of VS in the digester could also result as discussed in detail in chapter 5.

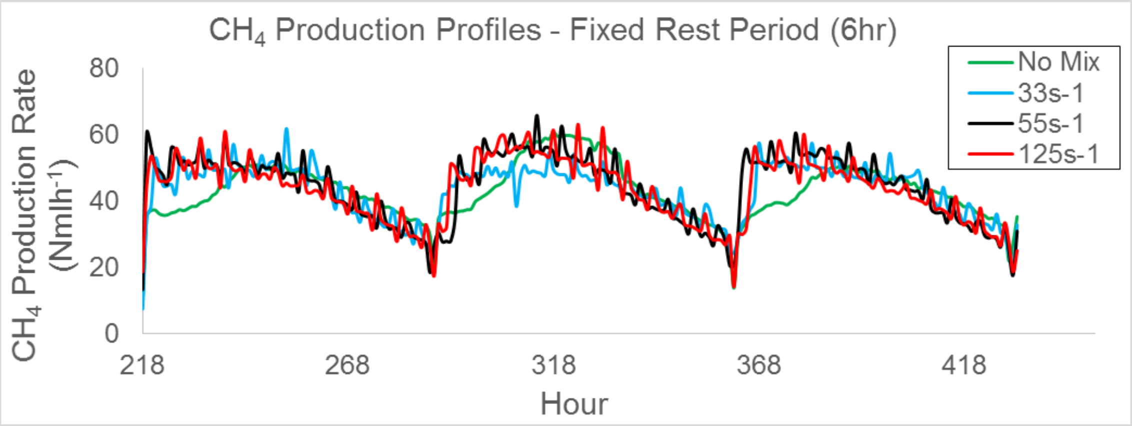


Figure 61 – CH_4 production between hours 219 and 290 (cycle 4)

The effects of mixer failure on CH_4 production was demonstrated when power to the digester mixed at a shear rate of $55s^{-1}$ was inadvertently interrupted at the start of feed cycle 3 (shown in black in Figure 62). The first cycle (cycle 2 of the experiment) demonstrated a typical profile resulting from normal mixing. However, when power to the $55s^{-1}$ digester pair was interrupted CH_4 production adopted a similar trend to the unmixed digester. Again, low rates of CH_4 production recovered during the latter stages of the cycle.

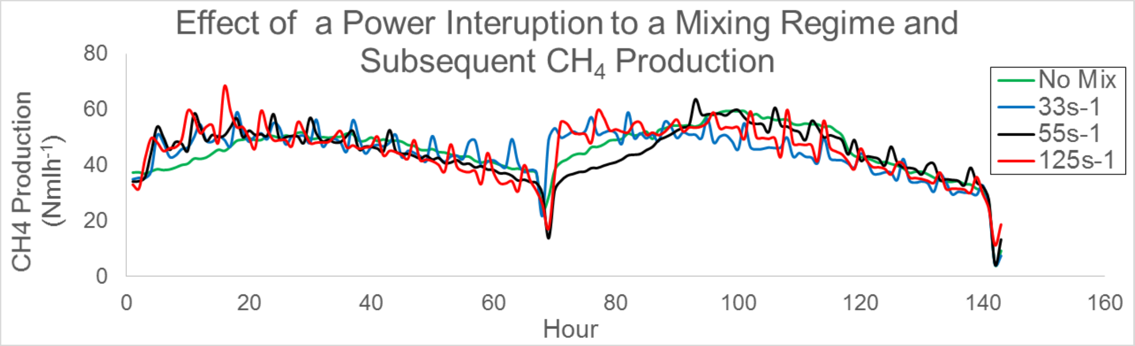


Figure 62 – Effect of interruption to mixing on CH_4 production

To identify potential differences in CH_4 production trends post-mixing, attempts were made to synchronise each feed cycle by feed time and mixing period before superimposing the profiles on top of one another to provide mean trends. However, differences in mixing periods when combined with a fixed 1-hour sample size did not support the technique.

4:3:3:3 Specific CH_4 Production Rate

A histogram of specific CH_4 production rates for all mixing regimes produced distribution curves with a common median of $0.020 Nml_{CH4}h^{-1}ml^{-1}_{substrate}$ (Figure 63). The non-mixed digester dominated the spectrum below the median whereas values for the mixed digesters were generally similar and mainly concentrated above the median. Comparable research could not be found in literature.

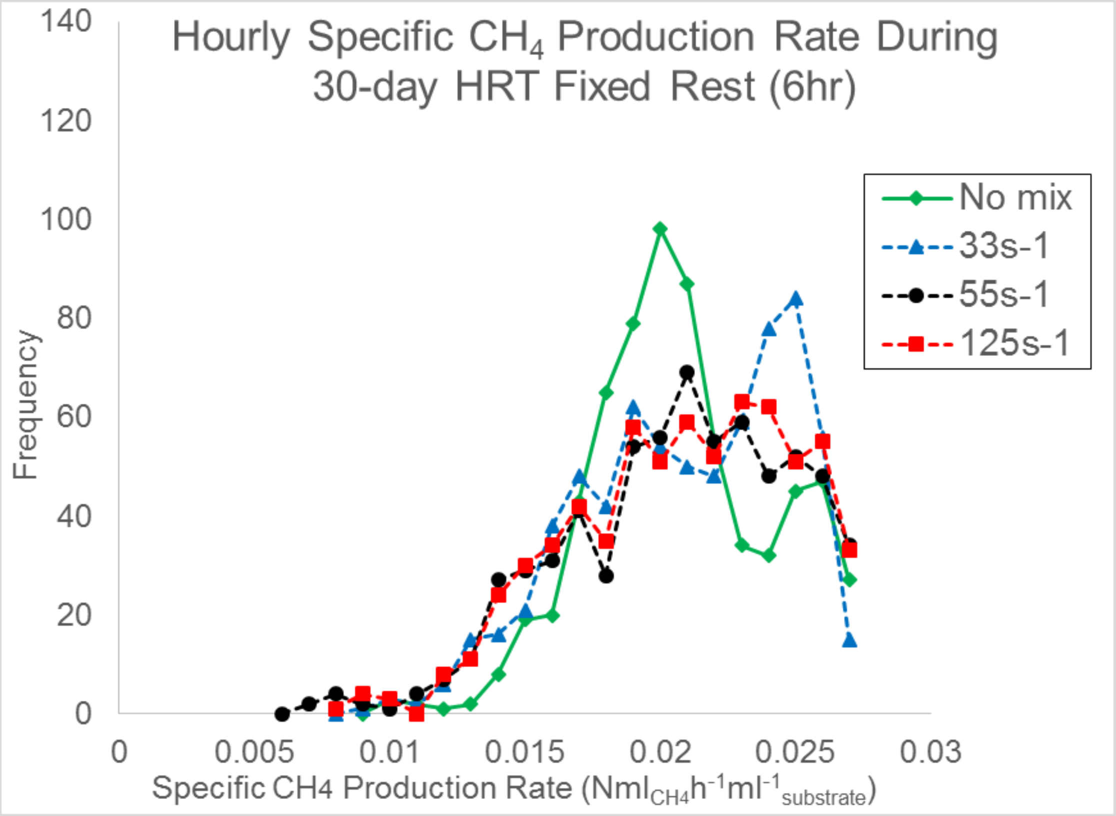


Figure 63 – Specific CH_4 production rate using a 30-day HRT, variable shear rate and fixed rest period (6hrs)

4:3:3:4 Changes in Substrate Characteristics

Despite the digesters being fed an average of $4.6g_{VS}d^{-1}$, the %VS of the substrate gradually reduced over the length of the experiment with the mixed digesters experiencing the largest reduction (circa 9 percent) whilst the substrate of the non-mixed digester reduced by approximately 2 percent (Table 22). Despite the wide variation in VS reduction between mixed and non-mixed digesters differences in CH_4 production was less than 1 percent (Table 25) and (Table 26) suggesting that the mixed digesters were more prone to VS washout. However, the reduction in VS content would likely increase the Newtonian characteristics of the substrate (as demonstrated in chapter 2) thereby improving mixing.

Digester	**Shear Rate**	**Volume**	**Substrate at Start**			**Substrate at End**			**ΔVS**
			TS	**VS**	**VS**	**TS**	**VS**	**VS**	
(#)	**(s^{-1})**	**(g)**	**(%)**	**(%)**	**(g)**	**(%)**	**(%)**	**(g)**	**(g)**
1	**Non-mixed**	1,800	8.5%	65.8%	114.8	8.9%	63.3%	113.0	-1.8
4	**33**	1,800	8.5%	65.8%	114.8	8.3%	63.6%	106.0	-8.8
2&3	**55**	1,800	8.5%	65.8%	114.8	8.2%	64.0%	105.4	-9.4
5&6	**125**	1,800	8.5%	65.8%	114.8	8.5%	62.1%	105.2	-9.6

Slurry fed to each digester over 38 days	Total	TS	VS	Total VS	VSd^{-1}
	(g)	(%)	(%)	(g)	(g)
	2,436	10.6%	67.8%	175.3	4.6

Table 22 – Changes in substrate solids content of digesters over 38 days using a 30-day HRT, variable shear rate and fixed rest period (6hrs)

4:3:3:5 Substrate Alkalinity

Alkalinity was monitored by periodically measuring the pH of the removed digestate. A consistent pH value of approximately 8 was maintained throughout suggesting a stable digestion process.

4:3:3:6 Process Efficiency Based on Volatile Solids Degradation

Basic process efficiency ranged from approximately 61 percent for the non-mixed digester to 64 percent for those mixed. Again, process efficiency took no account of VS washed out when digestate was removed (Table 25) and (Table 26). By estimating VS washout using the method previously described a ratio of VS pathways was produced using method A (Table 23) and method B (Table 24). Again, apportionment of VS digested and washed out varied significantly depending on the method used and could have a direct impact on fluid rheology and hence handling and eventually OPEX. Subsequent biodegradation efficiency was estimated at approximately 52 percent for all digesters using method A (Table 25) and 18-24 percent for non-mixed and mixed digesters, respectively when method B was used. A mean CH_4 conversion factor of $556ml_{CH_4}g^{-1}{}_{VS}$ was achieved using method B which was similar to that achieved when shear rate was fixed and rest period varied. This was again more than double that cited (Zeeman & Gerbens, 1996) and assumed in the method A calculations and previously published (Andersons Centre, 2010). Biodegradation efficiencies were again regarded as low as digester conditions were ideal for acclimatised mesophilic operations. Single-stage CSTR operations were again thought to be the cause.

Estimated CH_4 Production Ratio based on $240ml_{CH4}g^{-1}{}_{VS}$			
Shear Rate	**Digested**	**Remaining**	**Washed out**
Non-mixed	52.1	38.9	9.0
33	51.8	36.5	11.6
55	52.3	36.3	11.4
125	51.9	36.3	11.8

Table 23 – Estimated ratio of the different VS pathways over 38 days using method A, a 30-day HRT, variable shear rate and fixed rest period (6hrs)

Estimated CH_4 Production Ratio			
Shear Rate	**Produced**	**Remaining**	**Washed out**
Non-mixed	18.4	38.9	42.6
33	23.5	36.5	40.0
55	23.9	36.3	39.8
125	24.1	36.3	39.7

Table 24 – Estimated ratio of the different VS pathways over 38 days using method B, a 30-day HRT, variable shear rate and fixed rest period (6hrs)

4:3:3:7 Optimisation Based on Cumulative CH_4 Yield

System performance was once again compared using corrected YF and PF values to provide a performance comparison. Table 27 provides a summary of the measurements and calculations on which the comparison was based. The non-mixed digester was not included as the results would misrepresent the net energy benefits of not mixing which would be relatively substantial as no power was used. Moreover, mixing is necessary in fed-batch dairy farm operations, as explained in chapter 1. Again, comparable literature could not be found.

Rest Period	Total VS Fed (measured)	VS Remaining (measured)	VS Washed Out (estimated)	Theoretical CH_4 Equivalent based on $240ml_{CH4}g^{-1}{}_{VS}$				Process η	Degradation η
				VS Digested/CH_4 Produced		Remaining	Washed Out		
(hr)	(g)	(g)	(g)	(g)	(ml)	(ml)	(ml)	(%)	(%)
Non-mixed	290.1	113.0	26.1	151.1	36,257	27,114	6,261	61.1%	52.1%
33	290.1	106.0	33.7	150.4	36,103	25,439	8,088	63.5%	51.8%
55	290.1	105.4	33.1	151.6	36,389	25,302	7,940	63.7%	52.3%
125	290.1	105.2	34.3	150.6	36,151	25,242	8,239	63.7%	51.9%

Slurry Conversion to CH_4	0.24 $m^3kg^{-1}{}_{VS}$ 240,000 $mlkg^{-1}{}_{VS}$ 240 $mlg^{-1}{}_{VS}$	Remarks: Extracted from support research to IPCC Guidelines for National GHG Emissions, 2006

Table 25 – Biodegradation process efficiency of digesters over 38 days using method A, a 30-day HRT, variable shear rate and fixed rest period (6hrs)

Rest Period	Total VS Fed (measured)	VS Remaining (measured)	VS Washed Out (estimated)	CH_4 Equivalent				Process η	Degradation η
				VS Digested/CH_4 Produced		Remaining	Washed Out		
(hr)	(g)	(g)	(g)	(g)	(ml)	(ml)	(ml)	(%)	(%)
Non-mixed	290.1	113.0	123.6	53.5	36,257	76,550	83,784	61.1%	18.4%
33	290.1	106.0	116.0	68.1	36,103	56,180	61,489	63.5%	23.5%
55	290.1	105.4	115.4	69.3	36,389	55,344	60,574	63.7%	23.9%
125	290.1	105.2	115.1	69.8	36,151	54,439	59,584	63.7%	24.1%

Mean Slurry Conversion to CH_4	0.56 $m^3kg^{-1}{}_{VS}$ 555,627 $mlkg^{-1}{}_{VS}$ 556 $mlg^{-1}{}_{VS}$	Remarks: VS washout estimation assumes steady state well-mixed digester content when digestate extracted during feeding process.

Table 26 – Biodegradation process efficiency of digesters over 38 days using method B, a 30-day HRT, variable shear rate and fixed rest period (6hrs)

Shear Rate (s^{-1})	**CH_4-derived (m^3)**	**Equivalent (kWh)**	**Parasitic (kWh)**	**Net Power (kWh)**	**Parasitic (%)**	**PF**	**YF**	**YF (corrected)**	**PF*YFc**	**Net Rating**
33	0.0361	0.1325	0.0109	0.122	8.22%	1.00	0.99	0.27	0.27	1
55	0.0364	0.1335	0.0130	0.121	9.76%	0.84	1.00	0.27	0.23	2
125	0.0362	0.1327	0.0110	0.122	8.26%	0.99	0.99	0.27	0.27	1

Table 27 – Energy output of digesters over 38 days using a 30-day HRT, variable shear rate and a fixed rest period (6hrs)

4:3:3:8 Parasitic Energy Use and Power Factor

Although inducing lower shear rates demanded a lower voltage and current, the shear rate had to be applied for longer to achieve the required level of homogeneity. Mixing at shear rates of 33 and 125s^{-1} were the most energy efficient using virtually the same power (PFs of 1 and 0.99, respectively) followed by the digester mixed using a shear rate of 55s^{-1} (PF = 0.84). The worst performer (mixing using a shear rate of 55s^{-1}) used 20 percent more power than the most economic (mixing using a shear rate of 33s^{-1}) over 38 days. Parasitic energy used for mixing equated to approximately 8-10 percent of energy generated. Figure 64 illustrates the PF relationship of the mixing regimes.

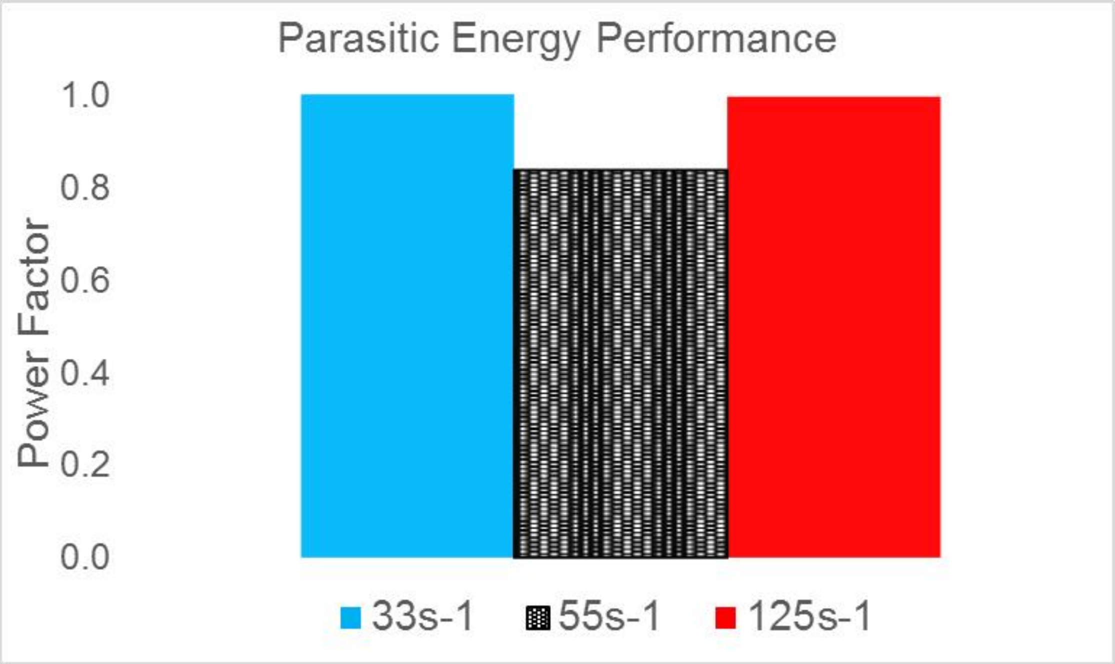


Figure 64 – Comparison of parasitic energy performance using power factor when HRT 30 days, shear rate varied and rest period fixed (6hrs)

4:3:3:9 CH_4 Yield and Yield Factor

CH_4 yields were virtually the same for all shear rates so there was very little difference in YF values after conversion to the kWh (Figure 65).

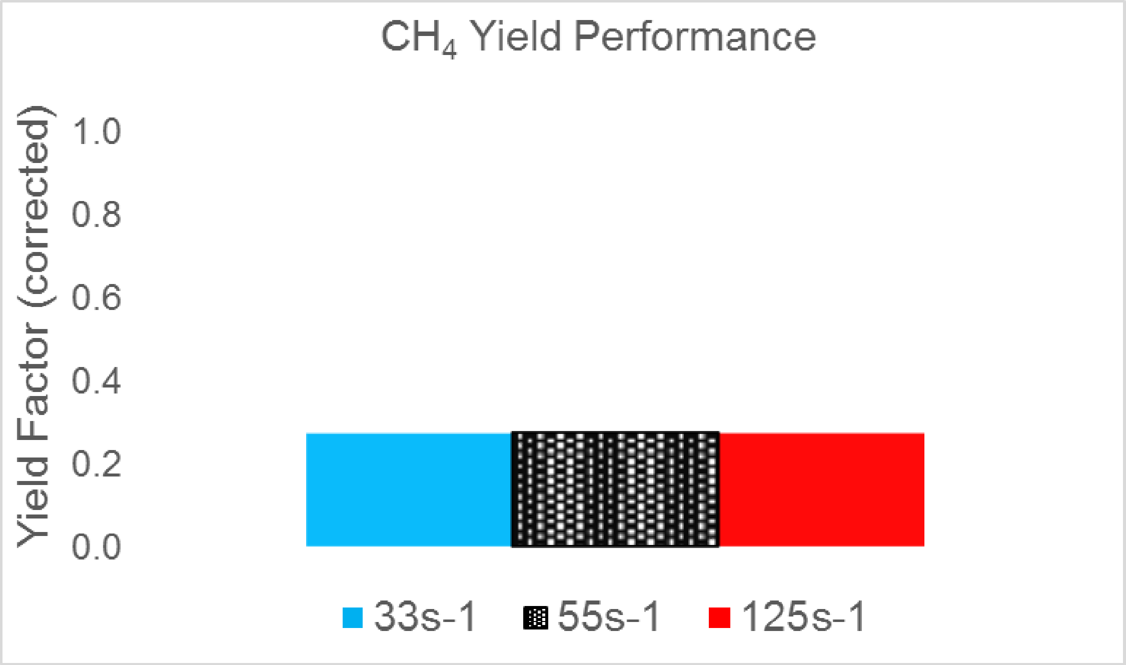


Figure 65 – Comparison on CH_4 yield performance using yield factor when HRT 30 days, shear rate varied and rest period fixed (6hrs)

4:3:3:10 Balancing CH_4 Yield and Parasitic Energy

With minimal difference between CH_4 yields achieved by the different shear rates, net energy output was mainly influenced by parasitic energy demand similar to the relationship identified in chapter 3. The regimes mixed using shear rates of 33 and 125s^{-1} were the best performers followed by the digester mixed at 55s^{-1} which was 16 percent less efficient (Figure 66).

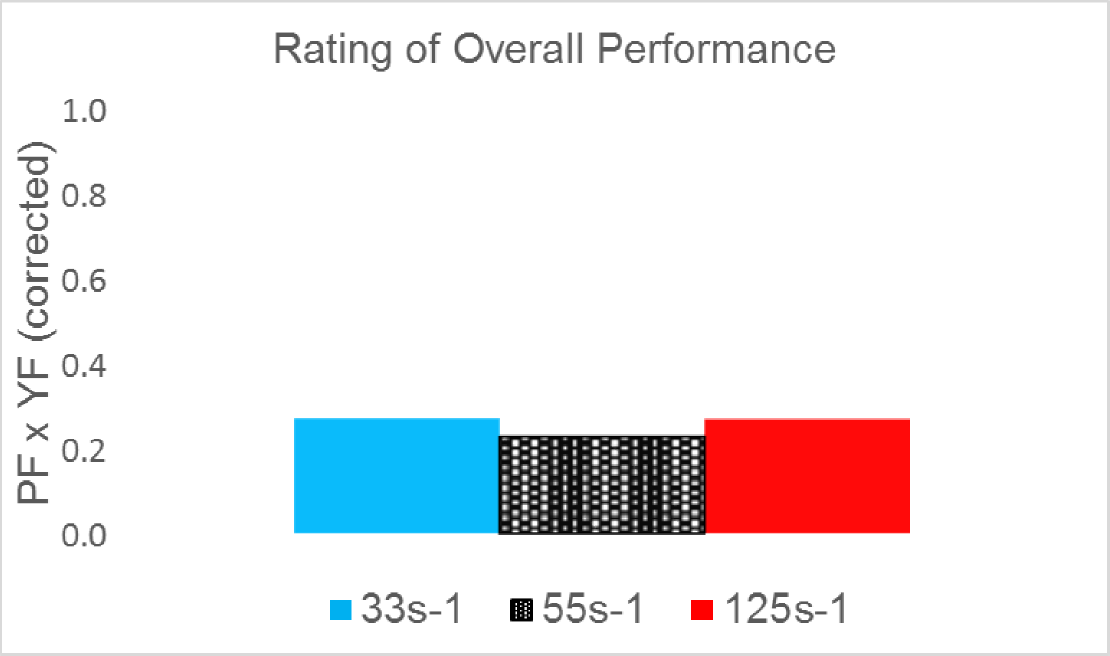


Figure 66 – Comparison of net energy production when HRT 30 days, shear rate varied and rest period fixed (6hrs)

4:3:3:11 Optimisation Based on Production Rate

Specific CH_4 production rate profiles were not used as a basis for optimising the rate of CH_4 production to maximise net energy output in this chapter as the main influence of the metric is directly related to HRT which is considered in detail in chapter 6.

4:4 Conclusions

Due to the unique method adopted in chapters 3 and 4 no literature could be found that explored the effects of the key metrics of shear rate, the number of mixing events and rest period on CH_4 production when a common mixing technique was applied. The analysis of the effects of different mixing regimes on CH_4 production when the process was intermittently fed is likely have a more direct relevance to on-farm AD operations than the earlier batch experimentation. However, batch analysis was necessary to identify the key mixer configurations to be monitored when digester availability was limited. The analysis of intermittently fed operations using an OLR of 2.3-2.6$g_{VS}l^{-1}d^{-1}$ supported the following conclusions:

- Varying shear rate had a minimal effect on CH_4 production in a homogenised digester when the rest period was fixed at 6hrs. However, OPEX would be influenced by an informed shear rate selection.
- The length of rest period associated with intermittent mixing had the greatest influence on long-term CH_4 yield in a homogenised digester with short mixing periods and short intervals producing the highest levels of CH_4 when a shear rate of $55s^{-1}$ was applied.
- Specific CH_4 production was higher when feeding and mixing coincided.
- CH_4 production rate was less responsive to feeding in an unmixed digester fed every 3 days than in mixed digesters. However, the CH_4 production rate eventually responded to recover and produce similar yields to other digesters before the next feed took place.
- Although resting can influence CH_4 yield, the energy savings associated with long periods of no mixing can realise substantial net energy gains, particularly over long periods and hence reduce OPEX.

Although the differences in gas yields of different mixing regimes were sometimes significant, the AMPTS II was programmed with an assumed biogas quality of 60 percent CH_4. Therefore, the effects of mixing regime on biogas quality and quantity may not be an accurate representation so the data should be used with caution.

4:5 Next Research Step

Although the results were informative, the 30-day HRT combined with a fixed substrate volume of 2000ml resulted in a relatively low OLR compared to typical feed rates of up to $4.8g_{VS}l^{-1}d^{-1}$ (Khanal, 2008). However, the typical feed rates are designed to accommodate a range of feedstock types with cow slurry having a relatively low CV and therefore likely to attract the higher rate. The batch data of chapter 3 will now be combined with the method used in the fed-batch experiments of this chapter to identify the effects that reducing HRT has on CH_4 production and digester performance.

CHAPTER 5 – EFFECTS OF MIXING ON A FED-BATCH PROCESS USING A 10-DAY HRT

5:1 Introduction

The temporal separation of shear rate and rest period of fed-batch operations (chapter 4) demonstrated that changing the rest period had a more significant effect on CH_4 production rate than varying the shear rate applied. The HRT of 30 days reflected the theoretical time required for cow slurry to be completely digested at mesophilic temperature. However, reducing the HRT to 10 days would match the period within which maximum rates of CH_4 production were achieved during a batch process (chapter 3). Moreover, lowering the HRT would allow smaller digesters to be used (thereby lowering CAPEX) which would require less energy to mix (reducing OPEX). However, increases in specific CH_4 production rates may not be as high as expected as biodegradation of the feedstock may not be achieved before being replaced when throughput is high (Bensmann et al., 2013). Reducing HRT whilst still accommodating the fixed volume of slurry produced daily during the farm operation would also increase the OLR to which the process was subjected thereby increasing the potential for process inhibition due to overloading (Kim et al., 2002). Identifying the effects of increasing OLR in response to reducing digester volume is therefore important not only to identify differences in CH_4 yield and production rate potential but also to confirm the ability of a smaller digester to maintain process stability at a higher OLR.

5:1:1 Aims

The aims of this chapter are to:

- Quantify the effects of mixing regime on methanogenesis and hence the rate of CH_4 production and cumulative yield using a 10-day HRT.
- Assess process biodegradation performance for each mixing regime.

- Compare the parasitic energy demanded by each mixing regime and produce a dimensionless power factor.
- Compare cumulative yields produced by each mixing regime and produce a dimensionless yield factor.
- Combine power factor and yield factor values for each mixing regime to produce an overall comparative rating on which a net energy performance hierarchy can be based.
- Identify any trend in CH_4 production rate that could enable the adjustment of the HRT to optimise CH_4 production.

5:2 Materials and Method

The equipment used and procedures adopted during this stage of the analysis were the same as those used in chapter 4. The original 30-day HRT analysed in that chapter was initially reduced to 20 days in this iteration until process stability was confirmed. HRT was then reduced to 10 days. Any differences to the procedures used in chapter 4 are highlighted, where appropriate.

5:2:1 Digester Procedure and Set-up

Varying shear rate when rest period was fixed at 6 hours had a minimal effect on CH_4 production using an HRT of 30 days. Therefore, similar variables were used to identify the effect that reducing HRT had on CH_4 production because they:

- Provided the opportunity to isolate resting as a variable that had a known effect on CH_4 production.
- Offered the opportunity to investigate if the minimal effect that shear rate had on CH_4 production using an HRT of 30 days changed when HRT was reduced for a fixed feedstock throughput (effectively an increase in OLR).
- Allowed the stable process achieved during the previous fed-batch experiment using a fixed rest period to continue uninterrupted using fully acclimatised digesters.

Continuity was provided by using the output substrate of the previous experiment (30-day HRT mixed using variable shear rate and fixed rest period) as the input substrate for the first experiment of this chapter. Table 28 lists the mixing regimes investigated.

Experiment	1 (Fixed Rest)	2 (Fixed Shear Rate)
Shear Rate (s^{-1})	33/55/125	125
Stirrer speed (rpm)	17.3/28.8/65.6	65.6
DC Voltage (V)	3.24/4.45/7.74	7.74
On Period (min/sec)	23m29s/19m33s/7m21s	7m21s
Off Period (hour)	6	1/6/12
HRT (day)	10	10

Table 28 – Mixing regimes used to identify the effect of intermittent mixing on CH_4 production when HRT was 10 days

5:2:1:1 Experiment 1: Variable Shear Rate and Fixed Rest Period (6hrs)

Only HRT was changed from the previous mesophilic experiment. The rest period was fixed at 6 hours and the paired digesters programmed to mix at shear rates of 55 and 125s^{-1} leaving a single non-mixed configuration and another mixed at a shear rate of 33s^{-1} (Figure 67). Again, configuring a digester pair mixed using 33s^{-1} was not possible because digester 1 would not reliably mix at low shear rates. The experiment was planned to run for 20 days (2 x HRT).

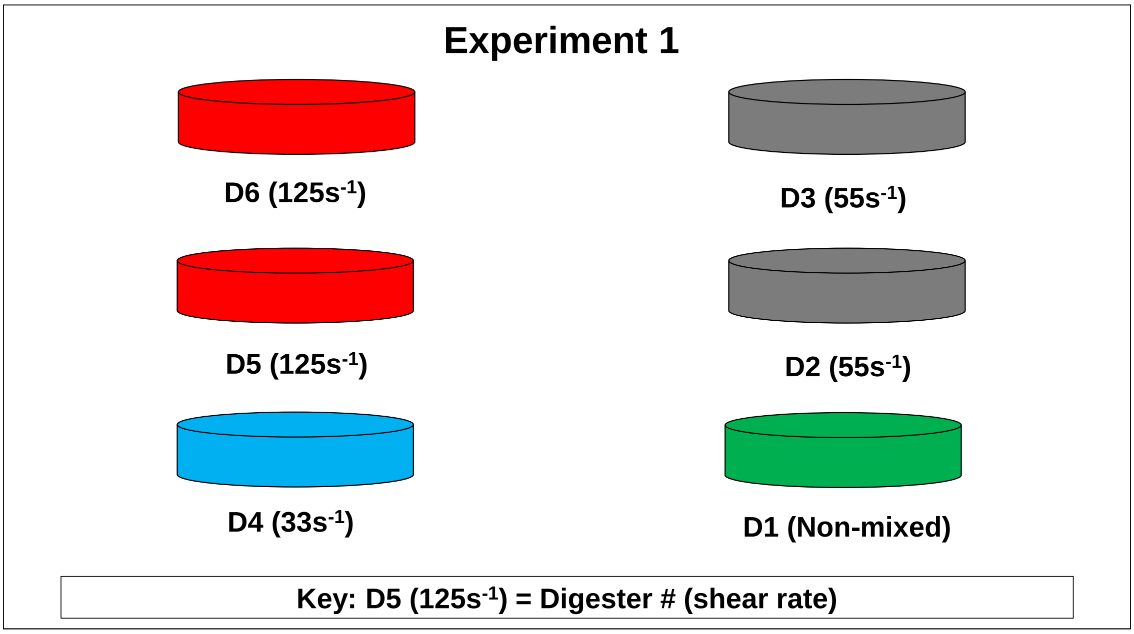


Figure 67 – AMPTS II configuration when HRT 10 days, shear rate varied and rest period fixed (6hrs)

5:2:1:2 Experiment 2: Variable Rest Period and Fixed Shear Rate ($125s^{-1}$)

The digesters were dismantled, serviced and cleaned before digestate from experiment 1 was communally mixed and redistributed between the 6 digesters providing each with 1800ml of acclimatised starter substrate. An additional 203g of cow slurry was added leaving approximately 10 percent gas headspace. The experiment was initiated at 37.5˚C. CH_4 outputs were monitored for 48 hours and discrepancies in CH_4 production noted. The digesters were paired (Figure 68) using the previous technique with pairs coinciding with the previous experiment. Rest periods of 1, 6 and 12 hours were again controlled by PLCs. A fixed shear rate of $125s^{-1}$ was selected as the level of agitation produced the most CH_4 during the batch analysis in chapter 3 and the variable shear rate analysis of chapter 4. Hence, the configuration would provide an estimate of the maximum CH_4 potential for the range of shear rates investigated when the rest period was fixed. Ideally, a shear rate of $55s^{-1}$ would have been investigated first to link the 30 and 10-day HRT data before exploring the potential of mixing at the higher shear rate. However, due to the limited time available shear rate was fixed using the best performing shear rate of the previous experiment to confirm if process stability was achievable using the highest CH_4-producing mixing intensity. A 10-day HRT was applied and the experiment programmed to run for 20 days (2 x HRT).

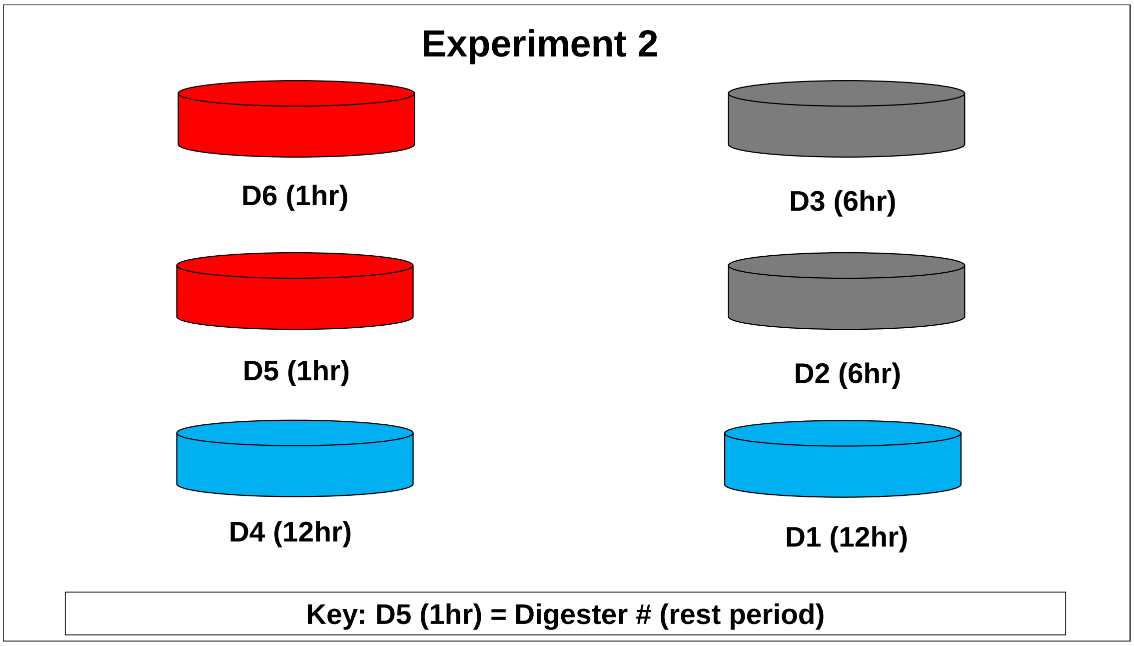


Figure 68 – AMPTS II configuration when HRT 10 days, rest period varied and shear rate fixed (125s^{-1})

5:2:2 Feedstock

HRT was reduced by maintaining the quantity of feed introduced during a feeding event but reducing the time interval between feed periods from 3 days to feeding on a daily basis. Solids content of the slurry and changes in OLR as HRT was reduced are summarised in Table 29.

HRT	**Start-up Substrate**		**Subsequent Feedstock**		
(days(expt))	**%TS**	**%VS**	**%TS**	**%VS**	**OLR ($g_{VS}l^{-1}d^{-1}$)**
30 (Fixed Rest)	8.5	65.8	10.6	67.8	2.4
20 (interim)	-	-			3.7
10 (Fixed Rest)	8.4	63.2	11.6	67.6	8.0
10 (Fixed SR)	12.6	47.7	11.4	68.0	7.9

Table 29 – Characteristics of start-up substrate, fed-batch feedstock and changing OLR

5:2:3 Data Comparison

Data analysis was limited to the outcomes of the 10-day HRT only as the 20-day HRT was introduced as an interim step.

5:2:4 Comparing Individual Digester Performance

The process performances of different regimes were compared using mean values of outputs from similar digester configurations. However, large variations between performances of digesters mixed using the same regime could be significant. Discrepancies would not only affect mean values but could also indicate differences in degrees of chemical stress being experienced by microbial communities in different digesters using the same mixing regime and OLR. This could become particularly relevant as OLR and the associated nutrient density of the substrate increased. To identify differences in the process performances of digesters mixed using the same regime, digester pairs were also monitored individually throughout this experiment and CH_4 production trends compared within each mixing regime.

5:3 Results and Discussion

5:3:1 Effectiveness of Experimental Technique

The proven experimental technique used in chapter 4 provided a satisfactory framework with which to investigate the effects that reducing HRT had on CH_4 production. The lack of measurements of CH_4 content of the gaseous products and the VS content of digestate when removed again reduced the efficacy of the research. RTD analysis would also have provided a better understanding of VS throughput and the potential for process stability issues when HRT was reduced. Experiment 1 had to be terminated after 15 days due to equipment failure. Experiment 2 went to term. An analysis of concentrations of volatile organic acids and total organic carbonate (FOS/TAC) was attempted using the digester contents at the end of experiment 2. This was introduced as an additional method of comparing process stability when CH_4 production of similarly configured digesters and pH values began to vary. However, the results of the manual titration technique were erratic and not repeatable. Also, a digestate handling error resulted in limited sample volumes being available for analysis so the procedure was abandoned. As a result, the potential onset of process instability indicated by variations in the CH_4 produced by a digester and a reduction in substrate pH could not be confirmed using the FOS/TAC method.

5:3:2 CH_4 Production Using a 10-Day HRT and Fixed Rest Period (6hrs)

5:3:2:1 Cumulative CH_4 Yield

Cumulative CH_4 yield increased in line with increases in the shear rate applied during mixing with higher shear rates providing higher yields (Figure 69). Mixing using a shear rate of $125s^{-1}$ realised the highest yield of 23,700Nml which was equivalent to $7.78m^3_{CH4}m^{-3}_{slurry}$ (or $12.97m^3_{biogas}m^{-3}_{slurry}$, assuming the biogas had a CH_4 content of 60 percent). This was approximately 65 percent of the mean potential biogas yield quoted ($20m^3_{biogas}m^{-3}_{slurry}$) by the Andersons Centre (2010). The digesters mixed using shear rates of 33 and $55s^{-1}$ produced similar yields that were 10 percent lower than the best performer whereas the non-mixed digester produced 40 percent less. The obvious impact that mixing had on CH_4 production confirmed earlier research (Karim et al., 2005a; Clark et al., 2012; Ghanimeh et al., 2012a) although those results were generalised so were not directly comparable with the detailed results of this study. At the time of termination the rates of change of yield profiles for shear rates of 55 and 125s^{-1} were still increasing suggesting that the process and therefore the rate of CH_4 production had yet to realise full potential.

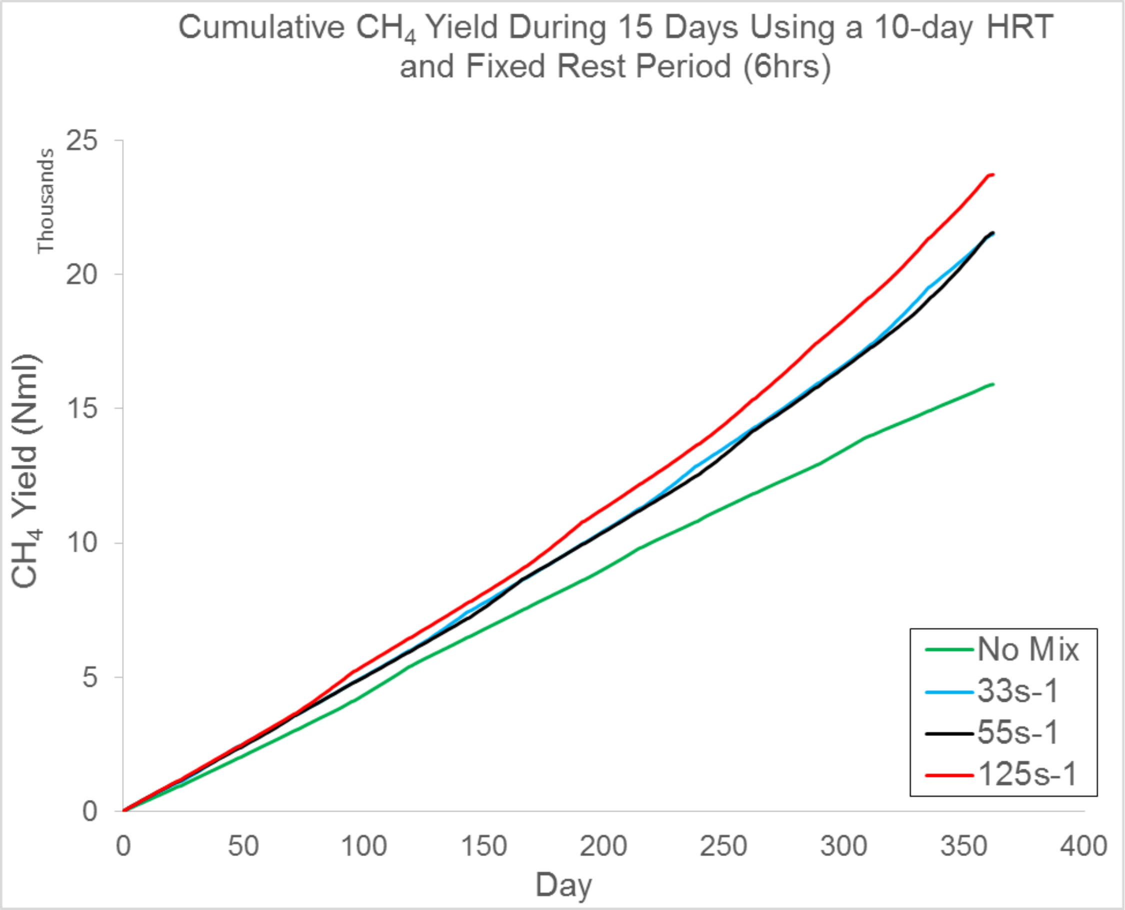


Figure 69 – Cumulative CH_4 yield achieved using a 10-day HRT, variable shear rate and fixed rest period (6hrs)

5:3:2:2 CH_4 Production Rate

The rate of CH_4 production gradually increased as the experiment progressed (Figure 70). Obvious reductions in CH_4 production, indicated by the sharp troughs every 24 hours, coincided with feeding times and were probably a result of the digesters being disconnected from the AMPTS II system to allow feeding to take place, resulting in a loss of accumulated gas pressure. However, this was similar for all digesters and observed in the previous experiments so was an accepted equipment limitation. Peak values of all mixed digesters coincided with mixing times with approximately 6 hours between peaks. The gradual increase in CH_4 production rate profiles confirmed that the digesters mixed using shear rates of 55 and $125s^{-1}$ had yet to stabilise when the experiment was terminated. At the time of failure the peak CH_4 production rate for the digester mixed using a shear rate of $125s^{-1}$ was approximately $116Nml_{CH4}h^{-1}$, a 107 percent increase on the lowest peak rate of production observed for that shear rate earlier in the experiment.

5:3:2:3 Underlying CH_4 Production Rate Cycle

The daily feeding routine reflected in the CH_4 production rate profiles of the mixed digesters (Figure 71) was easily identifiable. However, on closer inspection a 4-day cycle was also evident within which CH_4 production rate values at particular times within each feed cycle gradually increased. The rate of CH_4 production then decreased at the beginning of the fifth daily cycle before repeating the CH_4 production pattern. Figure 71 illustrates the cycle when a shear rate of $125s^{-1}$ was applied and when no mixing took place. However, the cycle was produced by all mixing regimes, although the trend was less obvious in the non-mixed digester. The reason for the 4-day cycle is not known and was not observed when the HRT was 30 days. The phenomena has not been previously reported although that maybe because past experimental methods have not been as detailed.

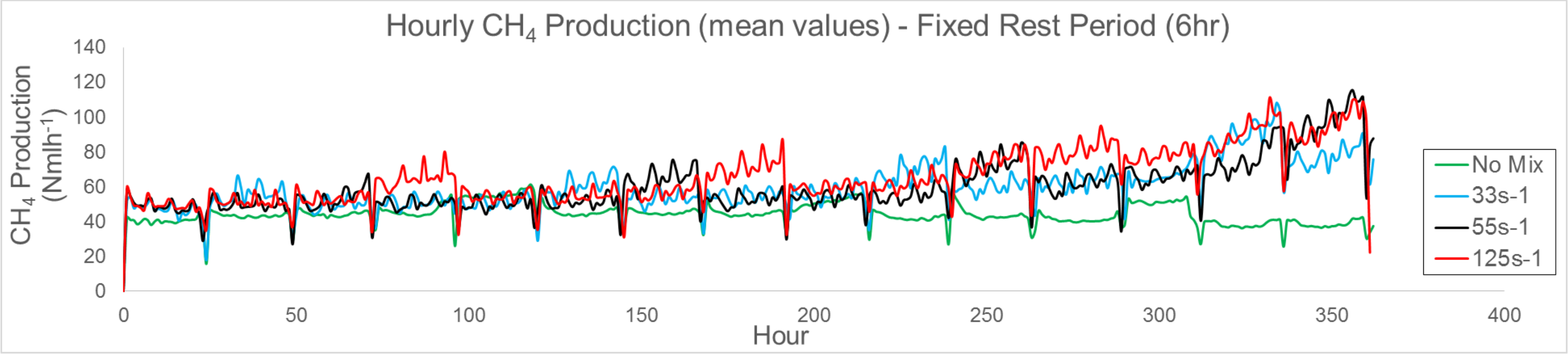


Figure 70 – CH_4 production rate achieved using a 10-day HRT, variable shear rate and fixed rest period (6hrs)

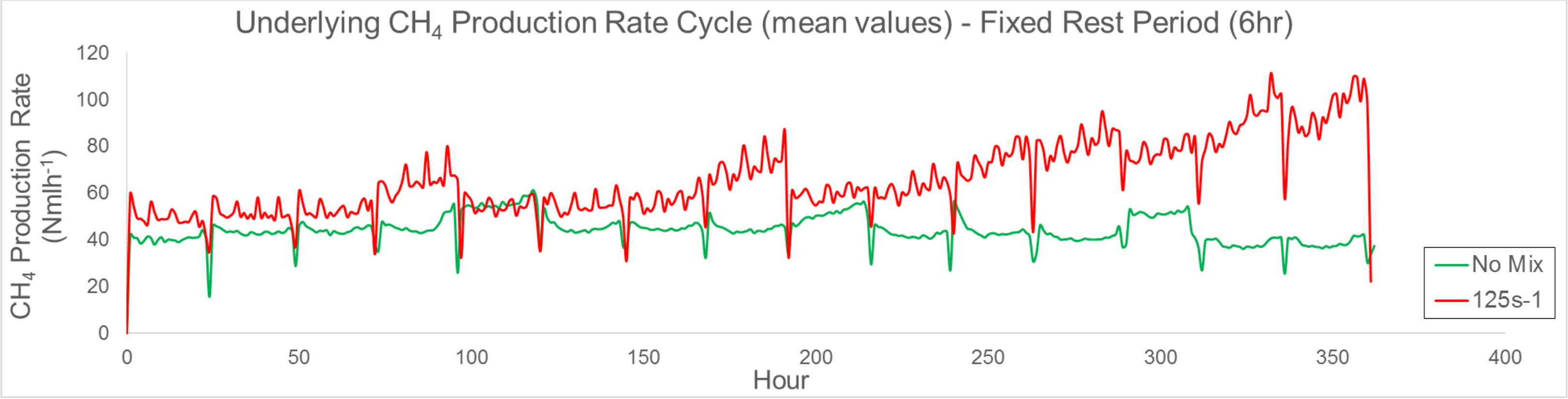
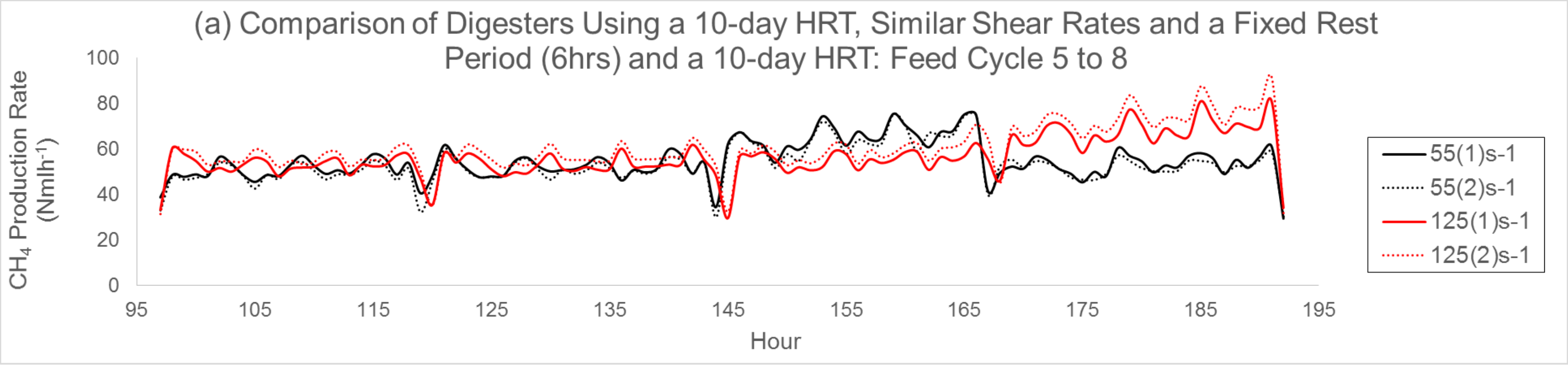


Figure 71 – Underlying 4-day CH_4 production rate cycle (mean values) using a 10-day HRT, shear rate of $125s^{-1}$ and fixed rest period (6hrs)

5:3:2:4 Comparing Individual Digester Production

The CH_4 production rate profiles using shear rates of 55 and $125s^{-1}$ (Figure 72a) and (Figure 72b) capture 4 feeding cycles at different stages of the experiment with the results being typical of those observed throughout. Discrepancies tended to be in the values of the rate at which CH_4 was produced rather than gradient trend or direction. Indeed, lower production during one feeding cycle was often compensated by higher production in a later feed cycle and so normalised over time. Again, past research was not sufficiently detailed to provide comparable data.


(a) Comparison of Digesters Using a 10-day HRT, Similar Shear Rates and a Fixed Rest Period (6hrs) and a 10-day HRT: Feed Cycle 5 to 8

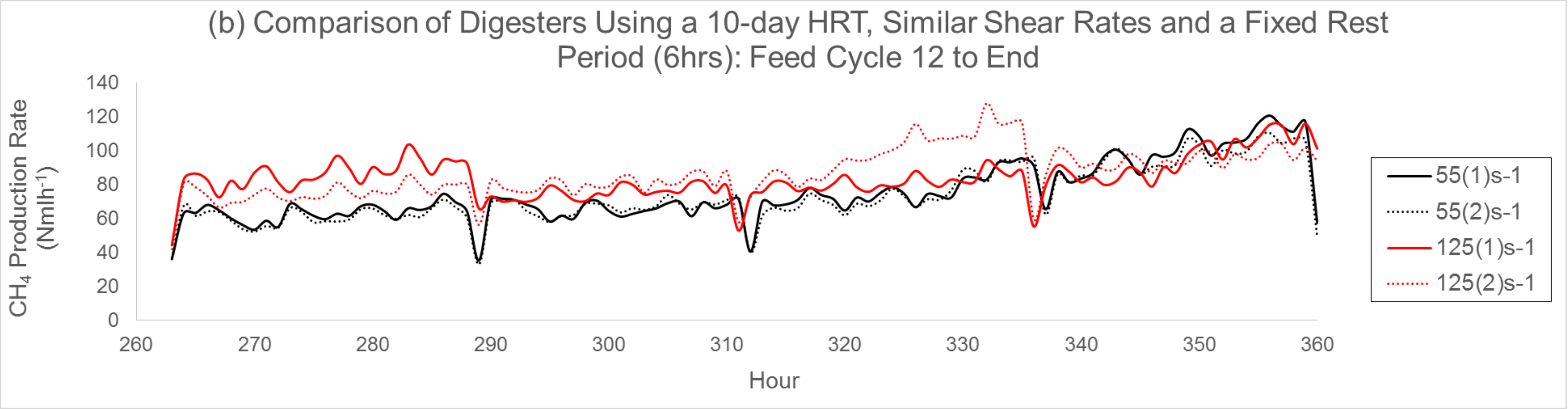

(b) Comparison of Digesters Using a 10-day HRT, Similar Shear Rates and a Fixed Rest Period (6hrs): Feed Cycle 12 to End

Figure 72 – Comparison of CH$_4$ production trends of digesters using a 10-day HRT, similar shear rates and a fixed rest period (6hrs) partway through the experiment (a) and at the end (b)

5:3:2:5 Specific CH_4 Production Rate

A histogram of specific CH_4 production rates produced by each shear rate (Figure 73) shows the profiles of the non-mixed regime and those mixed using shear rates of 33, 55 and $125s^{-1}$ based around medians of 0.022, 0.033, 0.035 and $0.036Nml_{CH4}h^{-1}ml^{-1}{}_{slurry}$, respectively. The specific CH_4 production rate values of the non-mixed digester were primarily focused around the median whereas the values of the mixed regimes were more widely distributed with the shear rate of $125s^{-1}$ producing the highest rate of production confirming a potential benefit of HRT reduction cited by Bensmann et al. (2013). However, lower HRT is only beneficial if process stability is maintained.

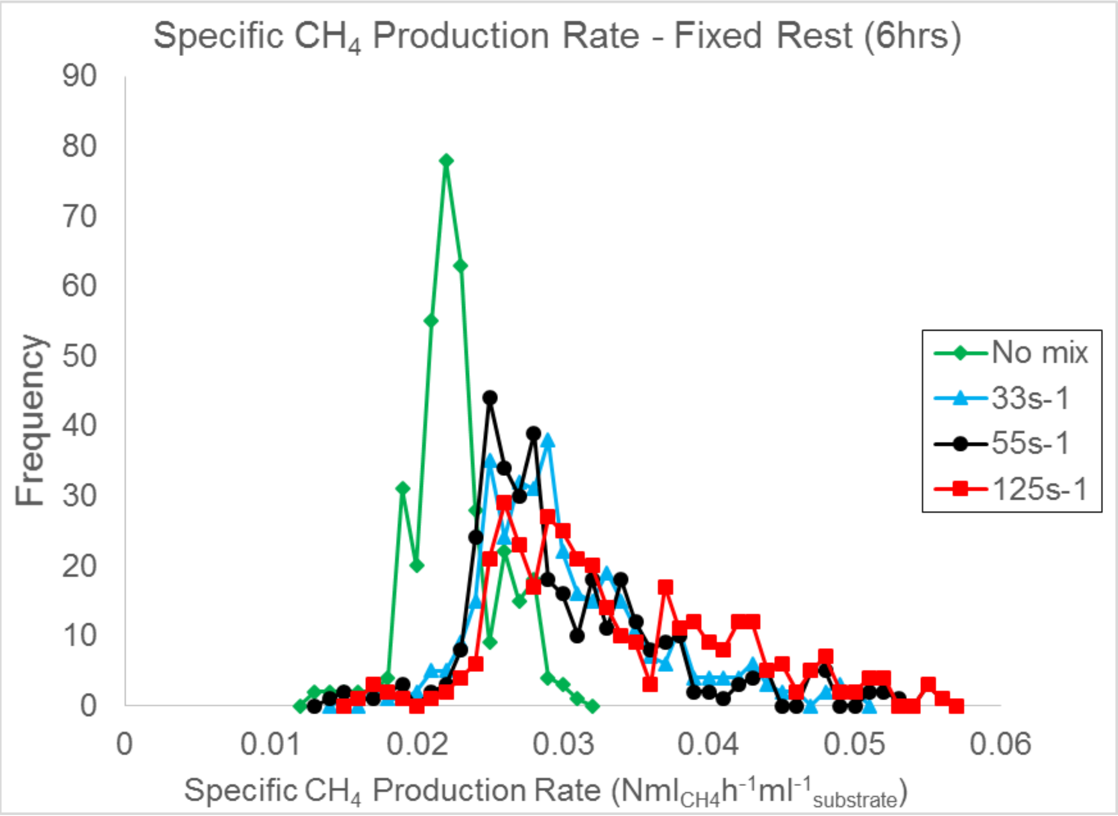


Figure 73 – Specific CH_4 production rates achieved using a 10-day HRT, variable shear rate and fixed rest period (6hrs)

5:3:2:6 Changes in Substrate Characteristics

The VS content of each digester was compared before and after the 15-day experiment with the mass of VS increasing despite CH_4 being produced (Table 30). This increase in VS concentration, rather than the decrease observed using a 30-day HRT was probably due to the rise in OLR when the HRT was reduced and would be expected to increase further until process stability was achieved. The use of RTD techniques would have provided a better understanding of the effects of changing HRT/OLR. A change in VS content would also effect substrate rheology and in turn parasitic energy demand and microbial activity.

Digester	**Shear Rate**	**Volume**	**Substrate at Start**			**Substrate at End**			**∆ VS**
			TS	**VS**	**VS**	**TS**	**VS**	**VS**	
(#)	**(s^{-1})**	**(g)**	**(%)**	**(%)**	**(g)**	**(%)**	**(%)**	**(g)**	**(g)**
1	**Non-mixed**	1,800	8.9%	63.3%	113.0	11.0%	63.5%	139.8	26.8
4	**33**	1,800	8.3%	63.6%	106.0	12.2%	59.0%	144.1	38.1
2&3	**55**	1,800	8.2%	64.0%	105.4	10.8%	62.1%	134.2	28.8
5&6	**125**	1,800	8.5%	62.1%	105.2	11.2%	61.7%	138.0	32.9

Slurry fed to each digester over 15 days	Total	TS	VS	Total VS	VSd^{-1}
	(g)	(%)	(%)	(g)	(g)
	2,842	11.6%	67.6%	223.1	15.9

Table 30 – Changes in substrate solids content of digesters over 15 days using a 10-day HRT, variable shear rate and fixed rest period (6hrs)

5:3:2:7 Substrate Alkalinity

The pH of the removed digestate was measured daily to compare digester acidity. All digesters shared a common pH value of approximately 7.8 when the HRT was first reduced to 10 days indicating a high process alkalinity for AD (Figure 74). Values then began to reduce, possibly due to an acidogenic microbial response to the increase in OLR which resulted in an increase in VFA production although this was not measured. By day 10, the pH began to recover but early termination of the experiment prevented a full assessment. However, the pH of the non-mixed digester was still reducing when the experiment ended. This may have been due to the digester's slow response to produce CH_4 after feeding (as demonstrated in chapter 4) and subsequent increase in VS. The 3-day feeding cycle of the 30-day

HRT experiment allowed time for the reduced rate of CH_4 production post-feeding to recover to realise similar yields to the mixed digesters prior to the next feed. However, the daily feeding regime reduced the inter-feeding period by 66 percent whilst feedstock volume remained constant which would limit the time for any recovery of CH_4 production. Jian et al. (1997) also reported process instability when OLR was increased.

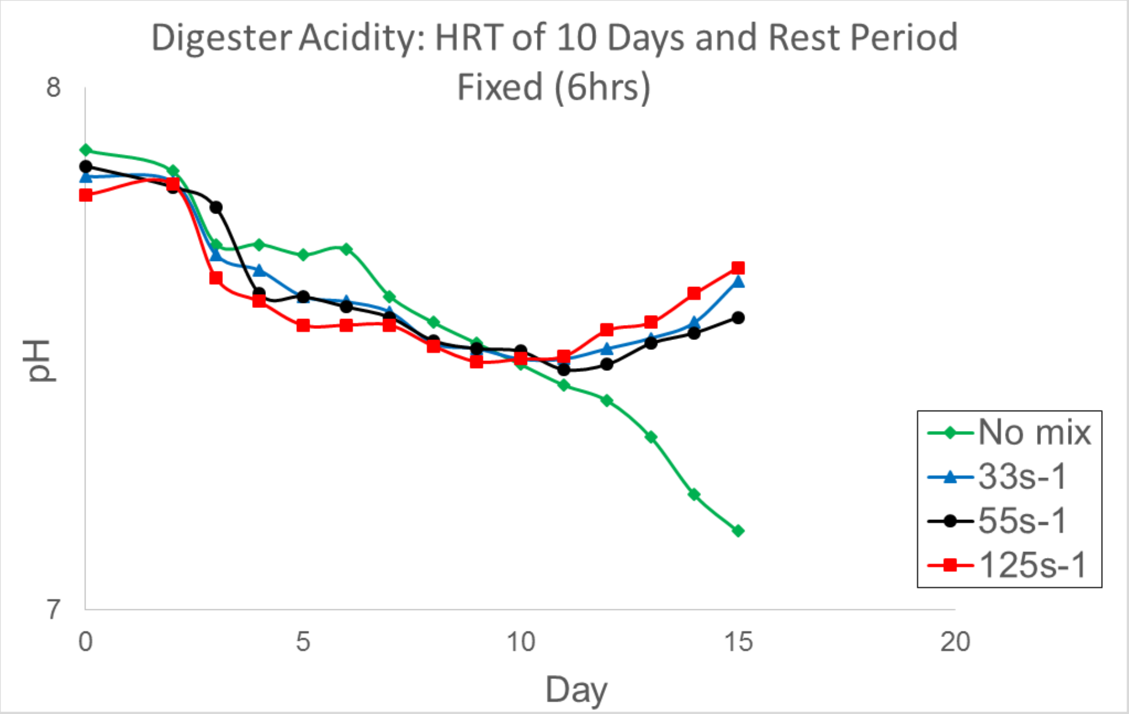


Figure 74 – Trends of pH over 15 days using a 10-day HRT, variable shear rate and fixed rest period (6hrs)

5:3:2:8 Process Efficiency Based on Volatile Solids Biodegradation

After 15 days the process efficiency based on VS residues at the end of the experiment was approximately 58 percent for all mixing regimes (Table 33) and (Table 34). Again, process efficiency took no account of VS washed out when digestate was removed. VS washout was estimated using methods A (Table 31) and B (Table 32) with significant differences in the results observed. This would affect substrate/digestate rheology (chapter 2) and therefore fluid handling characteristics and OPEX. Indeed the exponential effect of %TS on shear stress and apparent viscosity could have substantial consequences in terms of microbial activity and slurry management. Method A produced a reduction in VS digested and an increase in VS washed out to be expected if OLR increased and HRD reduced as time for the increase in VS to be exposed to microbial biomass and hence digested was reduced. However, results achieved using method B reduced VS digested to unrealistically low and in one case negative levels. RTD analysis may have provided prior warning and a better understanding of the extent of the issue. The digester mixed using a shear rate of 125s^{-1} achieved the highest biodegradation efficiency (30 percent) followed by those mixed at shear rates of 33 and 55s^{-1} (27 percent) when method A was used. The non-mixed digester achieved 20 percent (Table 33). The reduction in biodegradation efficiency when HRT was reduced/OLR increased coincided with an increase in estimated VS washout as would be expected in a CSTR. Meanwhile, biodegradation efficiency estimations using method B produced very low (circa 5 percent) and in one case a negative value which was not possible when significant levels of CH_4 were produced. This resulted in an exceptionally high and unrealistic mean CH_4 conversion factor of $1775ml_{CH4}g^{-1}{}_{VS}$. The cause of this anomaly may have been the relatively rapid increase in OLR between consecutive experiments using the same substrate resulting in a disruption in the previous steady state process. Kim et al. (2002) observed similar process instabilities and eventual process inhibition when increasing OLR. In addition, the length of the follow-on experiment limited the time for microbial adaptation and long-term process stability to be regained.

Estimated CH_4 Production Ratio based on 240 $ml_{CH4}g^{-1}{}_{VS}$			
Shear Rate	**Digested**	**Remaining**	**Washed Out**
Non-mixed	19.7	41.6	38.7
33	27.2	43.8	29.0
55	27.4	40.9	31.8
125	30.1	42.0	27.8

Table 31 – Estimated ratio of the different VS pathways over 15 days using method A, a 10-day HRT, variable shear rate and fixed rest period (6hrs)

Estimated CH_4 Production Ratio			
Shear Rate	**Produced**	**Remaining**	**Washed Out**
Non-mixed	4.6	41.6	53.8
33	-0.4	43.8	56.6
55	6.3	40.9	52.8
125	3.6	42.0	54.4

Table 32 – Estimated ratio of the different VS pathways over 15 days using method B, a 10-day HRT, variable shear rate and fixed rest period (6hrs)

5:3:2:9 Optimisation Based on Cumulative CH_4 Yield

PF and YF values were again used to compare system performance based on net energy gain. Table 35 provides a summary of the measurements and calculations on which the comparison was based. Again, the non-mixed digester was not included.

Shear Rate	Total VS Fed (measured)	VS Remaining (measured)	VS Washed Out (estimated)	Theoretical CH_4 Equivalent based on $240ml_{CH4}g^{-1}_{VS}$				Process η	Degradation η
				VS Digested/CH_4 Produced		Remaining	Washed Out		
(s^{-1})	(g)	(g)	(g)	(g)	(ml)	(ml)	(ml)	(%)	(%)
Non-mixed	336.1	139.8	130.0	66.3	15,914	33,547	31,209	58.4%	19.7%
33	329.1	144.1	95.4	89.6	21,511	34,592	22,892	56.2%	27.2%
55	328.6	134.2	104.5	89.9	21,571	32,214	25,073	59.1%	27.4%
125	328.3	138.0	91.4	98.9	23,733	33,126	21,938	58.0%	30.1%

Slurry Conversion to CH_4	0.24 $m^3kg^{-1}_{VS}$ 240,000 $mlkg^{-1}_{VS}$ 240 mlg^{-1}_{VS}	Remarks: Extracted from support research to IPCC Guidelines for National GHG Emissions, 2006

Table 33 – Biodegradation process efficiency of digesters over 15 days using method A, a 10-day HRT, variable shear rate and fixed rest period (6hrs)

Shear Rate	Total VS Fed (measured)	VS Remaining (measured)	VS Washed Out (estimated)	CH_4 Equivalent				Process η	Degradation η
				VS Digested/CH_4 Produced		Remaining	Washed Out		
(s^{-1})	(g)	(g)	(g)	(g)	(ml)	(ml)	(ml)	(%)	(%)
Non-mixed	336.1	139.8	180.8	15.5	15,914	143,114	185,118	58.4%	4.6%
33	329.1	144.1	186.4	-1.4	21,511	-2,175,801	-2,814,399	56.2%	-0.4%
55	328.6	134.2	173.6	20.7	21,571	139,687	180,685	59.1%	6.3%
125	328.3	138.0	178.5	11.8	23,733	278,509	360,252	58.0%	3.6%

Slurry Conversion to CH_4	1.78 $m^3kg^{-1}_{VS}$ 1,775,021 $mlkg^{-1}_{VS}$ 1,775 mlg^{-1}_{VS}	Remarks: VS washout estimation assumes steady state well-mixed digester content when digestate extracted during feeding process.

Table 34 – Biodegradation process efficiency of digesters over 15 days using method B, a 10-day HRT, variable shear rate and fixed rest period (6hrs)

Shear Rate (s^{-1})	CH_4-derived (m^3)	Equivalent (kWh)	Parasitic (kWh)	Net Power (kWh)	Parasitic (%)	PF	YF	YF (corrected)	PF*YFc	Net Rating
33	0.0215	0.0789	0.0046	0.074	5.89%	1	0.91	0.25	0.25	2
55	0.0216	0.0792	0.0056	0.074	7.04%	0.83	0.91	0.25	0.21	3
125	0.0237	0.0871	0.0047	0.082	5.40%	0.99	1.00	0.27	0.27	1

Table 35 – Energy output of digesters over 15 days using a 10-day HRT, variable shear rate and a fixed rest period (6hrs)

5:3:2:10 Parasitic Energy Demand and Power Factor

Despite the mixing period for the mixing regimes varying, the energy used by the digesters mixed using shear rates of 33 and 125s^{-1} were similar (PFs of 1 and 0.99, respectively) as shown in Table 35 with a PF of 1 representing the lowest energy applied to mix during the experiment (Figure 75). The digester mixed using a shear rate of 55s^{-1} used the most energy over the 15 days (PF=0.83). Parasitic energy demanded by the mixers using shear rates of 33, 55 and 125s^{-1} as a percentage of energy produced was 5.9, 7.0 and 5.4 percent, respectively. This relationship will change on scale-up.

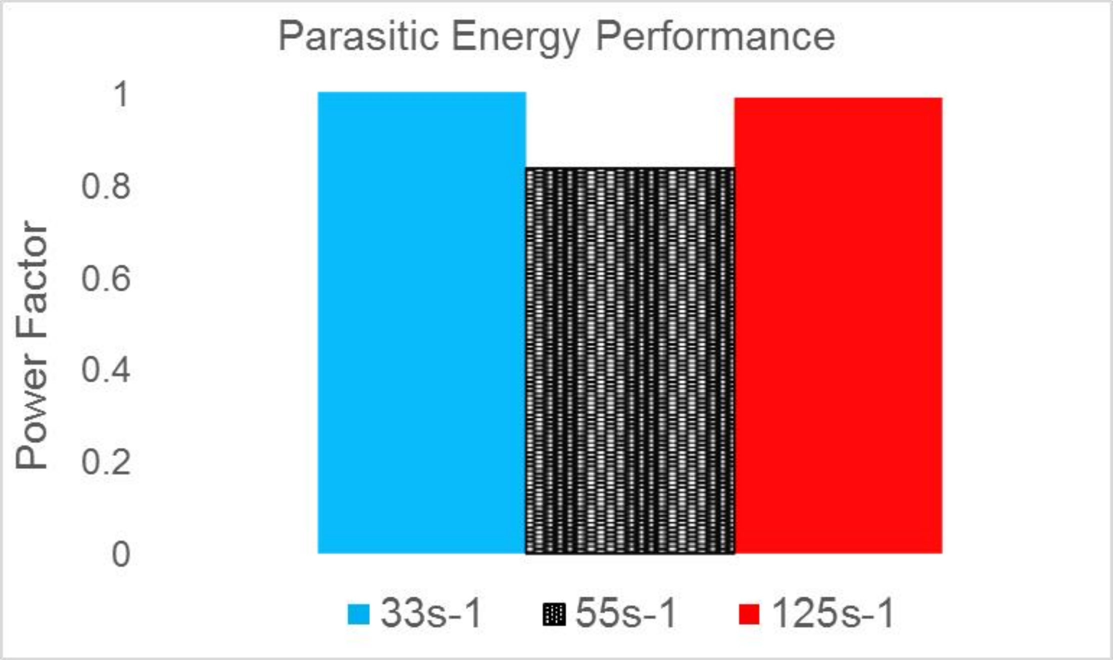


Figure 75 – Comparison of parasitic energy performance using power factor when HRT 10 days, shear rate varied and rest period fixed (6hrs)

5:3:2:11 CH_4 Yield and Yield Factor

A comparison of regimes produced a cumulative CH_4 yield hierarchy using corrected YF values. Although mixing with a shear of 125s^{-1} produced 10 percent more CH_4 than the other regimes, the significance of the difference reduced when the YF was corrected (Figure 76).

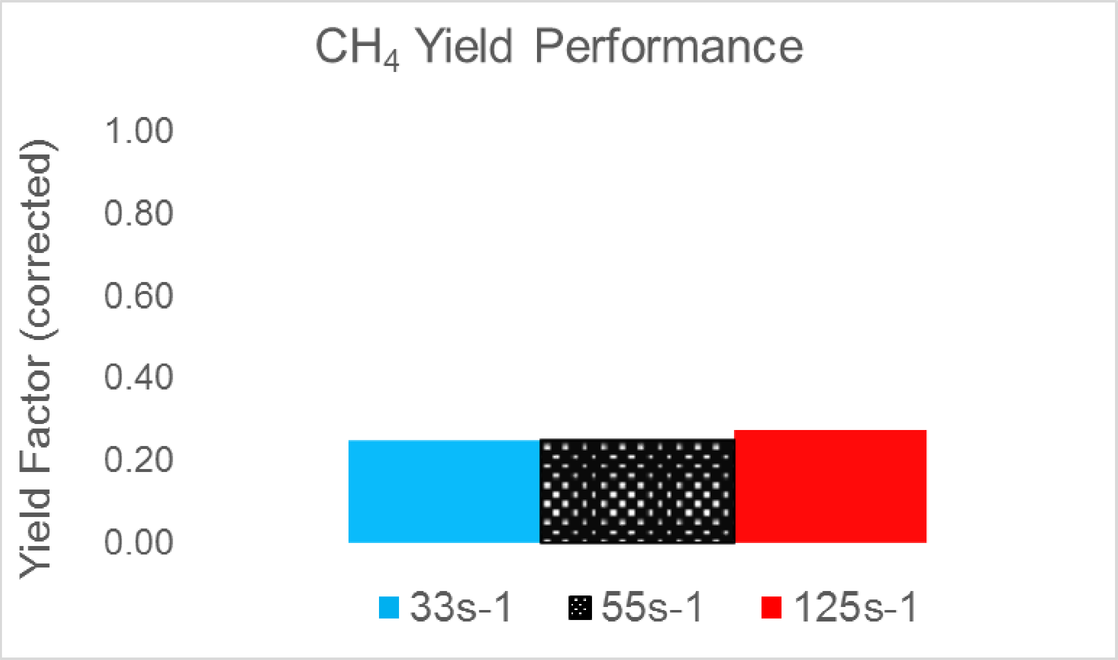


Figure 76 – Comparison of CH_4 yield using yield factor when HRT 10 days, shear rate varied and rest period fixed (6hrs)

5:3:2:12 Net Energy Output

Parasitic energy demand had the most influence when calculating net energy gain. The digester mixed using a shear rate of 125s^{-1} produced the highest net energy output closely followed by that mixed using a shear rate of 33s^{-1} (Figure 77). Mixing using a shear rate of 55s^{-1} produced the lowest net energy gain.

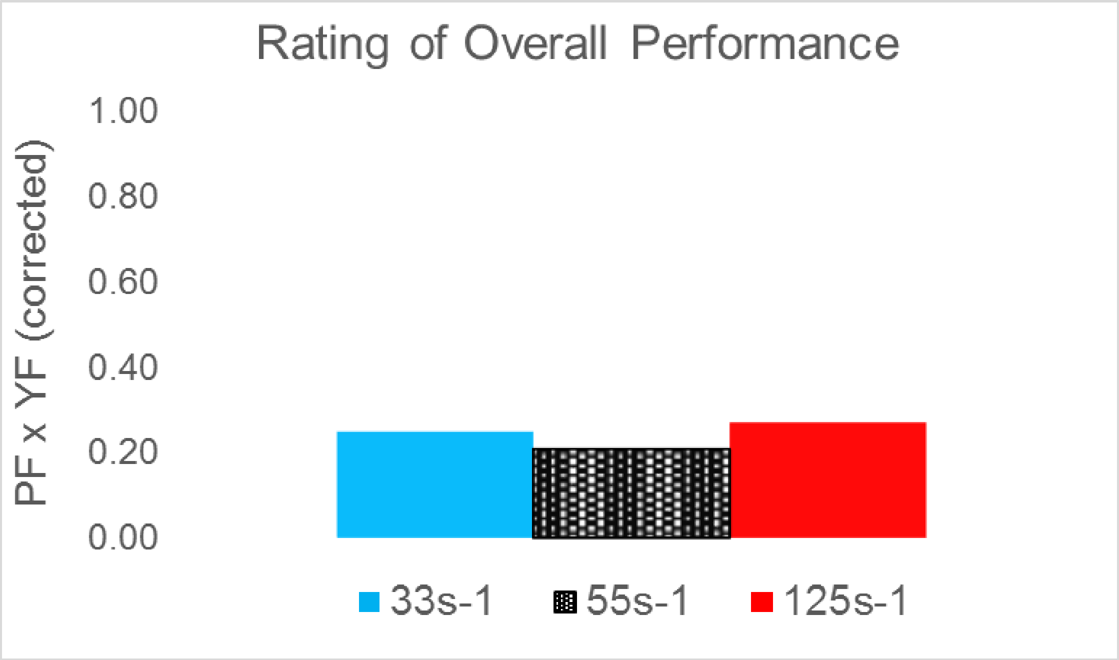


Figure 77 – Net energy comparison using a 10-day HRT, variable shear rate and fixed rest period (6hrs) using a 10-Day HRT and fixed shear rate (125s^{-1})

5:3:3 CH_4 Production Using a 10-Day HRT and Fixed Rest Period (6hrs)

5:3:3:1 Cumulative CH_4 Yield

Cumulative CH_4 yield increased as the period of resting reduced (Figure 78). Resting for 1 hour produced the highest yield of 42,000Nml which was equivalent to $10.3m^3_{CH4}m^{-3}_{slurry}$ (or $17.2m^3_{biogas}m^{-3}_{slurry}$), 86 percent of the mean potential biogas yield quoted by the Andersons Centre (2010). However, the HRT was a third of that required for complete digestion (Khanal, 2008) so would be expected to be lower. The digesters rested for 6 and 12 hours produced similar yields (less than 0.5 percent difference) that were approximately 2.5 percent lower than the best performer. However, towards the end of the 20-day experiment cumulative yields of the different mixing regimes started to converge as a consequence of a decline in the CH_4 production rate of both digesters rested for 1 hour, best illustrated by Figure 82.

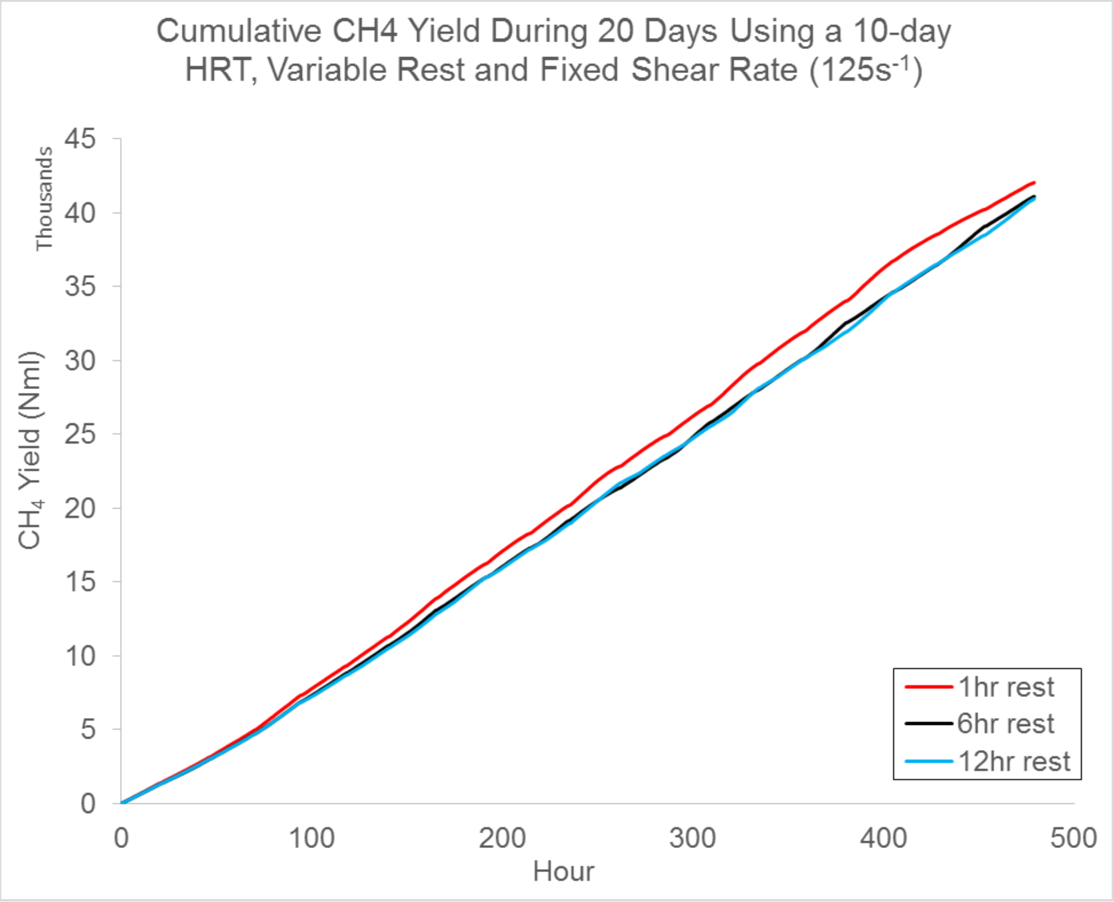


Figure 78 – Cumulative CH_4 yield achieved using a 10-day HRT, variable rest period and fixed shear rate ($125s^{-1}$)

Notably, a common mixing regime ($125s^{-1}$/6hr) to both 10-day HRT experiments produced very different CH_4 yields (Figure 69 and Figure 78). This is discussed in chapter 6.

5:3:3:2 CH_4 Production Rate

The rate of CH_4 production gradually increased during the first 13 days of the experiment and then peaked for 5 days before gradually decreasing. CH_4 production fluctuated in line with mixing periods (Figure 79). Again, the necessary dismantling of gas lines to allow feeding produced obvious troughs in production rate values every 24 hours. However, the period of peak rates of CH_4 production within each feed cycle varied depending on the rest period. The digester rested for 1 hour tended to produce most CH_4 just after feeding whereas the digesters rested for 6 and 12 hours invariably experienced a delay in peak CH_4 production that coincided with feeding and mixing times being out of synchronisation. The highest mean peak CH_4 production rate was produced on day 14 by the digester rested for 12 hours (137.6Nmlh^{-1}) which was approximately double the lowest peak rate of CH_4 production achieved for that rest period throughout the experiment. The other mixing regimes produced similar peak production values around that period in the experiment.

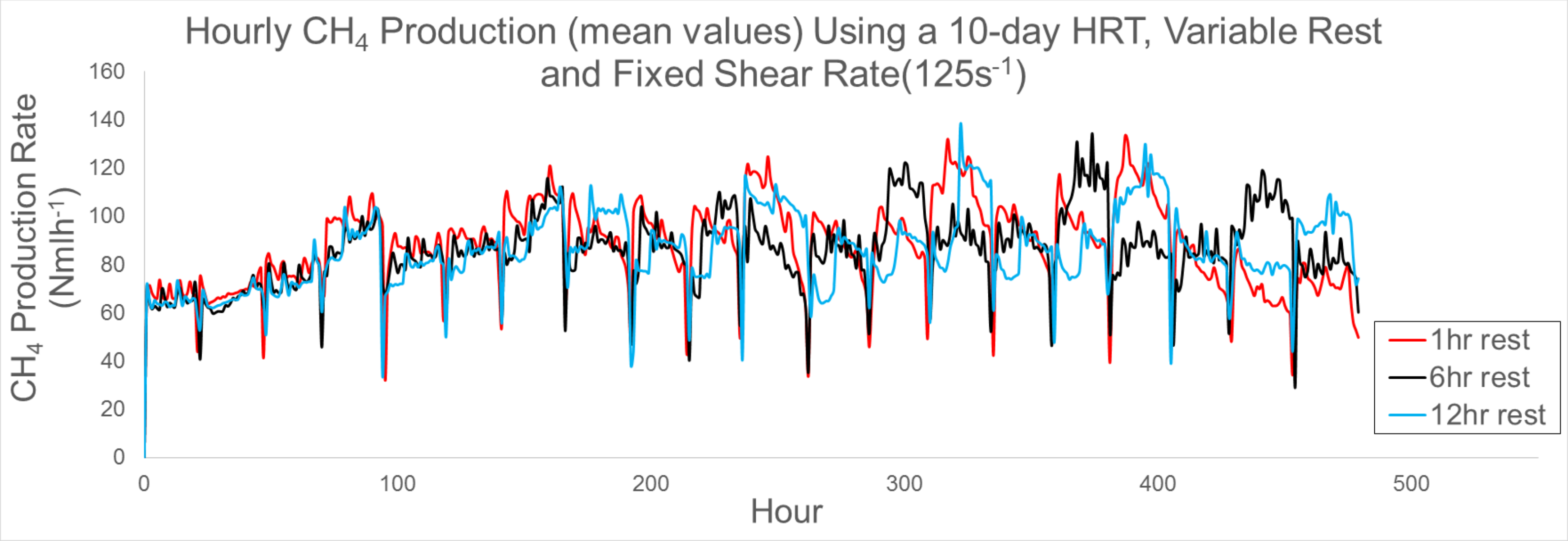
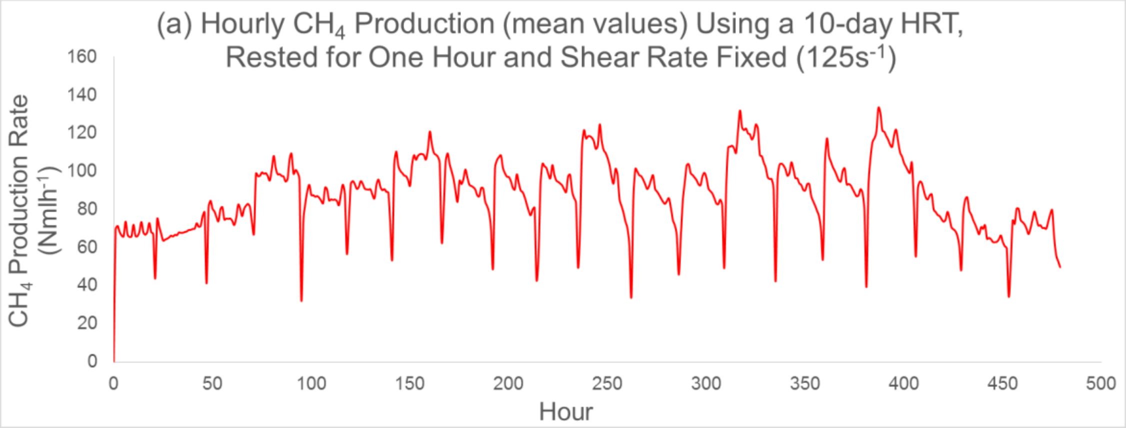
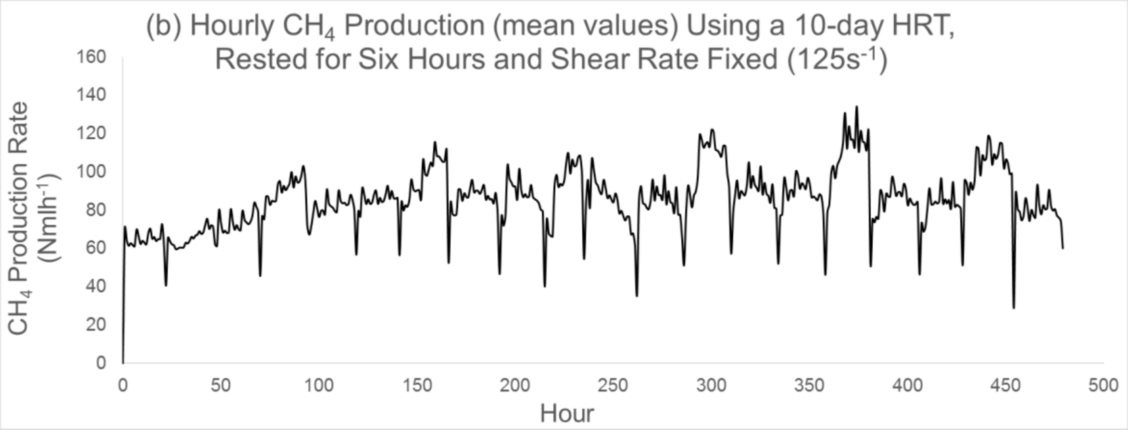


Figure 79 – CH_4 production rate achieved using a 10-day HRT, variable rest period and fixed shear rate (125s^{-1})

5:3:3:3 Underlying CH_4 Production Rate Cycle

When the shear rate was fixed ($125s^{-1}$) and rest period varied an underlying sinusoidal CH_4 production rate cycle was observed in all mixing regimes (Figure 80). CH_4 production rates gradually increased over the same period in each feed cycle during the first 4 days before decreasing and adopting a 3-day cycle. The latter started with relatively low CH_4 rates of production at the beginning of the cycle that gradually increased over 3 days before returning to original values. The 6-hour rest regime (Figure 80b) was the first to establish the pattern followed by the digesters rested for 1 (Figure 80a) and then 12 hours (Figure 80c), the latter providing the most obvious illustration of the pattern. Again, the reason for this underlying and repetitive fluctuation in CH_4 production values is not known and did not occur when the HRT was 30 days with a shear rate fixed at $55s^{-1}$. However, that may have been because the digesters were generally fed every 3 days rather than daily and so the introduction of new nutrients every 3 days may have masked the phenomenon (Figure 81). Only mixing using a 1 hour rest period at the higher HRT is provided for comparison but the absence of the pattern was common to all.





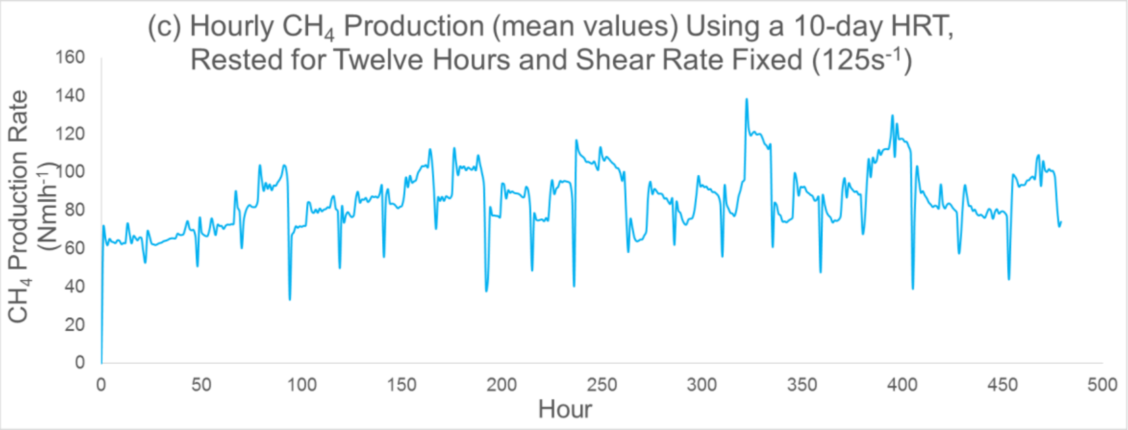


Figure 80 – Underlying CH_4 production rate cycles (mean values) using rest periods of (a) 1, (b) 6 and (c) 12 hours and shear rate fixed ($125s^{-1}$)

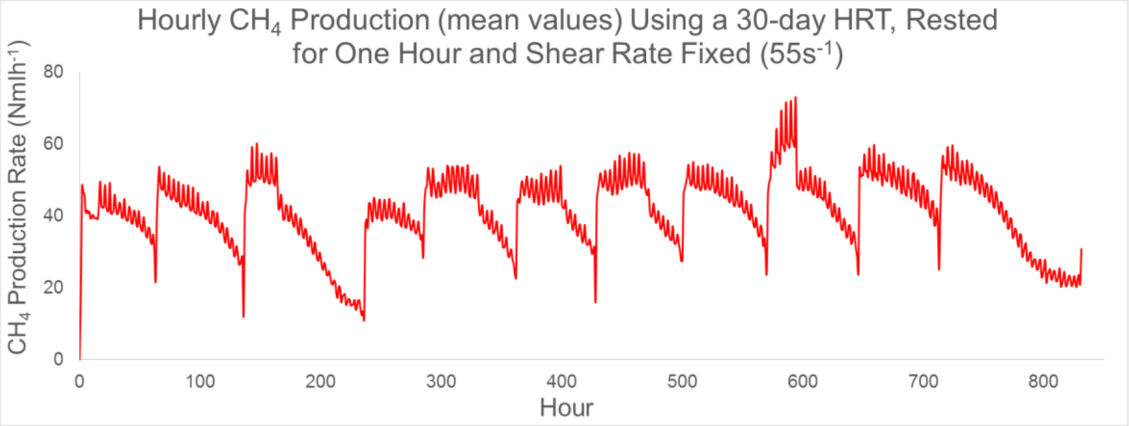


Figure 81 – Underlying CH4 production rate cycles (mean values) using a rest period of 1 hour and shear rate fixed ($55s^{-1}$)

5:3:3:4 Comparing Individual Digester Production

Discrepancies were observed between the performances of digesters mixed using the same regime as the experiment progressed. This may have been in response to the high OLR (Kim et al., 2002) and inadequate time for the volatile solids to completely biodegrade within the 10-day HRT. The profiles of different CH_4 production rates shown in Figure 82a and Figure 82b capture 4 feeding cycles at different stages of the experiment. Discrepancies tended to be in the levels of the CH_4 production rate rather than trend gradient or direction (Figure 82a). A similar discrepancy was observed when the rest period was fixed at 6 hours and the shear rate varied using a 10-day HRT. However, differences in CH_4 production rate between similarly mixing regimes were much larger when shear rate was fixed ($125s^{-1}$) and the rest period varied using the same HRT. Moreover, the gap between CH_4 production rates at similar points in the feeding cycle when the shear rate was fixed widened as the experiment progressed. This resulted in the performances of similarly configured digesters being very different on occasions by the end of the 20-day experiment (Figure 82b). The observation also explained why CH_4 production values for the mixing regime rested for 1 hour began to converge with those of other digesters towards the end of the experiment as the performance of both digesters declined. As CH_4 production is used as a common, if not ideal, indicator of digester performance (Ward et al., 2011a) the drop in CH_4 production may indicate a methanogenic community under chemical stress, possibly due to the high OLR. A FOS/TAC analysis of removed digestate was attempted as an independent check of process stability but failed to produce coherent results.

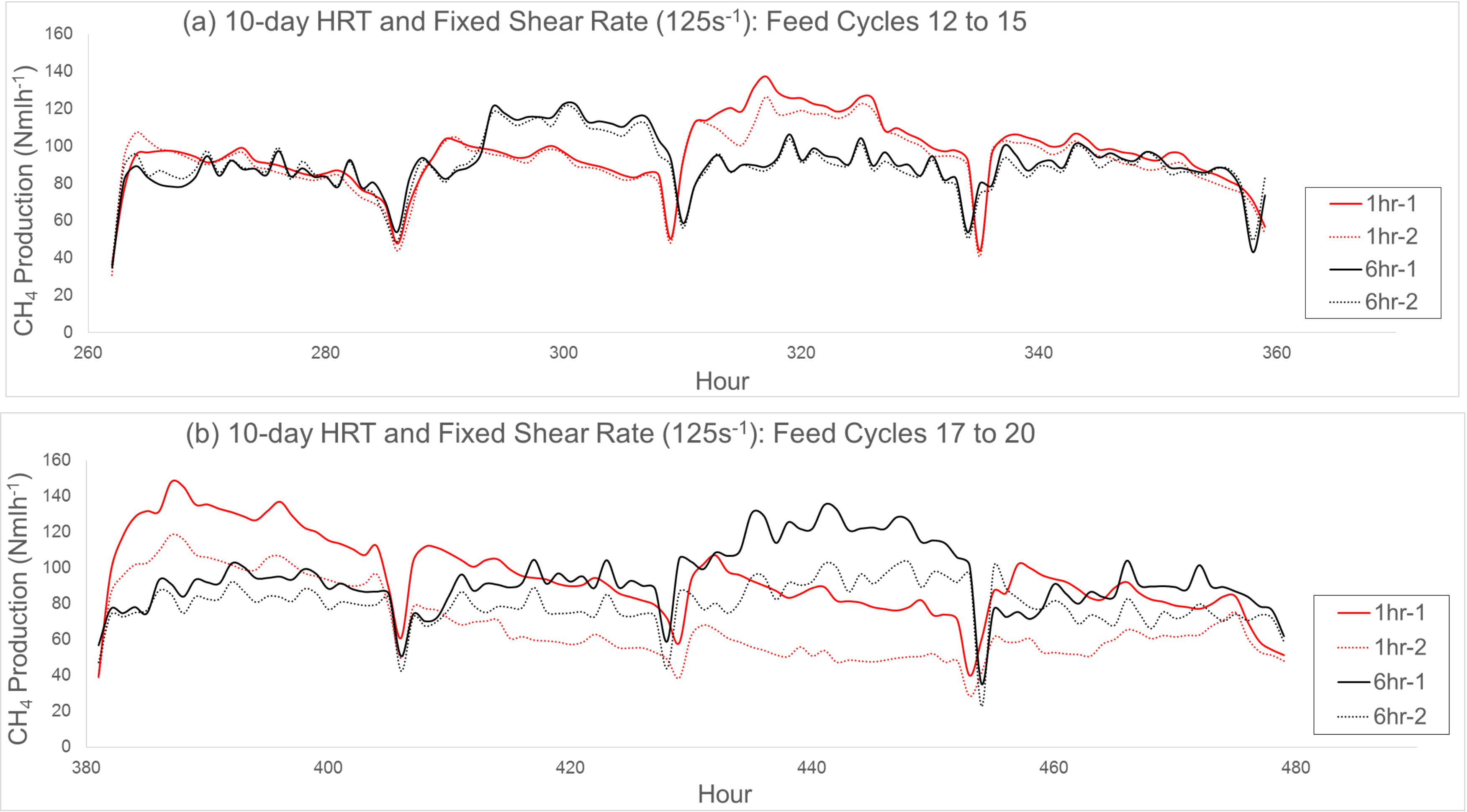


Figure 82 – Comparison of CH_4 production trends of similarly configured digesters using a 10-day HRT, variable rest period and fixed shear rate ($125s^{-1}$) (a) partway through and (b) at the end of the experiment

5:3:3:5 Specific CH_4 Production Rate

A histogram of specific CH_4 production rates for digesters rested for 1, 6 and 12 hours produced profiles based around medians of 0.042, 0.040 and 0.040$Nml_{CH4}h^{-1}ml^{-1}_{substrate}$, respectively (Figure 83). The profiles were very similar although the mixing regime rested for 1 hour indicated slightly higher specific CH_4 production rates over the length of the experiment.

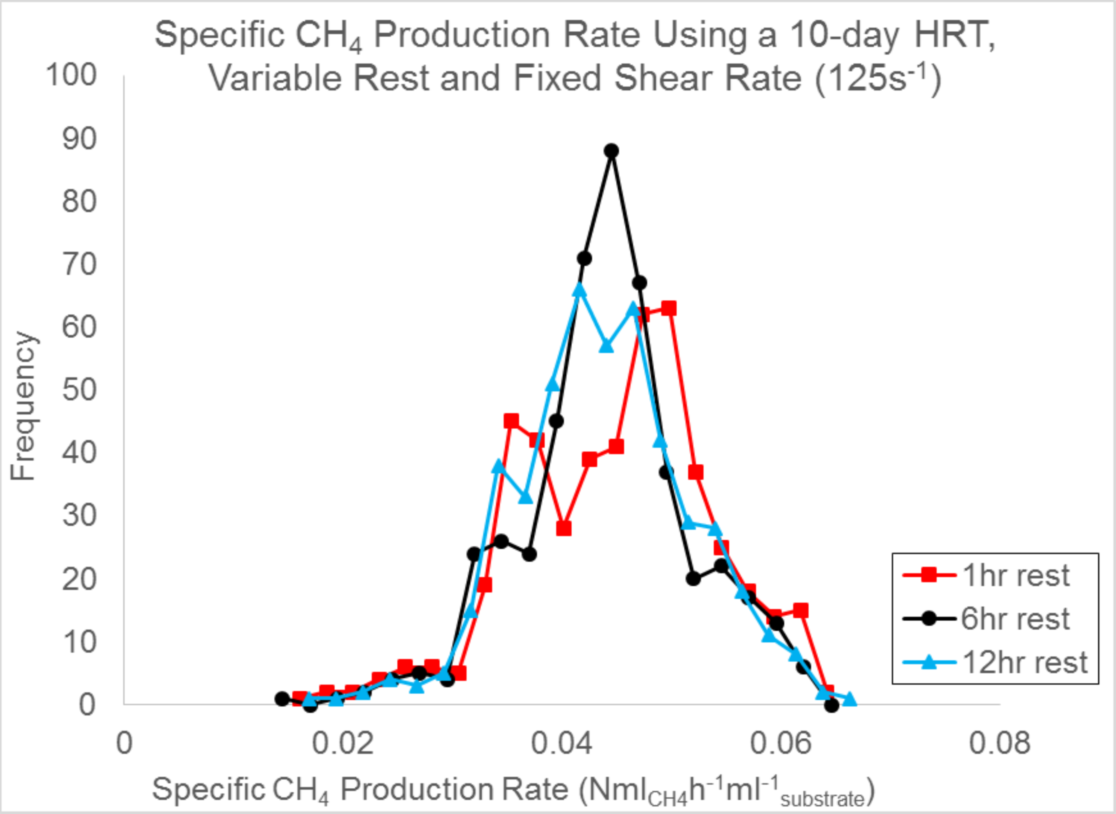


Figure 83 – Specific CH_4 production rates achieved using a 10-day HRT, variable rest period and fixed shear rate ($125s^{-1}$)

5:3:3:6 Changes in Substrate Characteristics

As per the variable shear rate/fixed rest experiment, the mass of VS increased despite CH_4 being produced (Table 36). Again, this was probably due to the high OLR. However, the size of the increase was much lower than that observed in the previous experiment which may indicate a recovery in process stability due to microbial adaptation to the high OLR throughout the majority of the experiment.

Again, RTD analysis may have provided a better understanding of the issues that HRT reduction would raise.

Digesters	**Rest Period**	**Volume**	**Substrate at Start**			**Substrate at End**			**∆ VS**
			TS	**VS**	**VS**	**TS**	**VS**	**VS**	
(#)	**(hr)**	**(g)**	**(%)**	**(%)**	**(g)**	**(%)**	**(%)**	**(g)**	**(g)**
5&6	**1**	1,800	12.6%	47.7%	123.8	10.5%	60.2%	126.8	3.0
2&3	**6**	1,800	12.6%	47.7%	123.8	10.6%	58.3%	124.0	0.2
1&4	**12**	1,800	12.6%	47.7%	123.8	10.6%	58.9%	124.4	0.6

Slurry fed to each digester over 20 days	Total	TS	VS	Total VS	VSd^{-1}
	(g)	(%)	(%)	(g)	(g)
	3,857	11.4%	68.0%	299.2	15.7

Table 36 – Changes in substrate solids content of digesters over 20 days using a 10-day HRT, variable rest period and fixed shear rate ($125s^{-1}$)

5:3:3:7 Substrate Alkalinity

All digesters shared a common pH value of approximately 7.8 at the start (Figure 84). Values remained stable (within 0.25) until day 19 when the pH of the 2 digesters mixed using a shear rate of $125s^{-1}$ reduced to 7.4 and 7.5. However, the decline was in one measurement on each digester on the planned final day of the experiment. Furthermore, the same profile had been observed in all digesters in the previous experiment where all but the non-mixed digester recovered over the following 4 days. Also, the measurements were still above 7.4 so relatively alkaline. However, the reduction in pH was after a period of reduced CH_4 production so does suggest the possibility of the onset of chemical stress within the digester. Extending the experiment was not possible as the equipment had to be returned.

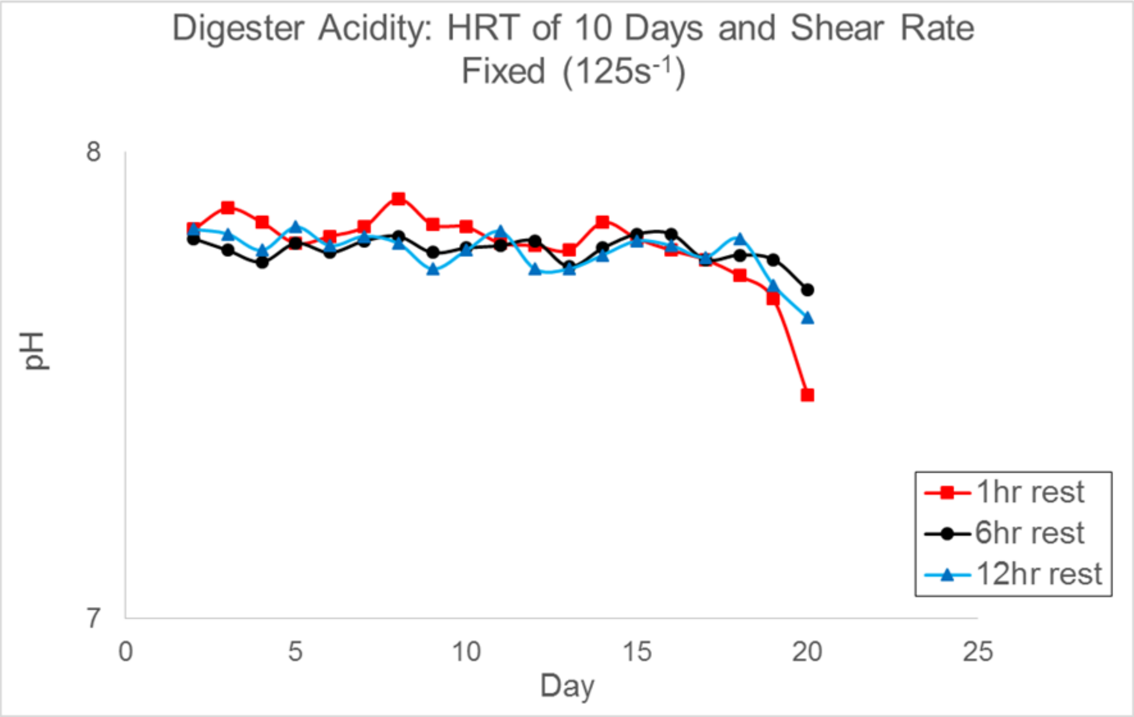


Figure 84 – Trends of pH over 20 days using a 10-day HRT, variable rest period and fixed shear rate ($125s^{-1}$)

5:3:3:8 Process Efficiency Based on Volatile Solids Biodegradation

After 20 days the process efficiency based on VS residues at the end of the experiment was approximately 71 percent for all mixing regimes (Table 39) and (Table 40). Again, process efficiency took no account of VS washed out when digestate was removed. VS washout was estimated to be 30 percent using method A (Table 37) and 53 percent using method B (Table 38). Biodegradation efficiencies of approximately 40 percent using method A (Table 39) and 18 percent using method B (Table 40) were achieved across all digesters. In both methods the reduction coincided with an increase in estimated VS washout when HRT was reduced (OLR increased). This would have similar rheological consequences to those previously discussed. A CH_4 conversion factor of $559ml_{CH4}g^{-1}_{VS}$ was estimated which was similar to that achieved using an HRT of 30 days and double the published estimates applied in method A (Zeeman & Gerbens, 1996).

Estimated CH_4 Ratio based on 240 $ml_{CH4}g^{-1}_{VS}$			
Rest Period	**Produced**	**Remaining**	**Washed Out**
1	41.4	30.0	28.6
6	40.5	29.3	30.2
12	40.3	29.4	30.3

Table 37 – Estimated ratio of the different VS pathways over 20 days using method A, a 10-day HRT, variable rest period and fixed shear rate ($125s^{-1}$)

Estimated CH_4 Production Ratio			
Rest Period	**Produced**	**Remaining**	**Washed Out**
1	16.3	30.0	53.7
6	18.2	29.3	52.5
12	17.9	29.4	52.7

Table 38 – Estimated ratio of the different VS pathways over 20 days using method B, a 10-day HRT, variable rest period and fixed shear rate ($125s^{-1}$)

5:3:3:9 Optimisation Based on Cumulative CH_4 Yield

Table 41 provides a comparison of the values and factors on which optimisation was assessed. PF and YF values were again used to compare system performance based on net energy gain. The non-mixed digester was not included.

Rest Period	Total VS Fed	VS Remaining	CH_4 Produced	Theoretical CH_4 Equivalent based on $240ml_{CH4}g^{-1}_{VS}$				Process η	Degradation η
				Potential		Remaining	Washed Out		
(hr)	(g)	(g)	(ml)	(m^3)	(ml)	(ml)	(ml)	(%)	(%)
1	422.9	126.8	42,042	0.102	101,505	30,423	29,040	70.0%	41.4%
6	422.9	124.0	41,107	0.102	101,505	29,750	30,647	70.7%	40.5%
12	422.9	124.4	40,941	0.102	101,505	29,858	30,707	70.6%	40.3%

Slurry Conversion to CH_4	0.24 $m^3kg^{-1}_{VS}$ 240,000 $mlkg^{-1}_{VS}$ 240 mlg^{-1}_{VS}	Remarks: Extracted from support research to IPCC Guidelines for National GHG Emissions, 2006

Table 39 – Biodegradation process efficiency of digesters over 20 days using method A, a 10-day HRT, variable rest period and fixed shear rate ($125s^{-1}$)

Rest Period	Total VS Fed (measured)	VS Remaining (measured)	VS Washed Out (estimated)	CH_4 Equivalent				Process η	Degradation η
				VS Digested/CH_4 Produced		Remaining	Washed Out		
(hr)	(g)	(g)	(g)	(g)	(ml)	(ml)	(ml)	(%)	(%)
1	422.9	126.8	227.0	69.1	42,042	77,077	138,046	70.0%	16.3%
6	422.9	124.0	222.0	77.0	41,107	66,206	118,574	70.7%	18.2%
12	422.9	124.4	222.8	75.7	40,941	67,267	120,475	70.6%	17.9%

Mean Slurry Conversion to CH_4	0.56 $m^3kg^{-1}_{VS}$ 559,400 $mlkg^{-1}_{VS}$ 559 mlg^{-1}_{VS}	Remarks: VS washout estimation assumes steady state well-mixed digester content when digestate extracted during feeding process.

Table 40 – Biodegradation process efficiency of digesters over 20 days using method B, a 10-day HRT, variable rest period and fixed shear rate ($125s^{-1}$)

Rest Period (hr)	CH$_4$-derived	Equivalent	Parasitic	Net Power	Parasitic	PF	YF	YF (corrected)	PF*YF$_c$	Net Rating
	(m^3)	(kWh)	(kWh)	(kWh)	(%)					
1	0.0420	0.1543	0.0331	0.121	21.45%	0.09	1.00	0.27	0.03	3
6	0.0411	0.1509	0.0061	0.145	4.04%	0.51	0.98	0.27	0.13	2
12	0.0409	0.1503	0.0031	0.147	2.05%	1	0.97	0.27	0.27	1

Table 41 – Energy output of digesters over 20 days using a 10-day HRT, variable rest period and fixed shear rate (125s^{-1})

5:3:3:10 Parasitic Energy Demand and Power Factor

As the mixing intensity and period were similar for all digesters parasitic energy demand was influenced by rest period so the range of values differed by a factor of 12. The regime mixed every 12 hours used the least energy so was allocated a PF of 1. The digesters rested for 6 hours and 1 hour produced PFs of 0.51 and 0.09, respectively (Table 41) (Figure 85). Parasitic energy demanded by the mixers rested for 1, 6 and 12 hours as a percentage of energy produced were approximately 21, 4 and 2 percent, respectively.

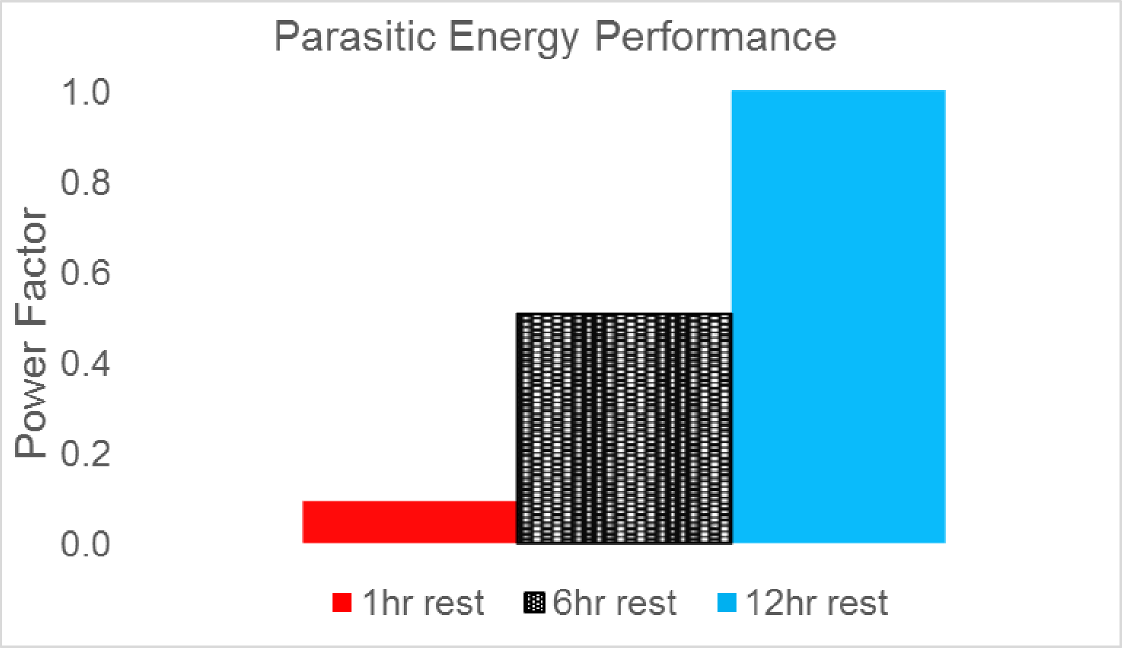


Figure 85 – Comparison of parasitic energy performance using power factor when HRT 10 days, rest period varied and shear rate fixed (125s^{-1})

5:3:3:11 CH_4 Yield and Yield Factor

All regimes produced a similar corrected YF of 0.27. Although mixing rested for 1 hour produced marginally more CH_4 than those rested for 6 and 12 hours, the significance of the difference reduced when the YF was corrected (Figure 86).

Figure 86 – Comparison of CH_4 yield using yield factor when HRT 10 days, rest period varied and shear rate fixed (125s^{-1})

5:3:3:12 Net Energy Output

Parasitic energy demand was the most influential factor when net energy gain was calculated. The digester rested for 12 hours produced the highest net energy followed by that rested for 6 hours (Figure 87). The digester rested for 1 hour produced the lowest net energy gain.

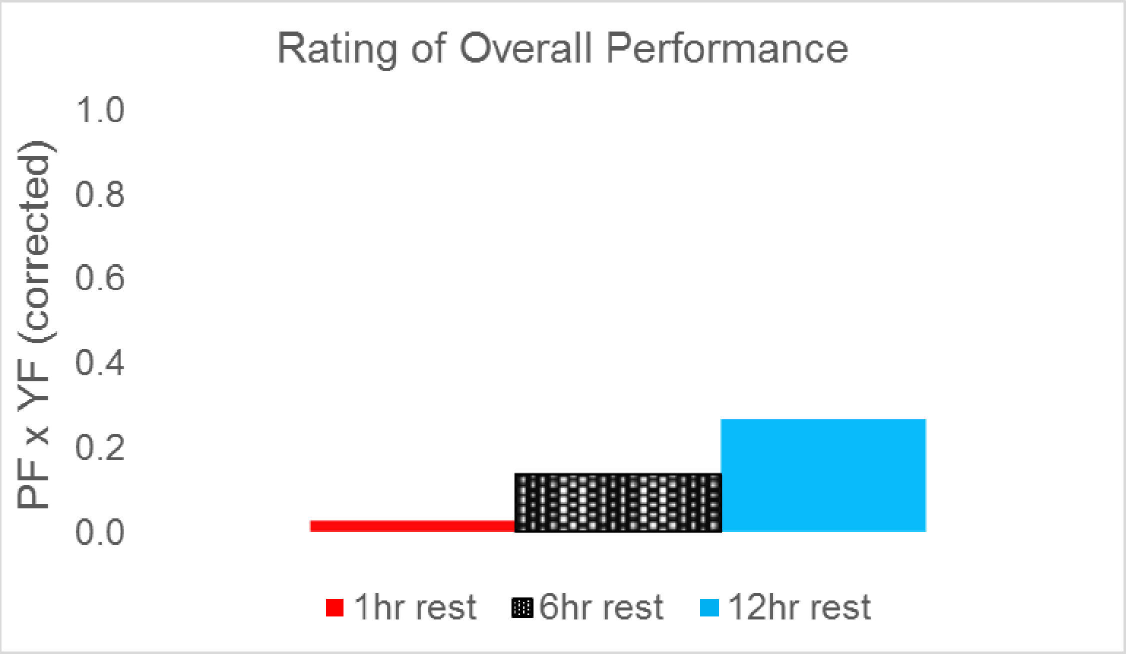


Figure 87 – Net energy performance comparison over 20 days using a 10-day HRT, variable rest period and fixed shear rate (125s^{-1})

5:4 Conclusions

Reducing HRT had a direct impact on digester performance with the degree of improvement depending on mixing regime. The analysis of fed-batch operations using a 10-day HRT supported the following conclusions:

- Varying shear rate had a significant effect on CH_4 production in a homogenised digester when the rest period was fixed. This contradicted results produced when the HRT was 30 days.
- Resting the substrate for 6 and 12 hours produced similar CH_4 yields but reducing the rest period to 1 hour increased CH_4 production.
- A secondary (underlying) sinusoidal CH_4 production rate cycle was observed in both experiments. The cause was not identified.
- Specific CH_4 production was higher when feeding and mixing coincided.
- The major benefit of resting on net energy produced is the energy savings associated with long periods with no mixing rather than the increase in energy production. This will directly influence OPEX and hence financial viability.

- Mixing using a shear rate of $125s^{-1}$ may destabilise the AD process over prolonged periods when the HRT is 10 days as indicated by the decline in CH_4 production rates at the latter stages of the fixed shear rate experiment.
- The importance of mixing increases when OLR is increased as indicated by the significant effect shear rate had on CH_4 production when the HRT was 10 days compared to having minimal effect when the HRT was 30 days.

Again, the assumed biogas quality of 60 percent CH_4 undermined the analysis so the effect of mixing regime on biogas quantity and quality may not be accurately portrayed. Hence, the data should be used with caution. RTD analysis would have allowed VS throughput to be accurately predicted thereby improving the understanding of the process. Measuring VS washout would also have improved the accuracy of the CH_4 conversion factor and allowed changes to the rheology of the digestate to be better understood.

5:5 Next Research Step

The results of chapters 6 and 7 will now be compared to better understand the effects of mixing regime selection when HRT is optimised to achieve:

- Complete biodegradation of cow slurry (30 days)
- Maximum CH_4 production rate (10 days).

CHAPTER 6 – OPTIMISING HRT FOR COW SLURRY

6:1 Introduction

The temporal separation of independent variables used in the fed-batch experiments in chapters 4 and 5 demonstrated that changing rest period and shear rate when mixing can influence digester performance. However, the broad range of parasitic energy demanded of the different mixing regimes significantly influenced net energy gain and hence the economics of each process. The outcomes of the experiments using the 2 HRTs applied are now compared with 30 days reflecting the time required for complete digestion of cow slurry at mesophilic temperatures (Khanal, 2008) and 10 days reflecting the period within the 30-day cycle when the rate of CH_4 production is highest. Comparing the net energy gains realised by each approach and the stability of each process as OLR changes will inform future financial modelling to identify the most economical way to process high volumes of low energy cow slurry that dairy farms have to manage on a daily basis.

6:1:1 Aims

This aims of this chapter are to:

- Identify differences in the performance of the mixing regimes using HRTs of 30 and 10 days by comparing:
    - Cumulative CH_4 yield.
    - CH_4 production rate.
    - Specific CH_4 production rate.
    - Biodegradation process efficiency.
    - Net energy output.
- Use analysis of variation techniques to statistically compare CH_4 produced by a mixing regime common to 2 experiments using the same HRT to better understand the extent of microbial adaptation observed.

6:2 Materials and Method

The results of chapters 4 and 5 were compared using simple graphical data comparison and ANOVA techniques.

6:2:1 Digester Procedure and Set-up

As described in chapter 4 and 5 and summarised in Table 42.

Experiment	**HRT**	**Shear Rate**	**Mixing Period**	**Rest Period**
	(day)	**(s^{-1})**	**(min/sec)**	**(hours)**
1 **(Fixed SR)**	30	55	23m29s (33s^{-1}) 19m33s (55s^{-1}) 7m21s (125s^{-1})	1/6/12
2 **(Fixed Rest)**	30	No-mix/33/55/125		6
interim	20	No-mix/33/55/125		6
3 **(Fixed Rest)**	10	No-mix/33/55/125		6
4 **(Fixed SR)**	10	125		1/6/12

Table 42 – Summary of experiments and mixing regime variables

6:2:2 Feedstock

The combined characteristics of the feedstock used in chapters 4 and 5 are presented in Table 43.

HRT (day)(experiment)	**Start-up Substrate**		**Subsequent Feedstock**		
	%TS	**%VS**	**%TS**	**%VS**	**OLR ($g_{VS}l^{-1}/d^{-1}$**
30 (Fixed SR)	10.0	67.6	14.8	72.4	3.6
30 (Fixed Rest)	8.5	65.8	10.6	67.8	2.4
20 (interim)	-	-			3.7
10 (Fixed Rest)	8.4	63.2	11.6	67.6	8.0
10 (Fixed SR)	12.6	47.7	11.4	68.0	7.9

Table 43 – Characteristics of start-up substrate, fed-batch feedstock and changing OLR

6:2:3 Data Comparison

Data was compared using 2 data sets from each experiment, as follows:

- Analysis of the solids content before and after each experiment was fundamental to calculating process efficiency and estimating biodegradation efficiency of each mixing regime at each HRT. Hence, results were compared using the complete data set covering the full length of each experiment. Both methods of predicting VS washout are included.
- As experiment length was selected to ensure that at least 1 HRT period of each process was captured experiments ranged in length from 15-38 days, depending on HRT and digester serviceability. Therefore, comparisons of process outcomes influenced by parasitic energy were based on reduced data sets restricted to the final 10 days (240 hours) of each experiment. This also ensured that the data represented periods during which each process had been given maximum opportunity to stabilise after changes to independent variables or digester reconfiguration. The selected period also provided the opportunity to compare processes after a reasonable period of exposure to high OLR when HRT was reduced.

6:2:3:1 Methanogen Community Kinetics

Improving the knowledge of the relationship between microbial community structure and AD function is important to understanding AD processes (Bocher et al., 2015). Mathematical quantitative structure activity relationship (QSAR) models have been developed to predict specific methane activity (SMA) for biomass but SMA can vary greatly between biomass samples. Hence, developing a method to predict the SMA for generic biomass would be challenging. Difficulties in refining such techniques increase when fundamental variables such as animal diet can affect methanogen communities in the rumen of livestock (Zhou et al., 2011). Therefore, accrediting the increase in CH_4 production specifically to HRT reduction, OLR increase or changes in methanogen community kinetics due to adaptation may not be reliable using this method. However, gaining an appreciation of the extent of possible changes in methanogen communities as a result of microbial adaptation was possible by analysing variations in CH_4 yields of certain mixing regimes using ANOVA techniques.

6:2:3:2 Analysis of Variation (ANOVA)

A statistical comparison of the effects of a mixing regime common to the 2 experiments subjected to a 10-day HRT was applied as they produced substantially different CH_4 yields. As one experiment followed the other with the same substrate being used, a statistical analysis of the variation between CH_4 yields realised provided an indication of the extent of microbial adaptation that occurred when all other variables were fixed.

6:3 Results and Discussion

6:3:1 Effectiveness of Experimental Technique

Comparing the results within experiments proved straightforward with no data issues observed as all results were relative and obtained within a relatively short timescale using a common substrate source. However, comparing the results from individual experiments was complicated by the same substrate being used from one experiment to the next. The practice provided the opportunity for microbial communities to adapt over time with no means of quantifying the impact of the microbial adaptation on CH_4 yield which confused the analysis. This made apportioning responsibility for CH_4 production to a specific variable difficult when data was considered as a whole. The issue is discussed fully at the appropriate section. RTD analysis of both HRTs would also have informed the comparison and provided a better understanding of the process.

6:3:2 CH_4 Production When Rest Period Fixed (6hrs)

6:3:2:1 Cumulative CH_4 Yield

Changing the shear rate produced a less than 1 percent difference in CH_4 yield when the HRT was 30 days and the rest period fixed (dotted lines in Figure 88). However, when the same shear rates were applied using a 10-day HRT, CH_4 production rates increased with the extent of the increase depending on the shear rate applied. CH_4 production was most influenced by HRT when the shear rate was $125s^{-1}$. Conversely, the non-mixed digester subjected to a 10-day HRT followed a similar straight-line trend to the yield profiles produced by all regimes when the HRT was 30 days with no improvement in CH_4 production observed as the experiment progressed.

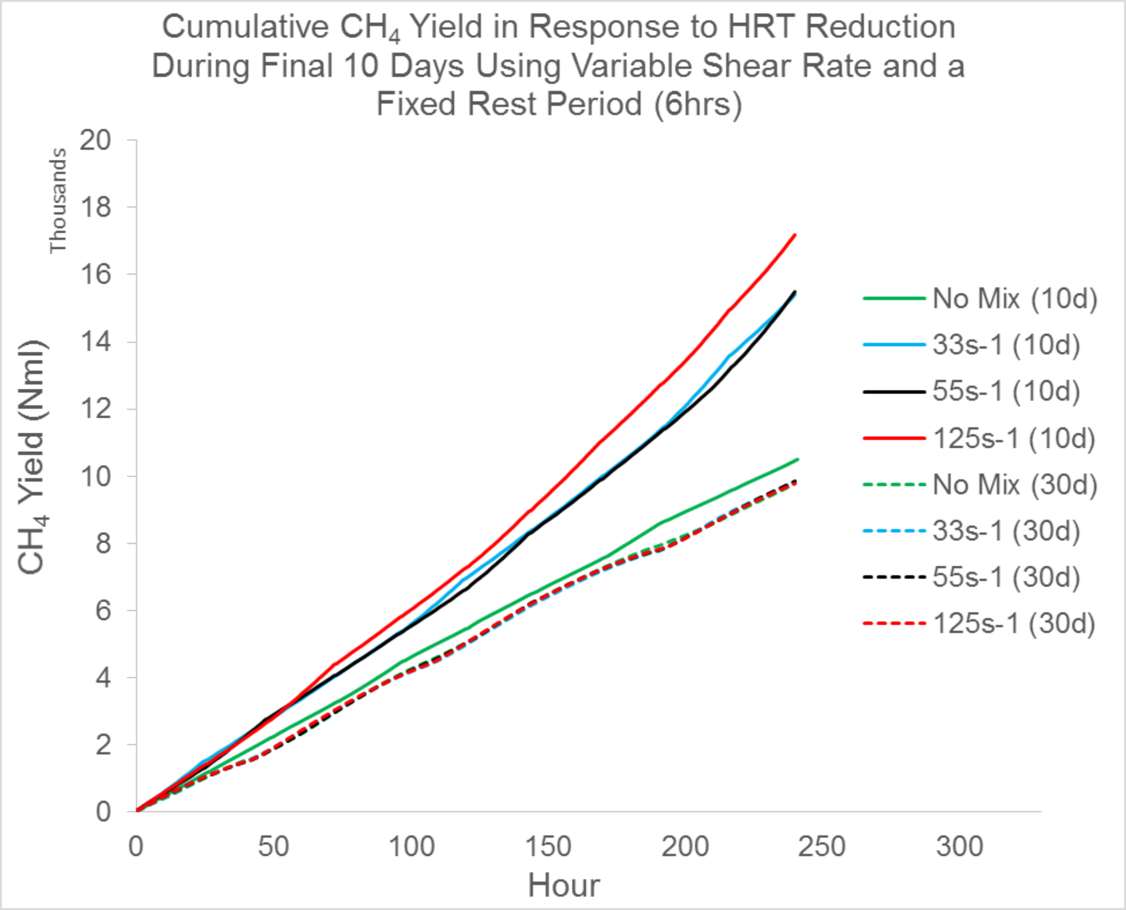


Figure 88 – Cumulative CH_4 yield during the final 240 hours when HRT reduced, shear rate varied and rest period fixed (6hrs)

A summary of CH_4 yield comparisons is presented in Table 44. After 10 days of mixing at a shear rate of 125s^{-1} with a 10-day HRT, CH_4 yield was 76 percent higher than that produced by the same shear rate when the HRT was 30 days. Mixing using shear rates of 33 and 55s^{-1} continued to produce similar CH_4 yields but 57 percent higher when HRT was reduced. The non-mixed digester produced a 7 percent increase in CH_4 yield at the lower HRT. As the rest period, temperature and OLR were fixed for all digesters using a similar HRT, differences in CH_4 yields could be directly attributed to changing shear rate. However, when the HRT was reduced, OLR increased and became an additional variable to be considered when results from experiments using different HRTs were compared. Shear rate changed from having virtually no influence when OLR was low (30-day HRT) to becoming significant when OLR increased (10-day HRT). Such an outcome suggests that the metabolism of the methanogens embedded in a digester accommodating higher nutrient-density feedstock (associated with the lower HRT) were more responsive when higher shear rates were applied.

Mixing Regime	30-day HRT				10-day HRT			
	Non-mixed	Shear Rate (s^{-1})			Non-mixed	Shear Rate (s^{-1})		
		33	55	125		33	55	125
Max Yield (Nml)	9,785	9,828	9,844	9,784	10,502	15,407	15,494	17,190
Δ between regimes (%)	0.01%	0.45%	0.62%	0.00%	0.00%	46.70%	47.54%	63.69%
Δ between HRTs (%)					7.33%	56.77%	57.39%	75.70%

Table 44 – Differences in cumulative CH_4 yields achieved during the final 240 hours using different HRTs when shear rate varied and rest period fixed (6hrs)

6:3:2:2 CH_4 Production Rate

From the outset there was a distinct difference between the rates at which CH_4 was produced by each mixing regime when the HRT was reduced to 10 days (Figure 89) which was not the case when HRT was 30 days. Shear rates applied during the 30-day HRT (dotted lines) produced similar and steady rates of CH_4 of approximately 40Nmlh^{-1}. The non-mixed digester produced CH_4 at a relatively similar rate overall although peak production was less obvious and occurred at different times to the mixed digesters for reasons explained in chapter 4. However, CH_4 production rates for all mixing regimes were significantly higher and more pronounced when the HRT was reduced to 10 days and gradually increased as the experiment progressed even though the OLR was fixed. At the end of the 10-day period, the range of peak CH_4 production rates achieved using a 10-day HRT increased by between 2.4 percent for the non-mixed digester and 240 percent for the digester mixed using a shear rate of 125s^{-1}. As the OLR was fixed throughout this increase in microbial metabolism may have been the result of microbial adaptation. The increase in CH_4 production rate over time suggests that methanogens were particularly adaptive.

Figure 90 represents the change (as a percentage) in CH_4 production rates for each mixing regime when HRT was reduced. The reason for the 2 peaks at hours 40 and 190 is not known but they have little relevance when considering the overall production profile. However, the trend for all mixed digesters does confirm that hourly CH_4 production was increasing as the experiment ended so rates of CH_4 production higher than those observed may be achievable. The non-mixed digester subjected to a 10-day HRT occasionally achieved a lower rate of production than the digester subjected to a 30-day HRT resulting in negative percentage values.

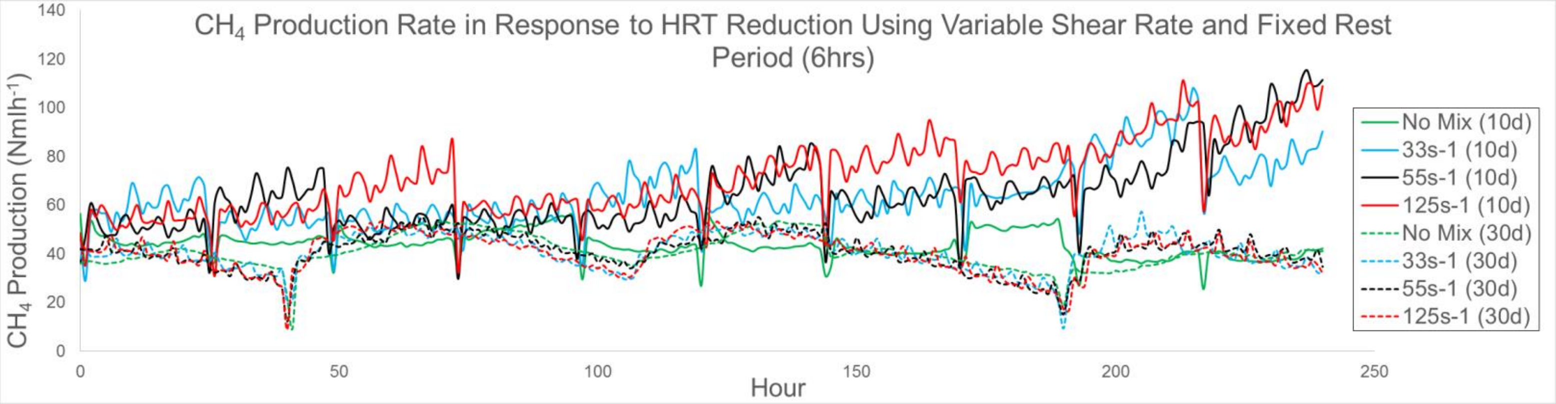


Figure 89 – CH4 production rate during the final 240 hours when HRT reduced, shear rate varied and rest period fixed (6hrs)

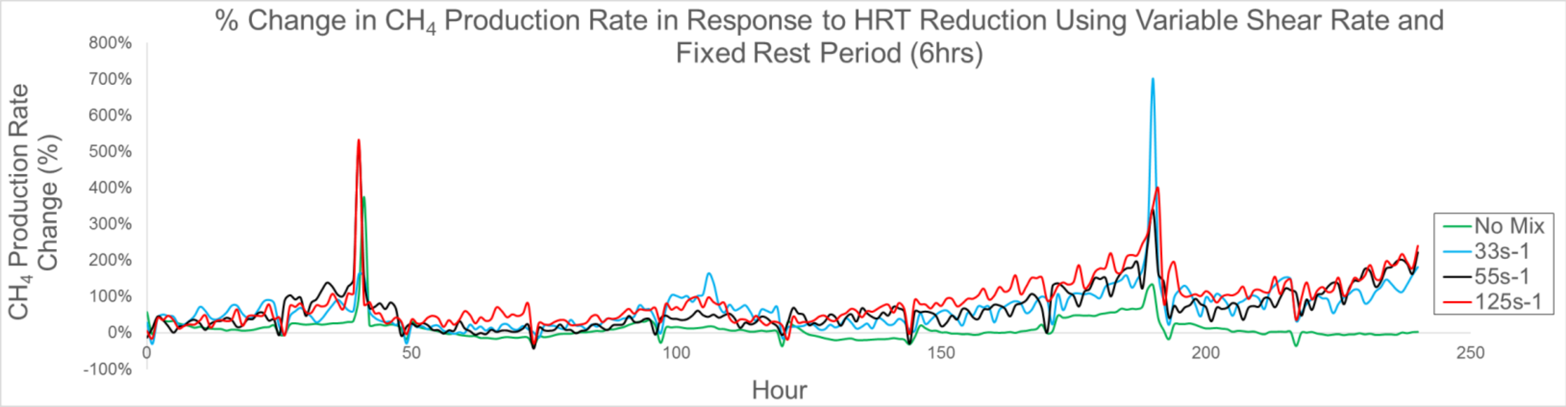
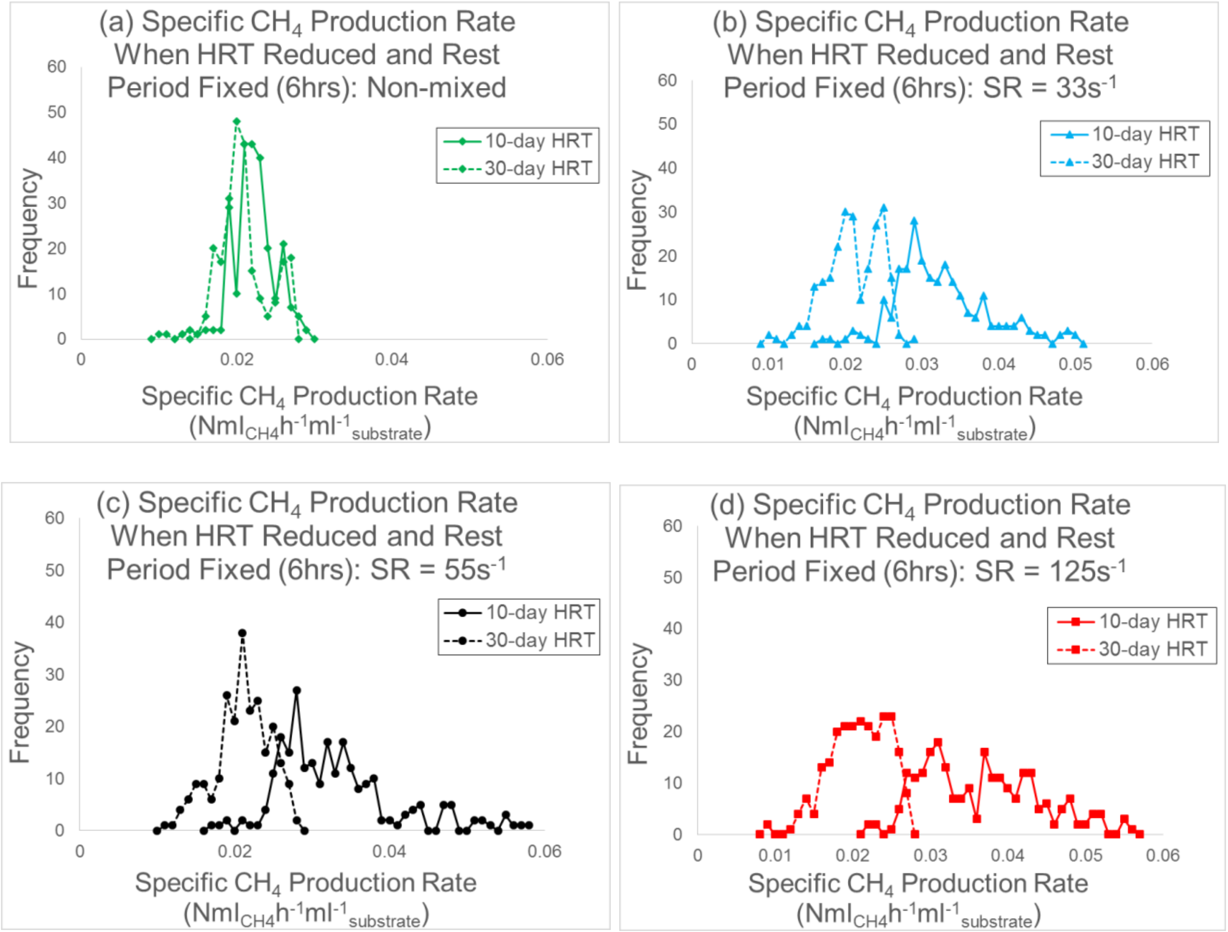


Figure 90 – Percentage variation in hourly CH4 production rate during the final 240 hours when HRT reduced, shear rate varied and rest period fixed (6hrs)

6:3:2:3 Specific CH_4 Production Rate

The specific CH_4 production rate of all regimes increased when HRT was reduced to 10 days with the most significant increases experienced by the mixed digesters (Figure 91). The non-mixed digester (Figure 91a) produced values that predominated around a median of $0.020 Nml_{CH4} h^{-1} ml^{-1}_{substrate}$ and experienced a relatively small increase when HRT was reduced. The profiles of the digesters mixed using shear rates of 33 (Figure 91b), 55 (Figure 91c) and $125 s^{-1}$ (Figure 91d) were based around median values of 0.034, 0.037 and $0.039 Nml_{CH4} h^{-1} ml^{-1}_{substrate}$, respectively. Specific CH_4 production rate values in response to reducing HRT tended to increase as shear rate increased, with $125 s^{-1}$ achieving the highest values.



(a) Specific CH_4 Production Rate When HRT Reduced and Rest Period Fixed (6hrs): Non-mixed

(b) Specific CH_4 Production Rate When HRT Reduced and Rest Period Fixed (6hrs): SR = $33s^{-1}$

(c) Specific CH_4 Production Rate When HRT Reduced and Rest Period Fixed (6hrs): SR = $55s^{-1}$

(d) Specific CH_4 Production Rate When HRT Reduced and Rest Period Fixed (6hrs): SR = $125s^{-1}$

Figure 91 – Comparison of Specific CH4 production during the final 240 hours when HRT reduced, shear rate varied and rest period fixed (6hrs)

6:3:2:4 Process Efficiency

The process efficiencies calculated in previous chapters for all mixing configurations proved to be of minimal value due to the coarse nature of the calculation so will not be considered further.

6:3:2:5 Biodegradation Efficiency

A far more useful comparison of the effects of HRT on CH_4 production of each mixing regime was made using biodegradation efficiency which significantly reduced when HRT was reduced (Table 45). The reduction occurred whichever method of estimating VS washout was used. However, results using method B indicate unrealistically low and even negative biodegradation efficiencies in the case of the digester mixed using a shear rate of $33s^{-1}$ rested for 6 hours which may have been due to a disruption of the steady state process when OLR increased.

Experiment	**HRT**	**Mixing Regime**	**Degradation η (Method A)**	**Degradation η (Method B)**
(#)	**(d)**	**SR(s^{-1})/Rest (hr)**	**(%)**	**(%)**
2	**30**	**Non-mixed**	52.1%	18.4%
		33 / 6	51.8%	23.5%
		55 / 6	52.3%	23.9%
		125 / 6	51.9%	24.1%
3	**10**	**Non-mixed**	19.7%	4.6%
		33 / 6	27.2%	-0.4%
		55 / 6	27.4%	6.3%
		125 / 6	30.1%	3.6%

Table 45 – Comparison of biodegradation process efficiencies for fixed rest mixing regimes when HRT was reduced (using methods A and B)

The impact of reducing HRT on CH_4 production is better portrayed in Figure 92. As method A used an assumed (previously published) CH_4 conversion factor, the reduced biodegradation efficiency highlighted in chapter 5 and portrayed using diamonds is obvious as a linear trend is produced. The reduction was probably caused by a combination of increasing acidogenesis (confirmed by the drop in pH observed in Figure 74) combined with a relatively slow methanogen response when OLR was increased which affected the steady state of the process. Kim et al. (2002) observed a similar response when intentionally overloading digesters. An increase in VS washout due to the reduction in HRT would have also effected the results.

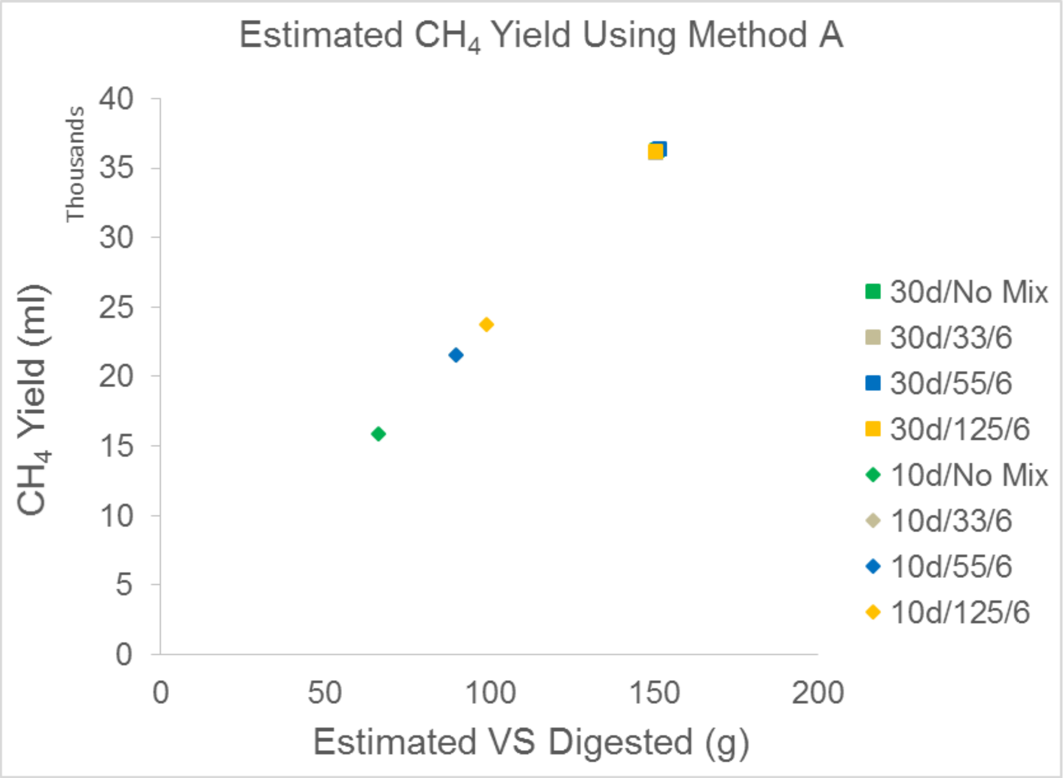


Figure 92 – Comparison of CH_4 yields of fixed rest mixing regimes when HRT was reduced (method A)

Results using method B are included for completeness (Figure 93) although biodegradation efficiency figures post HRT reduction using that method were unrealistic. RTD analysis may have helped clarify the issue.

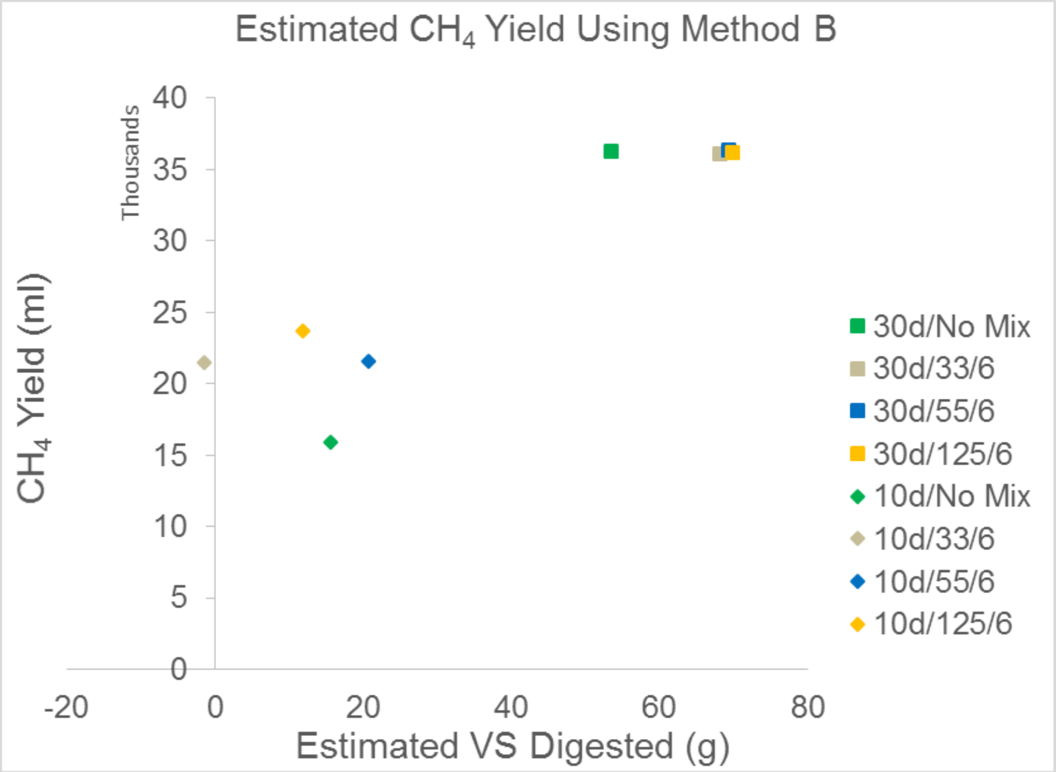


Figure 93 – Comparison of CH_4 yields of all mixing regimes when HRT is reduced (method B)

6:3:2:6 Digestate Quality

Changes in biodegradation process efficiency will affect the quantity and balance of undigested VS in the digestate and hence digestate rheology and effectiveness as a fertiliser. Rheological changes may be extensive and affect the handling characteristics of the digestate (particularly when spreading) which in turn could influence OPEX as outlined in chapter 2. Meanwhile, digestate quality will have a direct impact on the quantity of imported fertiliser that the digestate is intended to replace (The Soil Association, 2011). The reduction in biodegradation efficiency in response to changing the HRT will therefore influence the financial and environmental value of the digestate as well as CH_4 yield (Schnurer & Jarvis, 2010). Although this study did not include digestate analysis, changes in the quality and hence value of the digestate in response to manipulating HRT should be included when considering the financial viability of an AD system as a whole including the quality of the soil to which the digestate is applied (The Soil Association, 2011). Furthermore, the potential for carbon emissions to atmosphere from partially digested slurry spread on land will also increase.

6:3:2:7 Net Energy Output Based on Cumulative CH_4 Yield

YF and PF values gained using each HRT were compared (Table 46 and Table 47). Figure 88 presents the yield data in graphical form. The benefits of the shorter HRT in terms of CH_4 yield were substantial for all mixed digesters.

Net Energy Comparison: 30-day HRT										
Shear Rate (s-1)	**CH_4-derived (m3)**	**Equivalent (kWh)**	**Parasitic (kWh)**	**Net Power (kWh)**	**Parasitic (%)**	**PF**	**YF**	**YF (corrected)**	**PF*YF$_c$**	**Net Rating**
125	0.0098	0.0359	0.0032	0.033	8.81%	0.99	0.99	0.27	0.27	2
55	0.0098	0.0361	0.0037	0.032	10.19%	0.85	1.00	0.27	0.23	3
33	0.0098	0.0361	0.0031	0.033	8.66%	1.00	1.00	0.27	0.27	1

Table 46 – Energy output comparison during final 240 hours using a 30-day HRT when shear rate varied and fixed rest period (6hrs)

Net Energy Comparison: 10-day HRT										
Shear Rate (s-1)	**CH_4-derived (m3)**	**Equivalent (kWh)**	**Parasitic (kWh)**	**Net Power (kWh)**	**Parasitic (%)**	**PF**	**YF**	**YF (corrected)**	**PF*YF$_c$**	**Net Rating**
125	0.0172	0.0631	0.0032	0.060	5.01%	0.99	1.00	0.27	0.27	1
55	0.0155	0.0569	0.0037	0.053	6.48%	0.85	0.90	0.25	0.21	3
33	0.0154	0.0565	0.0031	0.053	5.53%	1.00	0.90	0.24	0.24	2

Table 47 – Energy output comparison during final 240 hours using a 10-day HRT when shear rate varied and fixed rest period (6hrs)

6:3:2:8 Parasitic Energy Demand

The mixing associated with each HRT used similar amounts of power to mix over a set period as HRT was defined by OLR with digester volume, mixing intensities and mixing times remaining constant (Table 46 and Table 47). Hence, comparing power used by different mixing regimes and HRTs could still be presented as a PF. However, the YF relationship were specific to an experiment so were irrelevant when comparing experiments using different HRTs. As the subsequent product of any PF and YF values would not be representative the analysis reverted to the kWh as the base unit of reference (Figure 94). Although this was a suitable means of comparing digester performance at lab-scale using digesters with similar volumes, the method would not be appropriate when commercially scaling up as a digester having an HRT of 10 days would be a third of the size of one retaining the substrate for 30 days when fed a constant mass of slurry each day. The smaller digester would therefore consume significantly less power than the larger digester to achieve the same degree of mixing as the volume/power relationship (specific to the mixing system used) is unlikely to be linear as digester volume increases (Doran, 2013). Therefore net energy gains achieved by reducing HRT/digester volume are likely to be greater when scaling up (para 1:5:10) than those demonstrated using this lab-scale experimental design. Such research was beyond the scope of this study but would be essential when modelling mixing systems as part of digester design. As indicated in Figure 94, the power used to mix using a shear rate of $55s^{-1}$ was 16 percent higher than that used by the other regimes.

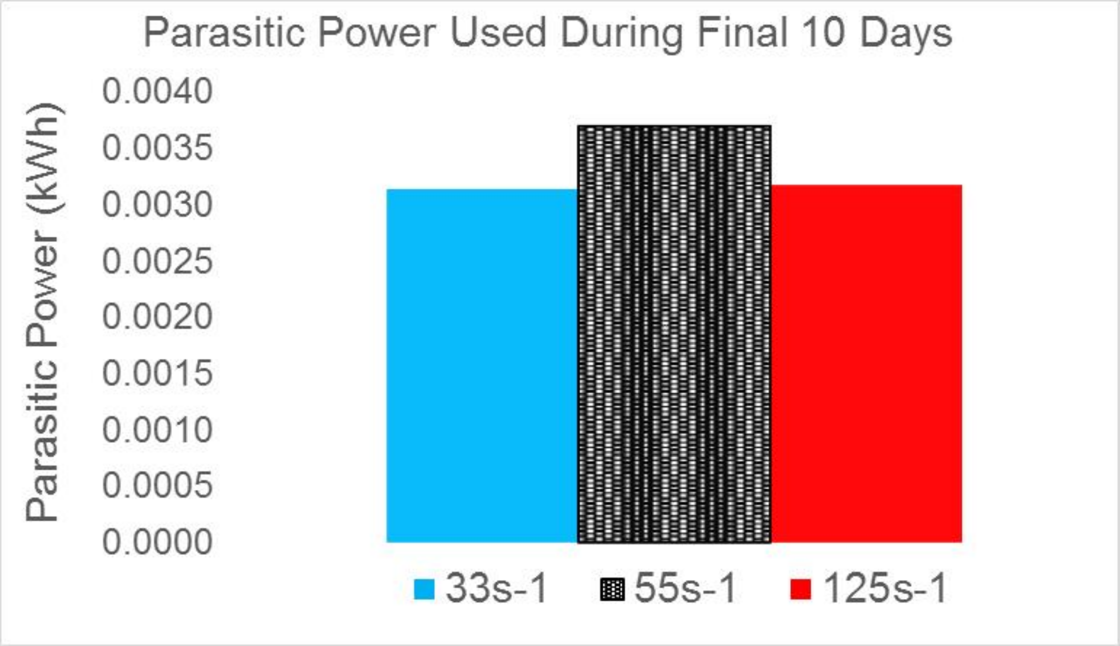


Figure 94 – Comparison of parasitic power used by each mixing regime during final 240 hours

6:3:2:9 CH_4 Yield

The CH_4 yield of each digester (in terms of kWh potential) was compared and the substantial gains associated with reducing HRT observed (Figure 95). CH_4 yields were similar using a 30-day HRT whereas mixing using a shear rate of 125s^{-1} produced higher yields when the HRT was 10 days.

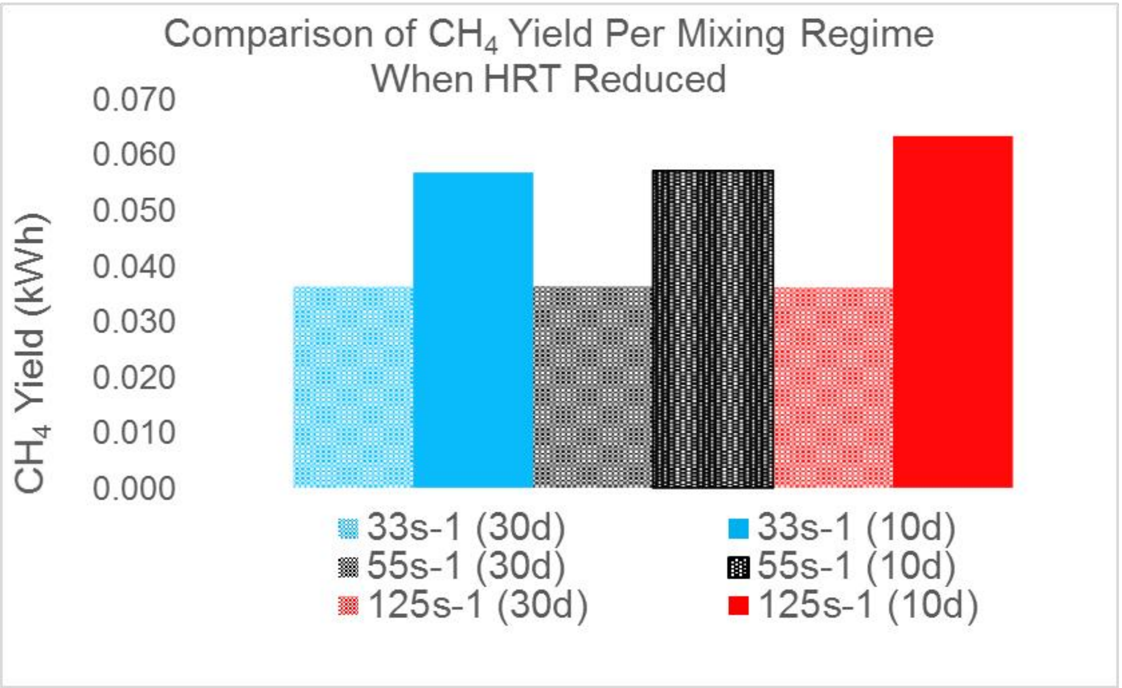


Figure 95 – Comparison of CH_4 yield for each mixing regime during the final 240 hours when HRT was reduced

6:3:2:10 Optimising the Process to Maximise Net Energy Production

Mixing using a shear rate of 125s^{-1} produced the highest net energy gain when all digesters were rested for 6 hours and an HRT of 10 days applied (Table 47) (Figure 96). Mixing using shear rates of 33 and 55s^{-1} produced similar net energy gains (13 percent lower than the best performer). Therefore, when optimising a digester to maximise net energy gain under such conditions a mixing shear rate of 125s^{-1} would be favourable. However, if using a 30-day HRT there was little difference in net energy production values (Table 46).

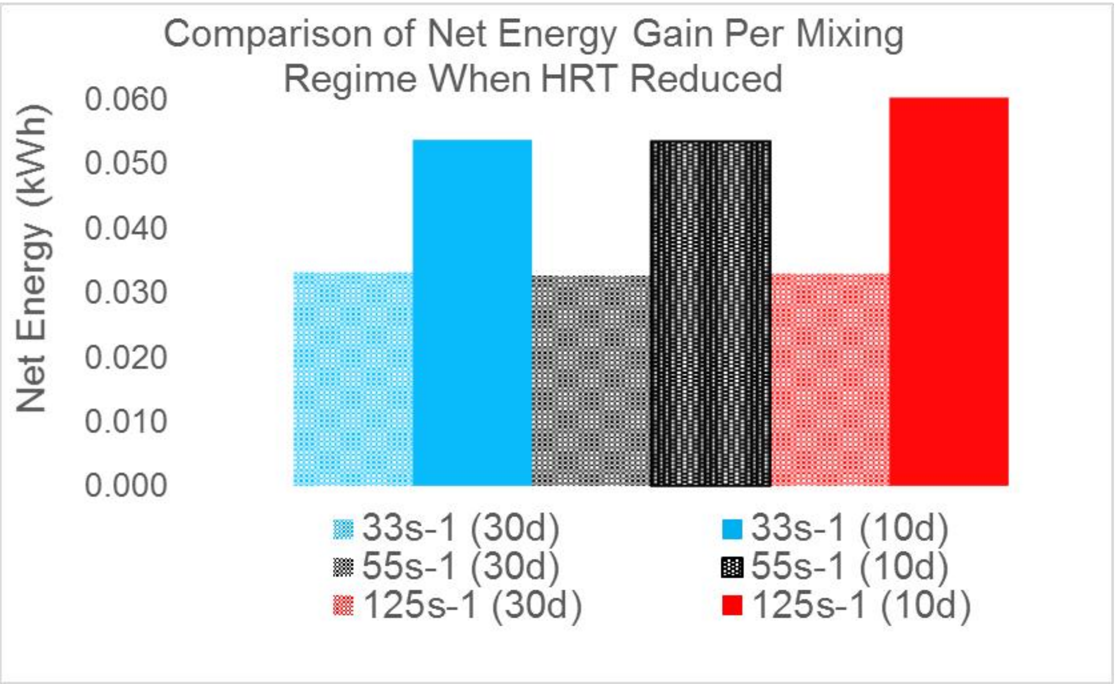


Figure 96 – Comparison of net energy production for each mixing regime during the final 240 hours when HRT was reduced

6:3:2:11 Optimising the Process to Maximise Specific CH_4 Production Rate

The difference in specific CH_4 production rate for all mixed regimes was significant when HRT was reduced (Figure 91). However, using the conditions and mixing system outlined a shear rate of $125s^{-1}$ rested for 6 hours produced the highest increase.

6:3:3 CH_4 Production When Shear Rate Fixed at $55s^{-1}$ when HRT was 30 days and $125s^{-1}$ when HRT was 10 days

6:3:3:1 Cumulative CH_4 Yield

Varying the rest period had minimal effect overall (less than 2 percent) on the CH_4 yields achieved by different mixing regimes within each HRT during the final 10 days of either experiment (Figure 97). Cumulative CH_4 yield trend lines generally ran in parallel within each HRT. However, the effect that reducing HRT had on cumulative CH_4 yield was substantial.

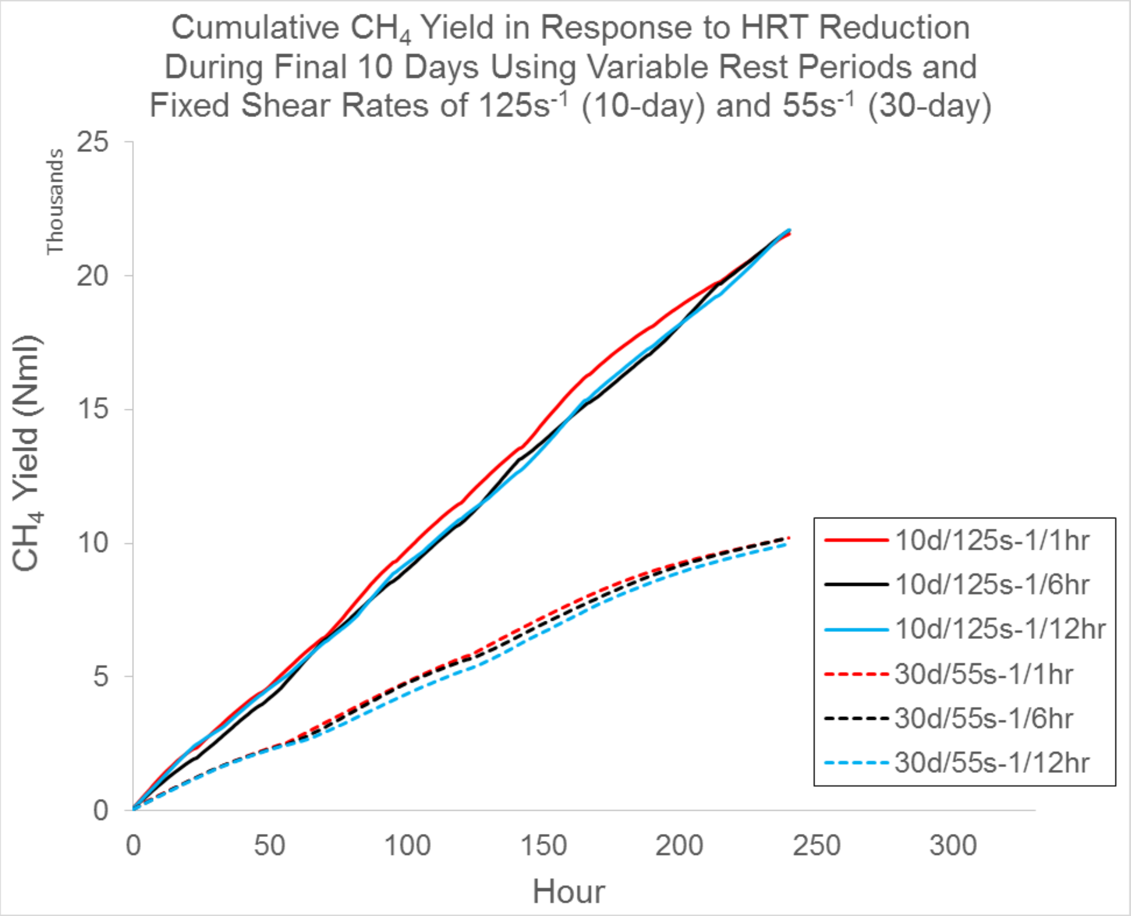


Figure 97 – CH_4 yield achieved during the final 240 hours when HRT was reduced, rest period varied and shear rate fixed at $55s^{-1}$ (30-day HRT) and $125s^{-1}$ (10-day HRT)

When HRT was reduced CH_4 yield increased by 112-117 percent (depending on the rest period adopted) (Table 48). However, the shear rate was fixed at $55s^{-1}$ when the HRT was 30 days and the rest period varied and $125s^{-1}$ when the HRT was 10 days and resting varied. Increasing shear rate to $125s^{-1}$ was observed to increase CH_4 yield when OLR was high but not when low (Figure 88). Hence, the probable cause of the increase was likely to be a combination of increasing OLR and shear rate. Furthermore, changes in the microbial density and biomass diversity as a result of microbial adaptation may also have been contributing factors as the inoculum used was stable digestate retained from the previous experiment.

Mixing Regime	**30-day HRT**			**10-day HRT**		
	Rest Period (hr)			**Rest Period (hr)**		
	1	**6**	**12**	**1**	**6**	**12**
Max Yield (Nml)	10,187	10,201	9,993	21,556	21,694	21,710
Δ between regimes (%)	1.94%	2.09%	0.00%	0.00%	0.64%	0.72%
Δ between HRTs (%)				111.61%	112.66%	117.26%

Table 48 – Differences in cumulative CH_4 yields achieved during the final 240 hours when using different HRTs, rest period varied and shear rates fixed at $55s^{-1}$ (30-day HRT) and $125s^{-1}$ (10-day HRT)

6:3:3:2 CH_4 Production Rate

Rest periods applied during the 30-day HRT (dotted lines) produced a steady undulating rate of CH_4 production that fluctuated around $40Nmlh^{-1}$ in response to the feeding cycle (Figure 98). CH_4 production rate more than doubled on numerous occasions when HRT was reduced and occasionally achieved over $90Nmlh^{-1}$. A plot of the differences achieved (as a percentage) when HRT was reduced is presented (Figure 99). Differences between the CH_4 production rates of mixing regimes using different rest periods were also much larger using a lower HRT and evident from the outset.

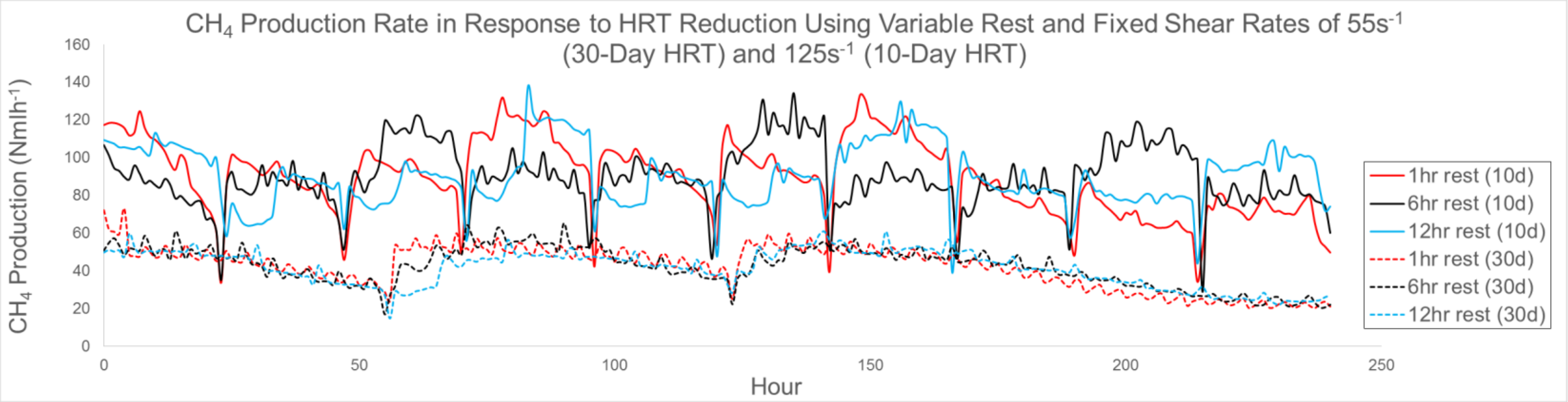


Figure 98 – CH$_4$ production rate during the final 240 hours when HRT reduced, rest period varied and shear rate fixed at 55s^{-1} (30-day HRT) and 125s^{-1} (10-day HRT)

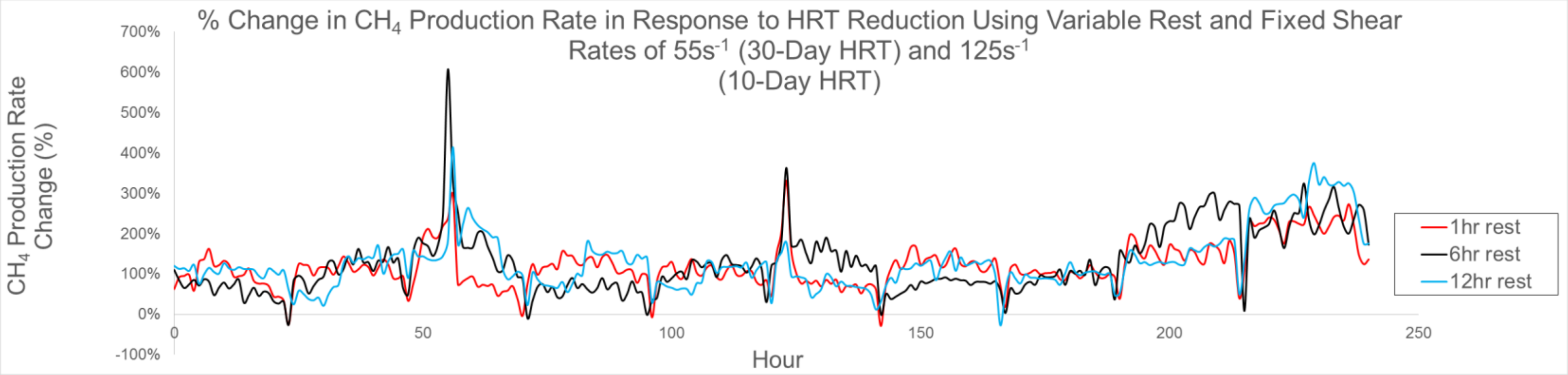


Figure 99 – Percentage variation in hourly CH$_4$ production rate during the final 240 hours when HRT reduced, rest period varied and shear rate fixed at 55s^{-1} (30-day HRT) and 125s^{-1} (10-day HRT)

6:3:3:3 Specific CH_4 Production Rate

The specific CH_4 production rate of all regimes increased significantly when HRT was reduced to 10 days (Figure 100). The median of the range of histogram values was $0.021Nml_{CH4}h^{-1}ml^{-1}_{substrate}$ for all mixing regimes subjected to a 30-day HRT. However, when HRT was reduced median values for regimes using 1, 6 and 12 hour rest periods approximately doubled to 0.040, 0.039 and $0.043Nml_{CH4}h^{-1}ml^{-1}_{substrate}$, respectively.

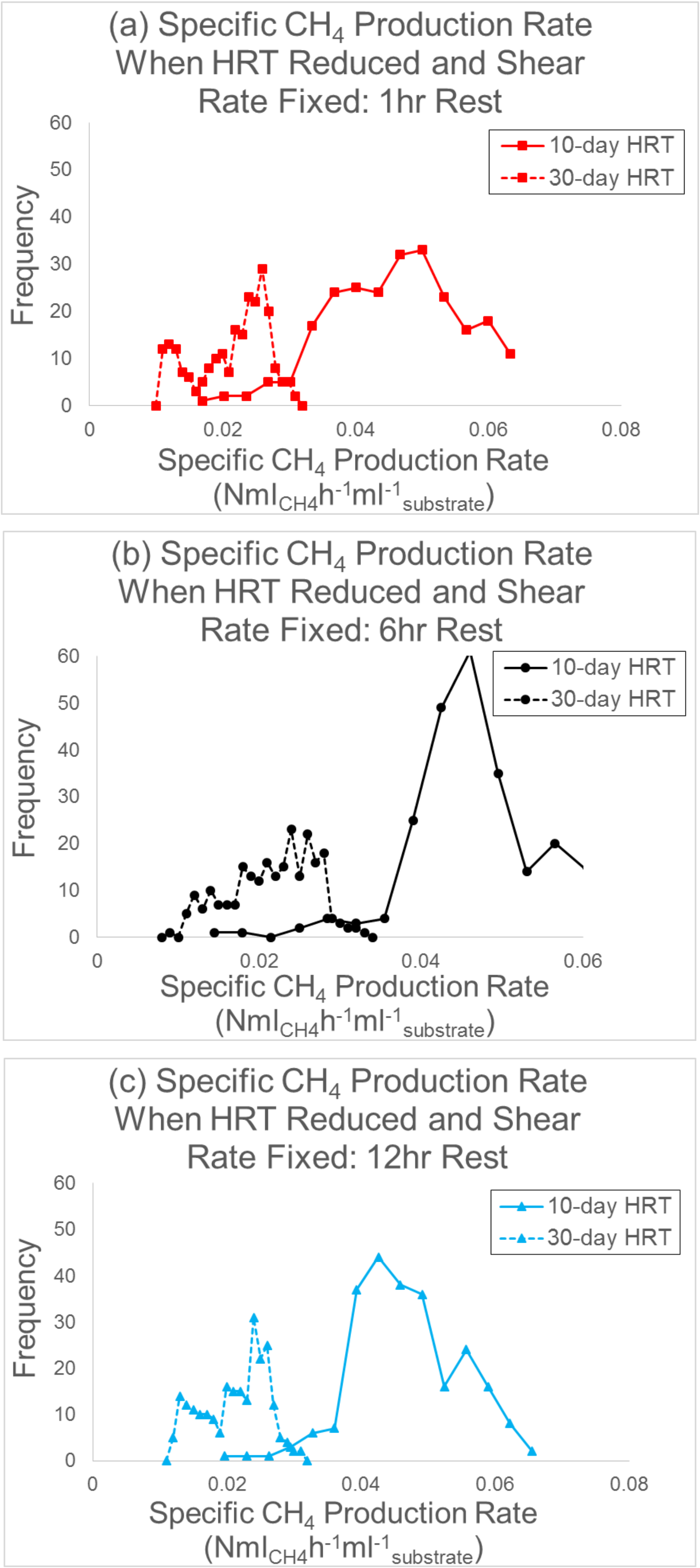


Figure 100 – Comparison of specific CH_4 production rate during final 240 hours when HRT reduced, rest period varied and shear rate fixed at 55s^{-1} (30-day HRT) and 125s^{-1} (10-day HRT)

6:3:3:4 Biodegradation Efficiency

Biodegradation efficiency reduced by approximately 15 percent (method A) and 20 percent (method B) when HRT was reduced (Table 49) despite a significant increase in CH_4 production. However, on this occasion pH measurements generally indicate a stable process (Figure 84) so the reduction was probably due to increase in VS washout that was evident using both estimation methods and likely due to the increase in OLR as a consequence of HRT reduction. This was confirmed by the CH_4 conversion rate increasing only slightly from 556 to $559ml_{CH4}g^{-1}_{VS}$ when HRT was reduced. Again, digestate quality and handling characteristics will be affected by any reduction in biodegradation efficiency and should therefore be considered in any financial modelling.

Experiment	**HRT**	**Mixing Regime**	**Degradation η (Method A)**	**Degradation η (Method B)**
(#)	**(d)**	**$SR(s^{-1})$/Rest (hr)**	**(%)**	**(%)**
1	**30**	**55 / 1**	49.4%	21.2%
		55 / 6	47.0%	21.2%
		55 / 12	46.1%	21.2%
4	**10**	**125 / 1**	41.4%	16.3%
		125 / 6	40.5%	18.2%
		125 / 12	40.3%	17.9%

Table 49 – Comparison of biodegradation process efficiencies for fixed shear rate mixing regimes when HRT was reduced (using methods A and B)

Figure 101 (method A) and Figure 102 (method B) represent biodegradation efficiency in terms of VS conversion to CH_4. The assumed (previously published) CH_4 conversion factor used in method A (portrayed using diamonds) is obvious with a linear trend evident.

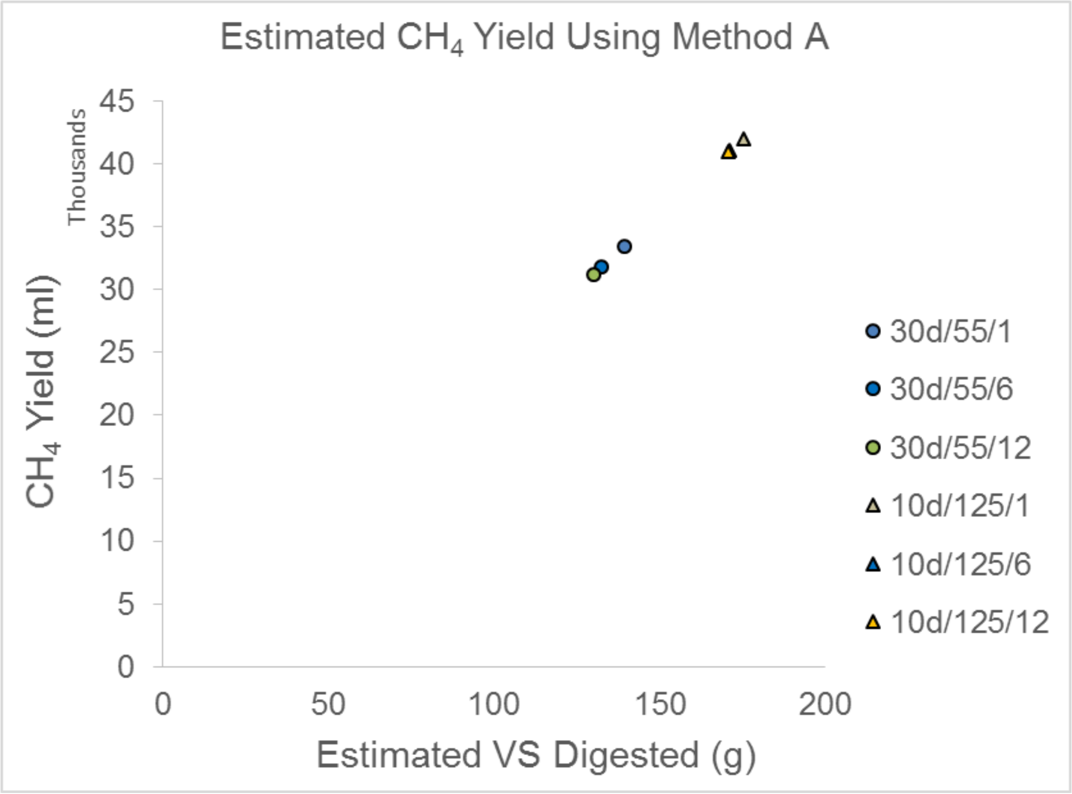


Figure 101 – Comparison of CH_4 yields of fixed rest mixing regimes when HRT was reduced (method A)

Alternatively, method B uses CH_4 conversion factors specific to this research which indicate a significant increase in CH_4 production when HRT was reduced. Again, RTD analysis would have improved the understanding of the process.

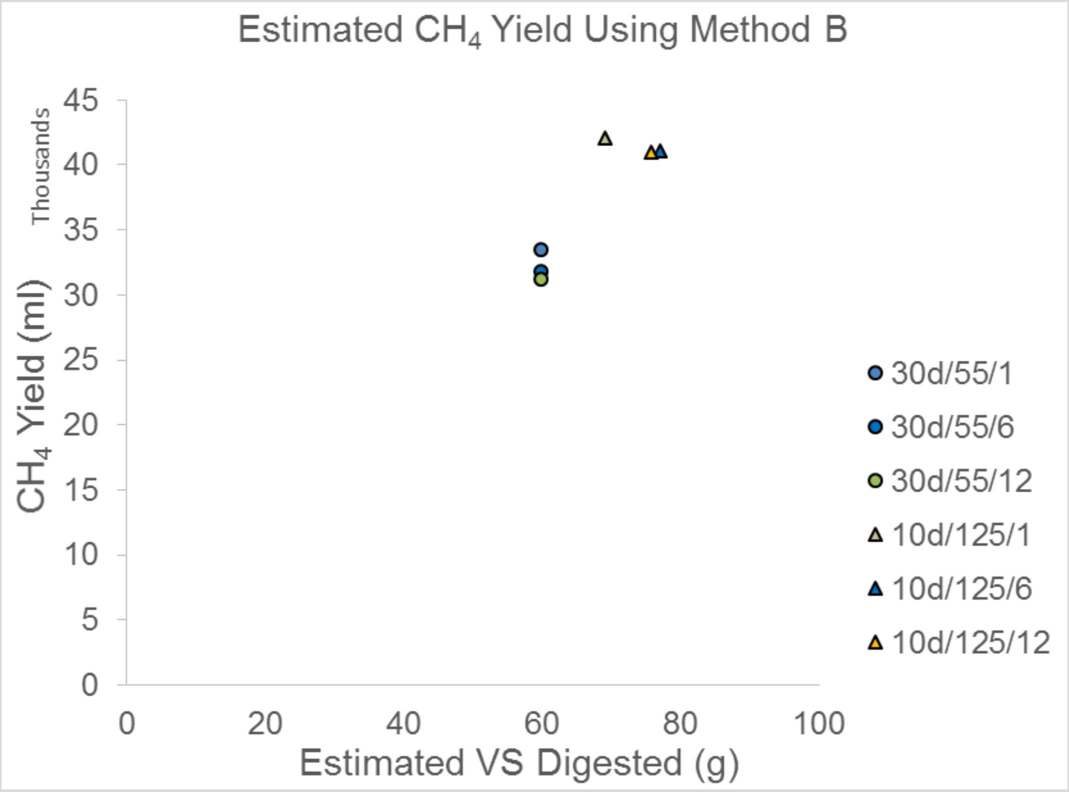


Figure 102 – Comparison of CH_4 yields of fixed shear rate mixing regimes when HRT is reduced (method B)

6:3:3:5 Net Energy Output Based on Cumulative CH_4 Yield

YF and PF values gained using each HRT were compared (Table 50 and Table 51). Figure 97 presents the yield data in graphical form. The benefits of the shorter HRT in terms of CH_4 yield were substantial for all mixed digesters.

Net Energy Comparison: 30-day HRT										
Rest Period (hr)	**CH$_4$-derived (m^3)**	**Equivalent (kWh)**	**Parasitic (kWh)**	**Net Power (kWh)**	**Parasitic (%)**	**PF**	**YF**	**YF (corrected)**	**PF*YFc**	**Net Rating**
1	0.0102	0.0374	0.0171	0.020	45.71%	0.11	1.00	0.27	0.03	3
6	0.0102	0.0374	0.0036	0.034	9.58%	0.53	1.00	0.27	0.14	2
12	0.0100	0.0367	0.0019	0.035	5.15%	1.00	0.98	0.27	0.27	1

Table 50 – Energy output comparison for the final 10 days of a 30-day HRT when rest period varied and fixed shear rate (55s^{-1})

Net Energy Comparison: 10-day HRT										
Rest Period (hr)	**CH$_4$-derived (m^3)**	**Equivalent (kWh)**	**Parasitic (kWh)**	**Net Power (kWh)**	**Parasitic (%)**	**PF**	**YF**	**YF (corrected)**	**PF*YFc**	**Net Rating**
1	0.0216	0.0791	0.0166	0.063	20.96%	0.09	0.99	0.27	0.03	3
6	0.0217	0.0796	0.0031	0.077	3.88%	0.50	1.00	0.27	0.14	2
12	0.0217	0.0797	0.0015	0.078	1.94%	1.00	1.00	0.27	0.27	1

Table 51 – Energy output comparison for the final 10 days of a 10-day HRT when rest period varied and fixed shear rate (125s^{-1})

6:3:3:6 Parasitic Energy Demand

Mixing times and the associated power required by each shear rate differed for the 240 hour period (Table 50 and Table 51). The digester rested for 1 hour used approximately 12 times the energy to mix as the digester rested for 12 hours (Figure 103). Again, these power relationships are specific to this lab-scale experiment and should not be used when scaling up (para 1:5:10).

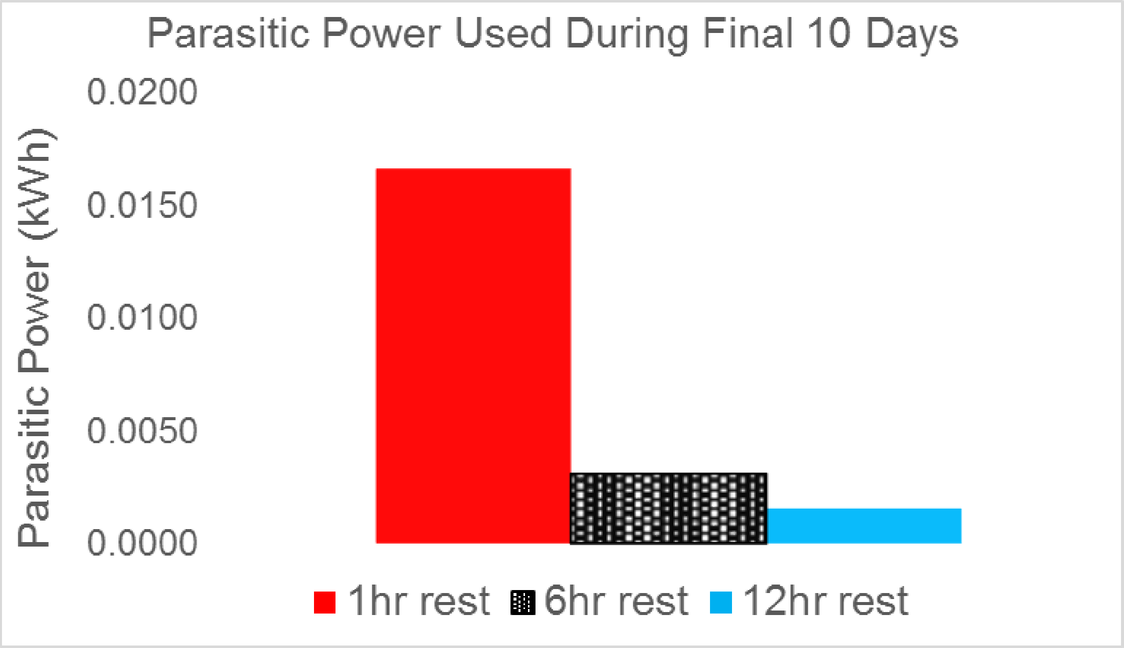


Figure 103 – Comparison of parasitic power used by each mixing regime

6:3:3:7 CH_4 Yield and Net Power Gain

As illustrated in Figure 104, comparing CH_4 yield indicated minimal differences between mixing regimes when the HRT was 30 days. CH_4 yield increased substantially when HRT was reduced but was again similar for all mixing regimes.

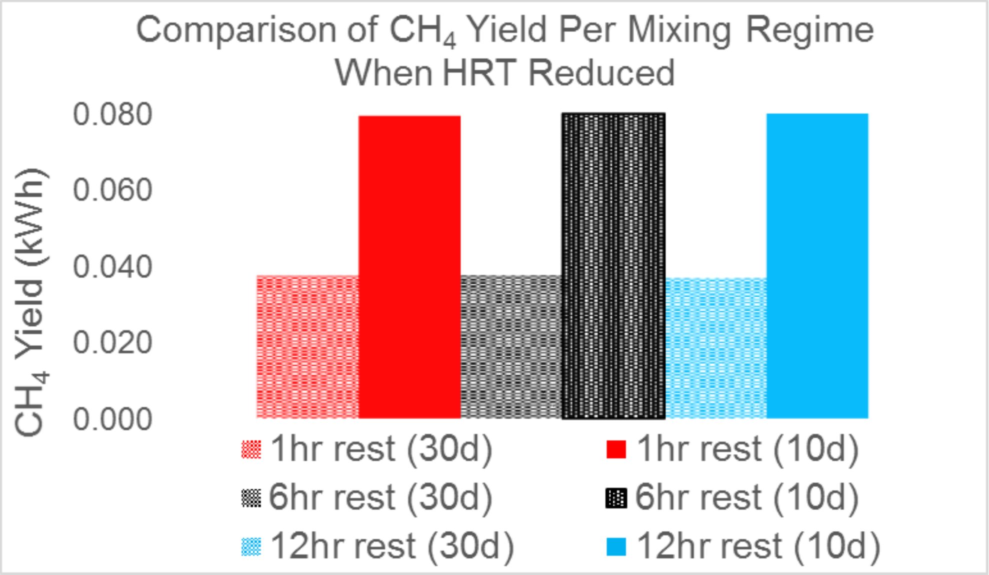


Figure 104 – Comparison of CH_4 yield for each mixing regime during the final 240 hours when HRT was reduced

6:3:3:8 Optimising process to Maximise Net Energy Production

Once again, the parasitic energy demanded by the mixing regimes was the most influencing factor when comparing net energy production. As CH_4 yields were similar within each HRT the higher energy consuming mixing regimes produced the lower net energy gains with mixing at $125s^{-1}$ being the worst performer (Figure 105).

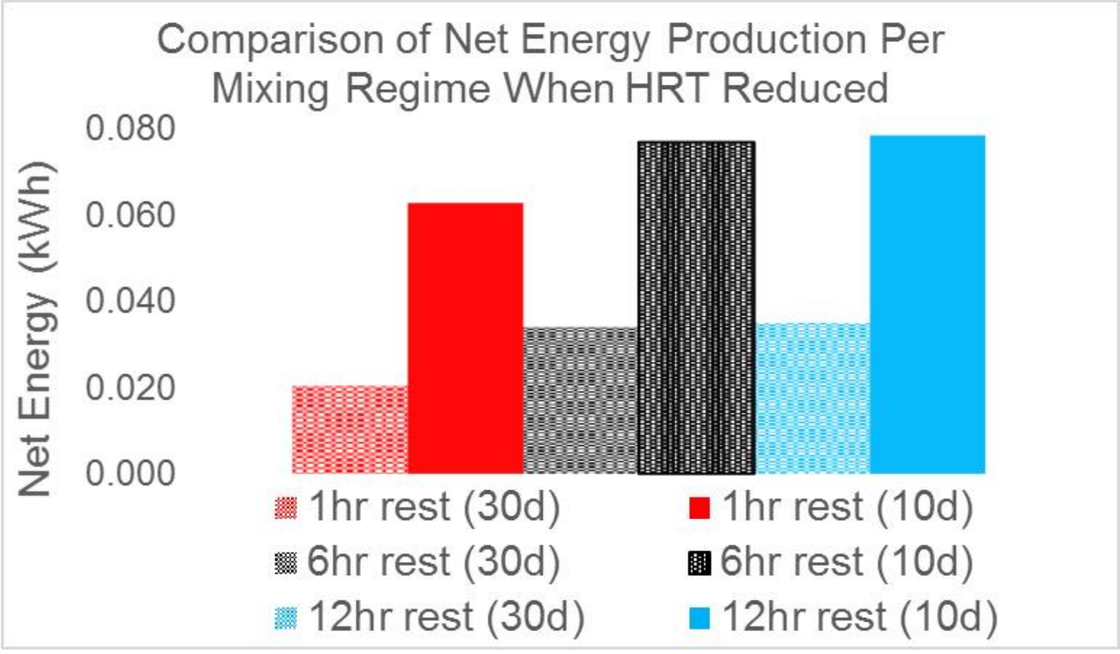


Figure 105 – Comparison of net energy production for each mixing regime during the final 240 hours when HRT was reduced

6:3:3:9 Optimising Process to Maximise Specific CH_4 production Rate

Specific CH_4 production rate increased significantly when HRT was reduced with no distinguishable difference observed between mixing regimes (Figure 100).

6:3:4 Comparison of All Mixing Regimes and HRTs

6:3:4:1 Cumulative CH_4 Yield

Only by comparing the results of all mixing regimes at each HRT can the impact of changing variables be fully appreciated (Figure 106). The results obtained without mixing have been omitted as the regime was not considered suitable for on-farm CSTR operations. Also, the profile '6hr/all/30d' captures all shear rates at that rest period and HRT as the differences in their CH_4 yields were minimal. The impact of reducing HRT from 30 to 10 days was significant with substantial increases in CH_4 production. The results of the different experiments produced 3 distinct data clusters with profiles reflecting CH_4 yields increasing as the experiments progressed. Data gathered using a 30-day HRT produced relatively similar values when compared to that produced when the HRT was reduced. However, more than one variable may have been responsible for the increase in CH_4 production.

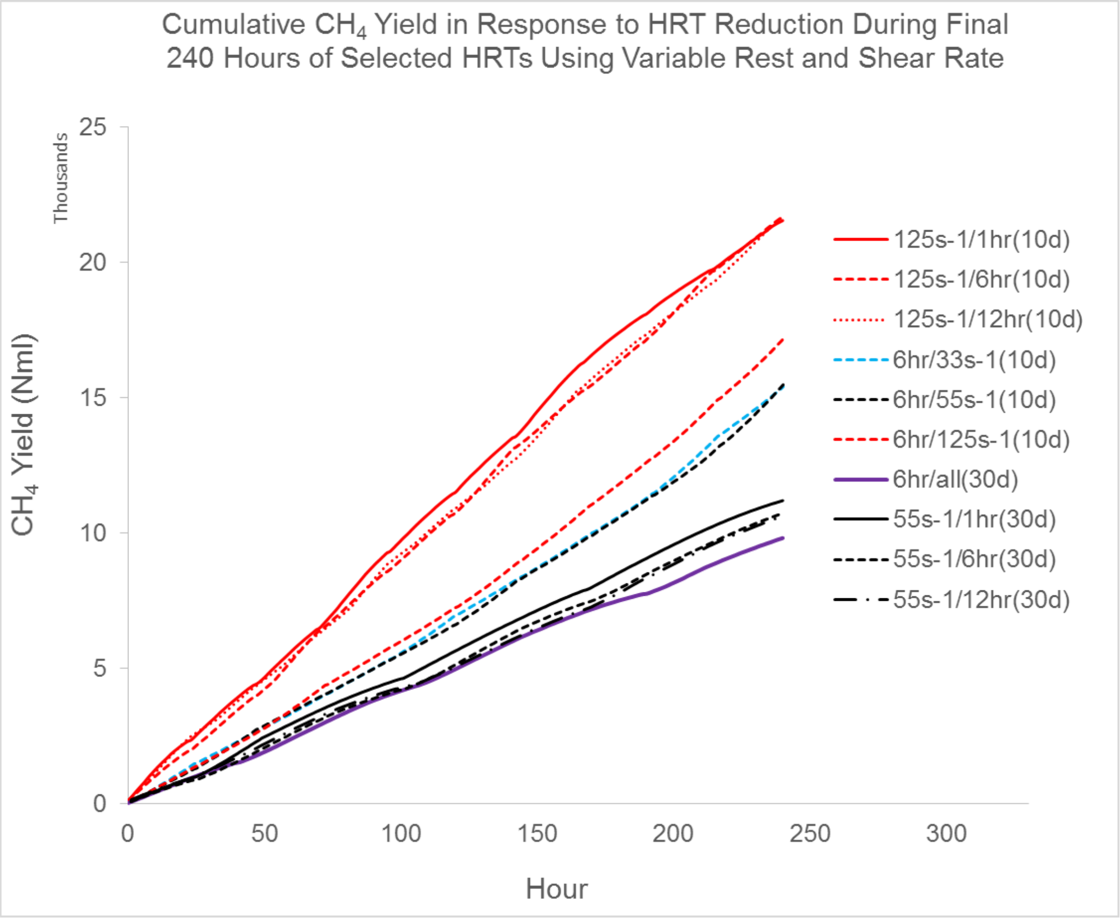


Figure 106 – CH_4 yield achieved during the final 240 hours of fed-batch experiments

6:3:4:2 Analysis of Variation (ANOVA) Within Experiments

The most significant impact that mixing regime had on CH_4 production was observed when the HRT was 10 days, the rest period fixed at 6 hours and the shear rate varied, producing an P-value of 0.36 (Table 52) indicating that the variation observed was likely to be significant rather than by chance. Varying rest period using an HRT of 30 days and fixing the shear rate at $55s^{-1}$ had the second greatest significance (P-value of 0.64). Varying shear rate when the rest period was fixed and the HRT was 30 days had a much smaller effect on CH_4 production, as did varying rest period with a fixed shear rate when the HRT was 10 days.

ANOVA Comparison			
Mixing Regime	**F**	**P-value**	**F-Crit**
30d HRT/Fixed SR (55s^{-1})/Variable Rest	0.46	0.64	3.35
30d HRT/Fixed Rest (6hr)/Variable SR	0.03	0.97	3.35
10d HRT/Fixed Rest (6hr)/Variable SR	1.05	0.36	3.35
10d HRT/Fixed SR (125s^{-1})/Variable Rest	0.01	0.99	3.35
All	46.40	7.62E-36	1.88

Table 52 – ANOVA comparison within and between results of experiments

6:3:4:3 Microbial Adaptation

The increase in CH_4 production was initially accredited to reducing HRT and the associated increase in OLR. However, in such circumstances mixing regimes common to 2 experiments subjected to similar HRTs should have produced similar results. The mixing regime using a 6 hour rest period and a shear rate of 125s^{-1} with a HRT of 10 days provides an excellent example (red dashed lines in Figure 106). Although the profiles from the 2 experiments follow similar trends the CH_4 produced by the latter (125s^{-1}/6hr/10d) produced 27 percent more CH_4 than the same mixing regime in the former (6hr/125s^{-1}/10d). A profile of hourly CH_4 production using the 6hr resting regime common to all experiments best illustrates the discrepancy (Figure 107). Note that the shear rates for the 30-day and 10-day retention times differ. Microbial adaptation during AD processes had been previously observed (McMahon et al., 2004; Clouzot et al., 2011; Lindmark et al., 2014).

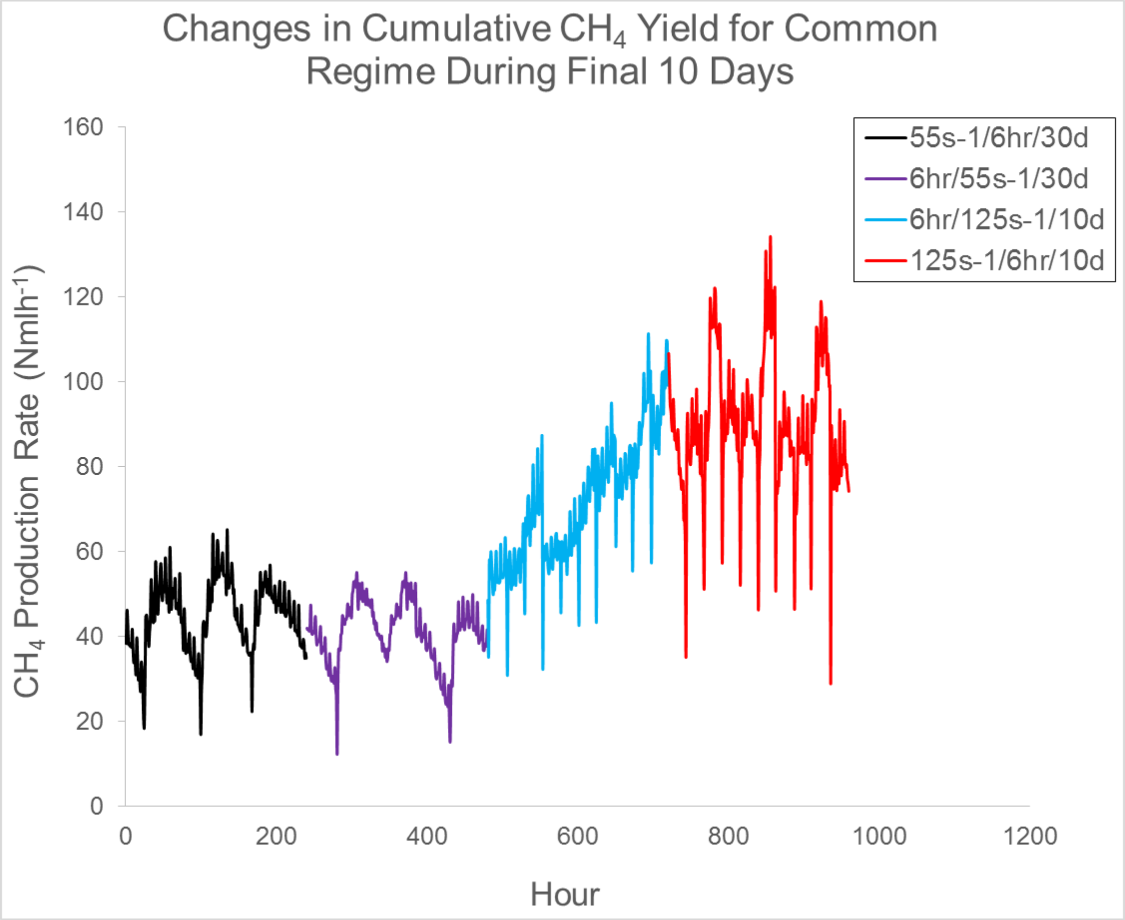


Figure 107 – CH_4 production rate achieved by a similar mixing regime but different HRTs

Hourly CH_4 production followed similar trends when the HRT was 30 days (black and purple) but gradually increased when HRT was reduced during experiment 3 (blue) before peaking and then reducing in experiment 4 (red). Similar mixer configurations and independent variable were used for the 10-day HRT experiments (blue and red profiles). However, the digestate of the first 10-day HRT experiment (blue) was used as the inoculum for the second (red). The technique was adopted to maintain process stability without the need for protracted acclimatisation periods and hence save valuable time when the length of period of granted access to the equipment was uncertain. However, digester acclimatisation and long term process stability may have improved microbial community diversity, population and kinetics within the substrate as the research progressed as also observed by Parawira et al. (2005) when processing potato waste at mesophilic temperatures. This adaptation of microbial communities over time will influence any statistical comparison.

An analysis of the variation between CH_4 yields of the digester configuration common to both 10-day HRT experiments (blue and red profiles in Figure 107) indicates that the differences of the means within the variation is likely to have significance rather than being by chance (P-value very low) thereby contradicting the null hypothesis that microbial adaptation did not occur (Table 53). As changes in microbial diversity and density were not measured throughout the research the extent of the influence they had on CH_4 production cannot be quantified. However, as microbial adaptation is likely to be the sole cause of the substantial increase in CH_4 yield the analysis is important and worthy of further research.

ANOVA Comparison			
10-day HRT	**F**	**P-value**	**F-Crit**
Common mixing regime: Rest (6hr)/SR (125s^{-1})	12.47	0.002	4.41

Table 53 – ANOVA comparison of CH_4 yield values of mixing regime common to both 10-day HRT experiments

6:4 Conclusions

The comparison of the performance of different mixing regimes when HRT was reduced from 30 to 10 days supports the following conclusions:

- Reducing HRT had a significant effect on CH_4 production rate and hence yield on all but the non-mixed digesters. This was likely due to the associated increase in OLR but may also have been due to changes in methanogen community kinetics as a direct result of long term process stability, microbial acclimatisation and methanogen adaptation. Reducing HRT would also reduce the digester volume required (CAPEX) and the energy used to mix (OPEX).
- Increasing shear rate to 125s^{-1} when OLR was high (10-day HRT) significantly increased methanogen activity and hence CH_4 production; shear rates of 33 and 55s^{-1} produced similar but lower results using a 10-day HRT. Conversely, increasing shear rate had minimal effect when the HRT was 30 days.

- Resting the substrate for 1 hour when shear rate was fixed resulted in a significant increase in methanogen activity and hence CH_4 production when either HRT was used. Meanwhile, digesters rested for 6 and 12 hours produced less but similar levels of CH_4 when a similar HRT was applied. However, process instability at the closing stages of the experiment using a 10-day HRT may indicate that the process is unsustainable using short rest periods when the OLR is high. This could prove costly in terms of CAPEX if a digester is sized incorrectly.
- An underlying cyclic variation in CH_4 production was observed with gas production gradually increasing during the length of most experiments.
- The method used to calculate basic process efficiency provided a very course indication of digester performance based on VS fed into the system. However, the application of the value calculated was limited as no distinction could be made between VS digested and VS washed out.
- Estimated biodegradation efficiency reduced in all digesters when HRT was reduced which coincided with increases in estimated VS washed out.
- A reduction in biodegradation efficiency will affect digestate quality (and therefore solids content and rheology as demonstrated in chapter 2).
- Net energy production was always more influenced by the parasitic energy demanded by each mixing regime than the CH_4 they produced. Hence, selecting a mixing regime should be a compromise between minimising OPEX (mixing energy) whilst producing acceptable CH_4 yield.
- Although microbial community diversity and density were not measured there were signs of microbial adaptation as the research progressed using the same substrate.

6:5 Next Research Step

The technical aspects of the research programme are now complete. The outcomes of all stages of the study will now be summarised and factors to be considered when designing a digester in support of dairy farm AD highlighted. Supplementary research required to progress this research theme will also be identified in the final chapter.

CHAPTER 7 – Synthesis of Research

7:1 Introduction

Designing and operating a cost-effective AD solution for dairy farm applications is challenging if slurry is the sole intended feedstock. Ideally, a technical solution should balance net energy production with installation and operational costs. Effective mixing is fundamental to AD process success but is also a major user of energy. Therefore, whatever the mixing technique adopted the mixing regime selected must be appropriate for the feedstock and be understood to be applied in the most cost-effective manner. However, cow slurry is a shear-thinning thixotropic 3-phase fluid so knowing the rheological response of the intended feedstock to mixing is fundamental to process success.

7:2 Rheometry

The AR2000 rheometer was adapted to accurately measure shear stress and apparent viscosity in representative dairy cow slurries. The equipment was calibrated (appendix 1) using guaranteed Newtonian calibration fluids having viscosities that captured the rheological extremes of cow slurries of 5-13%TS when subjected to a range of conditions common to dairy farm operations and the AD process. A 4-bladed rotor/cup geometry with an 8mm gap was selected to achieve accurate measurements without the need to pre-condition samples to the extent that they no longer represented their original state. Conversion coefficients were produced to calculate accurate rheological values. The rheological responses of different concentrations of CMC were also tested to identify solutions that could be substituted for cow slurry. This informed ERT modelling used to identify the length of mixing periods necessary to achieve 90 percent homogeneity when different shear rates were used.

Extensive rheological analysis (chapter 2) confirmed that dairy cow slurry demonstrates shear-thinning, thixotropic properties above 5%TS and follows the Herschel-Bulkley model of fluid flow. However, shear stress and apparent viscosity values were much higher than previously reported, possibly because pre-conditioning techniques applied to samples in past research were not practiced, so sample integrity was maintained prior to analysis. Solids content had the greatest effect on shear stress and apparent viscosity, followed by temperature, conditioning and finally shear rate. Shear stress and apparent viscosity increased exponentially as %TS increased whereas raising the temperature from 10-70˚C produced a linear reduction in both metrics. Conditioning (prolonged exposure to shear rate) caused a reduction in shear stress and apparent viscosity that recovered when the fluid was rested for 1 hour. The response of slurry to increasing shear rate was particular informative and influential when initially designing the experimental method that followed. Although shear stress increased linearly as shear rate increased, apparent viscosity initially reduced rapidly before the rate of decrease slowed substantially as shear rate increased through $20s^{-1}$ at which point the majority of shear thinning had taken place. Indeed, at shear rates above $20s^{-1}$ the fluids at all %TS adopted relatively near-Newtonian characteristics. This shear rate value is important, particularly if the intention is to intermittently mix a substrate as minimising the application of shear rate below $20s^{-1}$ could have a substantial influence on the parasitic energy required to mix. Moreover, stress experienced by microbial communities within the fluid, and by equipment components such as mixers and pumps, could be substantially reduced if mixing below that shear rate was minimised. Interestingly, changes in shear rate-induced stress above $20s^{-1}$ were minimal between mesophilic and thermophilic operating temperatures. Also, increasing shear rate was the only variable that produced opposing outcomes with shear stress increasing whilst apparent viscosity decreased. This could be particularly relevant if prioritising between achieving substrate homogeneity/heat distribution in a digester and attempting to minimise microbial shear stress. Measures that could be adopted to alleviate the issue include substrate dilution to reduce %TS, pre-heating of the substrate to reduce viscosity and avoiding long periods of dormancy to reduce opportunities for thixotropic recovery of the fluid. Extremes of shear stress and apparent viscosities were identified within the calibrated range of the equipment. Consistency coefficients (K) and behavioural index (n) values were also produced to allow results to be compared with other research. The benefits of these research outcomes to industry could be substantial if used to inform digester design, operational procedures and slurry management generally. Academic application of the results could also prove valuable to improve the understanding of microbial community response to shear stress and hence process stability and biogas production.

7:3 Batch Process Analysis

This improved rheological understanding of cow slurry was used to select a range of mixing intensities and intermittent mixing regimes described in chapter 3. An AMPTS II Bio-processor was adapted to monitor a batch AD process to compare different mixing regimes in terms of CH_4 yield and CH_4 production rate. Concurrent monitoring of the parasitic energy demanded of each regime was also carried out. When a fixed charge of feedstock was processed over 21 days CH_4 production was directly influenced by mixing intensity, the number of mixing events that occurred and the length of period during which the substrate was rested. Of the digesters that were mixed, a shear rate of $125s^{-1}$ tended to produce more CH_4 than digesters mixed using shear rates of 33 and $55s^{-1}$. Mixing periods varied as they were directly related to shear rate and had to ensure 90 percent homogeneity was achieved before mixing stopped. Resting for 1 hour tended to produce more CH_4 than resting for 3, 6 or 12 hours. The non-mixed and continuously-mixed digesters also performed well; however, mixing can be regarded as essential to dairy farm AD as the digester needs to be intermittently fed (and hence mixed) to distribute new feedstock and heat around the digester. Hence, the non-mixed regime was included for reference only. Conversely, continuous mixing was very energy intensive with relatively minimal gains in CH_4 produced so was not regarded as economically viable. Of the intermittently mixed digesters, lower shear rates rested for long periods used less energy to mix resulting in higher overall net energy production making them more economic. Indeed, parasitic energy demand had far more influence on net energy production than CH_4 yield. Overall, the digester mixed every 12 hours using a shear rate of $55s^{-1}$ produced the highest net energy yield. The operational significance of parasitic energy demand to net energy output is important to industry and will increase substantially compared to digester volume when scaling up. The rate of CH_4 production changed over the experimental period with approximately 80 percent of CH_4 being produced in the first ten days, an outcome that informed HRT selection in later experiments.

7:4 Fed-Batch Process Analysis

The outcomes of the rheological and batch AD analysis were now applied to a fed-batch process (chapter 4) that better suited the slurry management requirements of farm operations. A HRT of 30 days was initially selected to reflect the theoretical time required for cow slurry to completely biodegrade. Using a relatively low OLR, varying shear rate had a minimal effect on CH_4 production whereas the effect of resting was significant with short rest intervals (1 hour) producing the most CH_4. There was no significant difference in the CH_4 production rates achieved by the different mixing regimes throughout the experiment although specific CH_4 production rate was highest when feeding and mixing coincided. Again, the reduction in parasitic energy associated with longer rest periods outweighed any gains in CH_4 production resulting in digesters rested for 6 and 12 hours producing the highest net energy gains. All processes remained stable throughout.

HRT was then reduced to 10 days (chapter 5) to reflect the period in the biodegradation cycle of a single charge of feedstock when CH_4 production rate was highest as identified in the batch fed analysis. Changes in overall CH_4 yield and specific CH_4 production rates were investigated to inform any future modelling to reduce CAPEX by using smaller digesters. Reducing HRT significantly increased the CH_4 yields of all mixed regimes as OLR increased in response to HRT reduction. However, unlike the 30-day experiment, increasing shear rate to $125s^{-1}$ when HRT was 10 days caused a substantial increase in CH_4 production. This indicates that the importance of mixing intensity increases as OLR increases. Reducing the resting period also increased CH_4 production which was a similar response to that observed using the higher HRT. Parasitic energy was once again the major influence when net energy production was calculated resulting in mixing regimes that used longer rest periods realising higher net energy gains. Indeed, rest management could inform operational practice to improve net energy gain and hence revenue. The difference in CH_4 yields realised by individual mixing regimes within the 10-day HRT was also greater than that achieved when HRT was 30 days. Furthermore, an underlying 4-day fluctuating CH_4 production rate cycle was evident in all mixed digesters which was not observed using the 30-day HRT; the reason for this was never identified.

Specific CH_4 production rates were again higher when feeding and mixing coincided. Although substantial increases in CH_4 production were realised when HRT was reduced to 10 days there were indications of digester instability as CH_4 yields of mixing regimes using higher shear rates became erratic and the pH of their embedded substrates began to fall. This may have been due to the high OLR and a subsequent increase in VFAs over a prolonged period. Although the manipulation of HRT will primarily have operational implications by potentially providing an opportunity to reduce CAPEX and OPEX, changing HRT could also inform academic aims to improve understanding of microbial diversity and resilience within a biodegradation process. The changes in digestate quality in response to reducing HRT also has climate change consequences as the potential for carbon emissions from digestate spread on land will increase if the VS content is higher.

Reducing HRT had a significant effect on all mixing regimes as explained in chapter 5, with most CH_4 gains being realised by those digesters mixed using the higher shear rate and using a shorter rest period. Basic process efficiency proved to be limited as a comparison tool as VS washed out was not accounted for so any application of the metric should be used with caution. To address this shortfall alternative methods were adopted to estimate VS washed out so biodegradation efficiency could be estimated. Method A used published IPCC estimates of CH_4 potential per gram of representative cow slurry to estimate the apportionment of the likely pathways that VS might take within the process and hence VS washout. However, this method could not provide actual slurry/CH_4 conversion data for this research so a steady state process and substrate homogeneity when digestate was removed was assumed (method B). A CH_4 conversion factor of approximately double the IPCC reference figure was estimated. Although biodegradation efficiencies using the 2 methods varied, a reduction in response to reducing HRT was common and coincided with an increase in estimated VS washed out. However, method B did provide illogical results when HRT was first reduced probably because the steady state process on which the calculation relied was disrupted by the increase in OLR associated with the reduction in HRT. This was because the experiments ran from one into the other using the same substrate meaning that the microbial communities had little time to adapt to the increase in OLR. Results differed when resting was varied and shear rate fixed as the experiments using different HRTs were the first and last to take place with approximately 60 days (the other 2 experiments) between them. Again, the substrate was common to both. When compared (chapter 6), the biodegradation efficiency associated with the reduction in HRT reduced by 4-7 percent depending on method used which may have been due to an improvement in the microbial community through adaptation as VS washout was again estimated to have increased by approximately 20 percent. Of course, any increase in VS washed out will affect the rheology, quality and value of the digestate and the substrate left in the digester. Microbial adaptation was evident when the CH_4 yields of a mixing regime common to 2 experiments using a 10-day HRT ran from one experiment into the other. Only one mixing regime was common to both experiments ($125s^{-1}$ rested for 6hrs) but a substantial increase in CH_4 production was observed with no change in any variables. Hence, a change in the microbial community was accredited with causing the increase through adaptation. Unfortunately, the microbial diversity and densities within the substrate could not be measured to confirm the hypothesis.

7:5 Application of Research Outcomes

This research was intended to inform the design and operational procedures of AD systems used on dairy farms when slurry is the sole feedstock. Therefore, any suggested application of the outcomes will be biased to support decision making in that sector. However, the research will also be useful to the wider AD community whether involved in research, design, manufacturing or plant operations. The following outcomes are summarised for consideration:

- Shear stress and apparent viscosity values were higher than previous research suggested which should inform digester design, equipment selection and operating procedures.
- Operating %TS was the most influential factor when managing the shear stress induced within a substrate and the subsequent change in apparent viscosity. Hence substrate dilution using water, or the removal of solids through separation, may be beneficial when designing and operating a system.

- Heating feedstock/substrate prior to mixing or pumping may reduce the parasitic energy demanded of those practices and also the mechanical stress experienced by microbial communities and engineering components.
- Intermittent mixing at short intervals can minimise opportunities for settling and thixotropic recovery of the substrate thereby avoiding a return to high levels of apparent viscosity.
- Mixing should be applied to induce a shear rate of at least $20s^{-1}$ across the digester contents (if possible) to overcome high levels of apparent viscosity and achieve near-Newtonian fluid characteristics.
- Differences in shear stress induced in substrate at mesophilic and thermophilic temperatures were minimal.
- Highest rates of CH_4 production were achieved in the first 10 days of the substrate being introduced to the AD process which may support shorter retention times.
- High intensity intermittent mixing using short rest periods produced highest CH_4 yields on most occasions.
- Parasitic energy demand was the most influential factor when calculating net energy production and will increase in importance when scaling up.
- In the intermittently fed process, specific CH_4 production was highest when mixing and feeding coincided.
- Process stability was maintained in all digesters when the HRT was 30 days using a relatively low OLR.
- CH_4 production significantly increased in all mixed digesters when HRT was reduced (OLR increased).
- The difference between the CH_4 production rates within each mixing regime was greater using an HRT of 10 days than when an HRT of 30 days was applied.
- Mixing intensity had a greater effect on CH_4 production when OLR was high.
- VS washout was estimated to increase when HRT was reduced which reduced the CH_4 production potential of the feedstock introduced to the system and the rheology and quality of the digestate removed.

- An HRT of 10 days may be too low for processing cow slurry at mesophilic temperatures as the high OLR may cause process instability during prolonged operations.
- There was evidence of significant microbial adaptation to their environment and OLR over time.

7:6 Suggested Improvements to Research Method Used

Although several substantive research outcomes where achieved a review of the methods and procedures used suggest the following changes could have improved the value of the data captured:

- A means of reducing the opportunities for evaporation of water from CMC solutions over a 12 hour period should be identified to allow the solution's thixotropic characteristics to be better modelled.
- The AMPTS II Bio-processor should be located within a fume cabinet so that gas lines and motors do not have to be disconnected when feeding takes place.
- The CH_4 content and total volume of the gaseous products of all digesters should be measured to accurately calculate and compare changes in biogas quality and quantity in response to different mixing regimes.
- Volatile solids content of digestate removed at each feed should be measured to quantify the amount and variation of VS washed out as intermittently fed experiments progress so that process and biodegradation efficiencies can be accurately calculated.
- FOS/TAC analysis should be used to complement CH_4 production and pH measurement to confirm and quantify the level of process instability, should the condition be suspected.
- RTD techniques should be applied to better understand the transit of nutrients through the system, particularly the effects of HRT reduction on VS washout.
- A similar baseline inoculum should be used at the start of each experiment if attempting to isolate the effects of HRT on methanogen activity and hence CH_4 production.

- Microbial diversity and density should be measured periodically to quantify the proportion of CH_4 increase that can be specifically accredited to microbial adaptation.

7:7 Suggested Further Research

To gain more knowledge of how mixing can improve the financial viability of dairy farm AD and to answer questions raised by this study the following additional research is suggested:

- All experimental work using digesters should be repeated to improve the efficacy of the study. Actual CH_4 produced and total biogas volume should be measured to provide a more accurate indication of the effects of mixing regime on biogas quality and quantity.
- Modelling of CH_4 production from low nutrient feedstock such as partially digested cow slurry using different mixing regimes to identify the most economic mixing regime for digestate. This would identify opportunities to reduce OPEX.
- A study to identify the cause of the underlying sinusoidal CH_4 production rate cycle when the HRT was 10 days but which was not apparent when the HRT was 30 days. This may inform our understanding of the effects of shear and chemical stress on microbial communities.
- Some experiments had to be terminated whilst the CH_4 production rate was still increasing. The potential of those mixing regimes should be researched further using extended experiments of 3 x HRT to quantify the maximum CH_4 production rates achievable without inhibiting the process to inform operation practices.
- The full range of AD experiments should be repeated using larger scale proof of concept digesters (at least $1m^3$) and a mixing technique appropriate for farm AD operations to give an improved understanding and appreciation of the potential of net energy production when scaling up.
- Initiate specific energy modelling whenever the digester volume or the mixing technique changes to ensure that net energy gain calculations are

relevant and scale up implications in terms of mixing energy are understood.

- A microbial analysis of AD biomass to identify microbial diversity and adaptation characteristics of microbial communities over time when subjected to different mixing regimes and HRTs. This would inform process optimisation through mixing regime.
- RTD studies to better understand the effects of reducing HRT on VS retention, washout and short-circuiting when the daily OLR of a dairy farm is fixed.
- Investigate interim HRT periods to identify the most economically viable HRT for each mixing regime when processing cow slurry.
- Investigate the potential of improving the financial model of a dairy farm AD system by augmenting cow slurry with grass silage.

APPENDIX 1 – ADAPTING THE AR2000 RHEOMETER

1:1 Introduction

1:1:1 Overview

The rheological challenges associated with measuring cow slurry are generally caused by sample inconsistency, complexity and volume. The latter was particularly relevant to this analysis as samples had to represent substrates encountered in daily slurry handling operations on dairy farms. The wide range of variables to which samples were to be subjected suggested a controlled stress/controlled rate rheometer would be most appropriate so the TA Instruments AR2000 rheometer was selected.

1:1:2 Limitations of Controlled Stress/Rate Rheometer Geometries

The AR2000 offers a wide range of geometry options and guidance on their application (TA Instruments, 1996a) with the following limitations:

- Cone and plate (horizontal) configurations consist of a rotating cone above a static plate to provide an accurate means of analysing small samples and is generally used for single phase homogenous fluids with sub-micron particles. Cow slurry is 3-phase with relatively large accumulations of solid matter that require large sample volumes so the geometry was not considered suitable.
- Parallel plates are similar in design and size to the cone and plate but rely on 2 identical circular discs/plates as used by Baroutian et al. (2013) when analysing sewage sludge. But the maximum gap between the plates should be no more than 10 times greater than the largest particle size to ensure acceptable levels of accuracy (TA Instruments, 1996a).

Hence, parallel plate geometries were not considered appropriate for measuring cow slurry.

- Concentric cylinders (also known as bob and cup) consist of a cylinder/drum rotating within a fixed cup that holds the fluid to be measured as used by Achkari-Begdouri & Goodrich (1992) to analyse Moroccan dairy cattle manure. This arrangement is generally used for less viscous fluids that would be difficult to retain in the previous geometries. Interestingly, the gap between the cylinder and serrated cup used in that study was only 1.2mm with no mention of pre-shearing of samples prior to analysis. Again, accuracy is defined by the gap between the cylinder and cup wall so the geometry was regarded as unsuitable for cow slurry with suspended particulates that can be the same size or larger than the gap (Bongenaar et al., 1973). Indeed, the application of a technique with such a physical limitation would likely mechanically break down the particulates and flocs that influence the fluids rheology.
- Rotor and cup configurations are similar to concentric cylinders but with a bladed rotor or vane replacing the inner bob to provide increased interaction with the fluid. This reduces the relevance of the size of the gap between the rotor blade tip and the cup wall. Such an arrangement was used by Markis et al. (2014) when investigating the effects of the rheological properties of primary and secondary waste water treatment sludge on the AD process. As is quite common in that industry, samples were extensively pre-sheared prior to analysis.

1:1:3 Aims

The aims of this appendix are to:

- Identify a suitable AR2000 rheometer geometry that could accommodate and analyse appropriately sized samples of cow slurries between 5 and 13%TS without changing the characteristics of the sample.
- Compare a short list of geometry configurations to identify the most accurate for the task.
- Calibrate the rheometer and geometry to provide conversion coefficients to accurately carry out the rheological analysis in chapter 2.

- Identify a suitable transparent substitution fluid to replace cow slurry in experiments requiring techniques not conducive with cow slurry.

1:2 Materials and Method

1:2:1 The Rheometer

An AR2000 Rheometer, manufactured by TA Instruments and supported by Rheology Advantage software, is a controlled stress/controlled rate rheometer capable of supporting a wide range of sample types using a broad selection of geometries (TA Instruments, 1996a). Under normal circumstances, automatic temperature control of the common geometries provided is achieved by housing the components (and sample) in an enclosed chamber. Temperature is normally controlled automatically across a range of shear rate profiles; a pre-shear facility is also available. However, if a concentric cylinder or rotor/cup geometry is used, the relatively large arrangement requires an external water jacket in which the geometry of choice is housed. All profiles are computer-controlled with parametric measurements available as graphical or text outputs and hence easily exportable to other software applications (TA Instruments, 1996a).

After extensive consultation with TA Instruments a vertical axis rotating 4 bladed Rushton rotor solution was suggested to encourage high interaction with the substrate sample contained in a temperature-controlled cup. However, the rotor/cup arrangement that was identified was not provided as standard equipment and had not been tested using such complex substrates. A selection of rotors and cups were provided with an electrically-heated/water-cooled chamber in which the cup could be seated. No guarantees of accuracy were provided as the attachments had not been calibrated for such an undertaking; indeed, the Company declared an interest in the outcome of such research and so agreed to loan the equipment in return for access to the subsequent calibration data. Heating using the system’s heating control facility was possible, but could not be controlled automatically as the attachment geometry would not accommodate the system’s in-built Nitrogen cooling facility.

1:2:2 Using a Substitution Fluid

Substituting a transparent fluid with characteristics similar to cow slurry may support visual analysis techniques such as the use of coloured tracers and time lapse photography. Substrate contamination can also by observed visually. If the fluid content is primarily water, the fluid may also support techniques such as electrical resistance tomography (ERT) which may not work in cow slurry. Sodium Carboxymethyl Cellulose (CMC) is a recognised polymer substitute for non-Newtonian shear-thinning fluids (Cavadas & Pinho, 2001; Wu & Chen, 2007). Eshtiaghi et al. (2012) identified CMC (Sigma Aldrich M_w 700,000) as following power law model characteristics at shear rates above $10s^{-1}$ but questioned the ability of the polymer to replicate yield stresses associated with Herschel-Bulkley fluids. However, in that work CMC concentration was below 1.5 percent (w:w) so the viscosity values may not be representative of the high %TS cow slurries analysed in this study. CMC is simple to store and prepare, safe to handle and odourless. Furthermore, useful experimental life can be prolonged by adding a biocide to stop biological growth contaminating the fluid (Cavadas & Pinho, 2001). The CMC analysis carried out in this study was designed to support visual and ERT trials to inform the experimental design in later chapters.

1:3 Results and Discussion

1:3:1 Overview

The identification of a robust analytical method for use in subsequent rheological analysis adopted an evolutionary approach to identify appropriate rheometry techniques that would provide accurate measurements.

1:3:2 Rheometer Feasibility Testing

Prior to extensive viscosity calibration, a range of rotor/cup geometry options were tested to confirm their ability to accommodate suitably sized samples of cow slurry in the 90ml cup provided, without restricting the rotor’s freedom of movement. Geometries ranged in terms of mass and shape so the rheometer was calibrated to account for the geometry in use. Key specification and calibration values are listed at Table 54.

Geometry	Heated Jacket	Small Cup	Large Cup	Small Rotor	Large Rotor
TA Instruments Item Name	AR Series smart-swap concentric cylinder peltier jacket (with plumbing adaptor)	HA grooved concentric cylinder cup with removable steel base	HA aluminium large diameter concentric cylinder cup with removable steel base	AR-G2 smart-swap wide gap vane rotor (with heat break)	AR-AG smart-swap vane rotor
Part Number	533201.901	545610.901	545615.901	546027.901	546027.901
Composition	Aluminium	Aluminium with stainless steel base	Aluminium with stainless steel base	Stainless steel	Stainless steel
Diameter	-	30mm/34mm (4mm groove)	44mm	15mm	28mm
Length/depth	-	80mm	60mm	38mm	42mm
Number of Blades	-	-	-	4	4
Blade Offset	-	-	-	90˚	90˚
Instrument Inertia	-	-	-	15.61	15.61
Geometry Inertia	-	-	-	1.667	3.002
Total System Inertia	-	-	-	17.27	18.61
Remarks		Reduces sample slip at cup wall	Approximately 90ml capacity		

Table 54 – Geometry specification and inertia values

The following configurations were considered:

- Small rotor and large smooth cup (SRLC) with a 14.5mm gap
- Small rotor and small serrated cup (SRSC) with a 7.5mm gap
- Large rotor and large smooth cup (LRLC) with a 8mm gap
- Large rotor and small serrated cup (LRSC) with a 1mm gap

1:3:3 Choice of Variables and Associated Values

Key independent variables to be measured and evaluated to ensure the rheometer was fit for purpose were:

- Shear stress and apparent viscosity values from previous literature (Table 55) to capture the equivalent expected when analysing 5-13%TS.
- Temperatures of 20-80°C as required by the calibration fluids used.
- Shear rate of 0-250s^{-1}.
- Resting periods ranging from 1-12 hours during feasibility testing of CMC.

Author	Pre-shear	%TS	Shear Rate	Temp	Shear Stress	Apparent Viscosity
	Y/N	(%)	(s^{-1})	(˚C)	(Pa)	(Pas)
El-Mashad et al. (2005)	Y	9.1-10.7	87.5-238	30-60	15-140	0.30-0.97
Wu 2012, Wu (2013)	N (CFD)	2.5-15.0	3-702	35	-	0.006-2.93
Achkari-Begdouri & Goodrich (1992)	N	2.5-12.1	3-702	20-60	<1-40	0.01-0.16
Mbaye et al. (2014)	Y	5.16-6.09	<1-450	37	-	0.03-2.00

Table 55 – Key process variables used (and measured) by previous authors when analysing cow slurry

1:3:4 Temperature Control

After some experimentation, manual temperature control was achieved using the rheometer electrical heating system augmented by a manual cooling arrangement consisting of a syringe, hoses and a chilled water reservoir. This arrangement supported a procedure with a static temperature profile that could be heated to the required temperature by the system and maintained within +-0.1°C using manual chilled water circulation. The tendency for samples to overheat due to internal heat generation by the equipment and in some cases ambient room temperature was thereby addressed even when the laboratory temperature climbed as high as 27˚C and the sample needed to be retained at 10˚C. Testing started at 10˚C and all the necessary analysis was carried out at that temperature before any increase was initiated. A stepped increase from low to high temperatures proved more manageable and made best use of the time available. After charging the cup and descending the often relatively cold rotor into the sample the required temperature and shear rate test profile was programmed into the system. Once the sample achieved the target temperature a selected shear rate profile would begin. On successful completion of all profiles at that temperature, the apparatus was then raised to the next temperature and the procedure repeated.

1:3:5 Rheometry

The substrate/equipment viability trials carried out prior to the formal analysis were thorough and resulted in minimal refinement of experimental procedure being necessary once the analysis task was underway.

1:3:6 Equipment Calibration and Geometry Selection

The 1mm gap associated with the large rotor/small serrated cup was regarded as too small to accommodate slurry as damage could occur if debris, such as grit, became trapped between the rotor and the serrated cup wall so this configuration was discarded. Measurements gained using the remaining geometries and a guaranteed Newtonian calibration fluid were compared to identify the most suitable geometry. Suitability depended on the trend line of a profile produced by the rheometer correlating with that of the calibration fluid and the resultant R^2 value, rather than providing the nearest values to that gained.

The remaining rotor/cup geometries were tested using various shear rate profiles, up to and including 250s^{-1} and at specific calibration temperatures designated by the manufacturer (Table 56). A calibration fluid (TA Instruments S600) was initially selected to capture viscosity values quoted in previous research (Achkari-Begdouri & Goodrich, 1992). A comparison of the fluid viscosity range and the values to be captured is presented at Figure 108. Measurements achieved using the S600 fluid followed expected viscosity profiles although values differed between geometries as outlined in Figure 109.

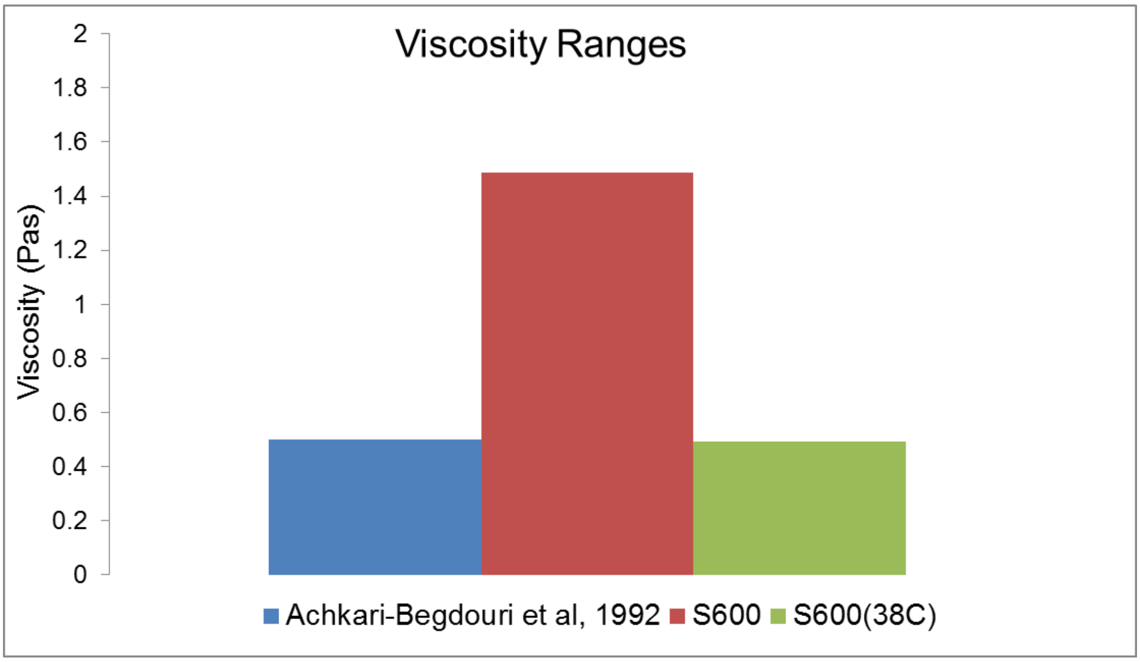


Figure 108 – Comparison of the S600 calibration fluid and previous research values

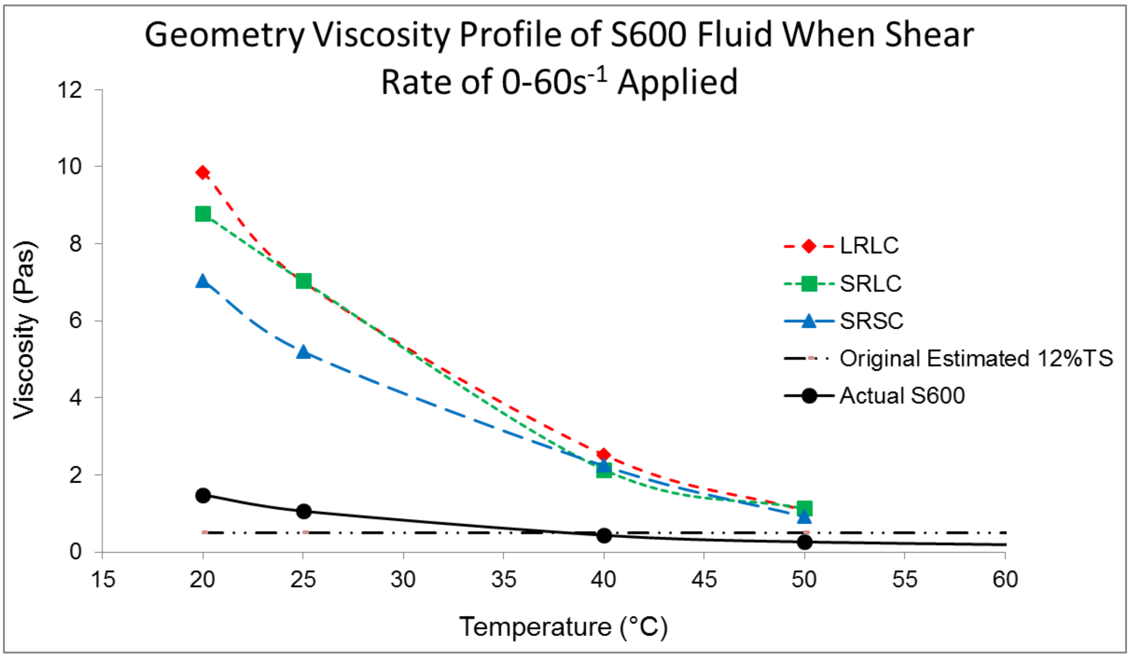


Figure 109 – Comparison of viscosity profiles of different geometries using the S600 calibration fluid

At first, the S600 fluid provided reasonable correlation (values) at temperatures between 20˚C and 50˚C. However, the standard error associated with shear stress and viscosity measurements when a shear rate greater than 60s^{-1} was applied was consistently higher (circa 10 percent) than considered acceptable. After experimenting, shear rate profiles were limited to 0-60s^{-1}, which reduced the standard error to less than 5 percent. To minimise opportunities for thixotropy, shear rate was increased within this range at 10s^{-1} increments every 10 seconds and viscosity measured, meaning a shear rate profile would take 60 seconds to complete. This was adopted as the standard shear rate profile (SSRP). By reducing the opportunity for thixotropy within a shear rate profile rheological measurements were strictly controlled to reflect the fluid in a particular rheological condition, important information when attempting to mix efficiently (Eshtiaghi et al., 2013). Experiments were then designed to provide the conditions likely to be experienced by a fluid at various stages throughout the AD process. Similar R^2 correlation values of 0.997 were achieved using LRLC and SRSC geometries. The SRLC arrangement gave an R^2 value of 0.996.

However, when slurry was introduced and the correction factor applied, calculated apparent viscosity values were much higher than those observed in previous research (Achkari-Begdouri & Goodrich, 1992; El-Mashad et al., 2005). This may have been due to the way samples in previous research were handled or pre-treated prior to measuring. Also, the equipment used may have imposed limitations that influenced the accuracy of the measurements. Accordingly, a more viscous calibration fluid (Rheotek N4000) was sourced to capture the range of viscosity values that were likely to represent the farm slurry being used. Table 56 provides a comparison of the calibration fluid properties and Figure 110 a visual comparison of viscosity values achieved using both fluids.

Calibration Fluids:	**Temp**	**(°C)**	**20**	**25**	**38**	**40**	**50**	**80**
TA Instruments S600	**Viscosity**	**(Pas)**	1.49	1.06	0.49	-	0.26	0.08
Rheotek N4000	**Viscosity**	**(Pas)**	17.35	10.83	-	3.06	1.47	-

Table 56 – Details of S600 and N4000 calibration fluids

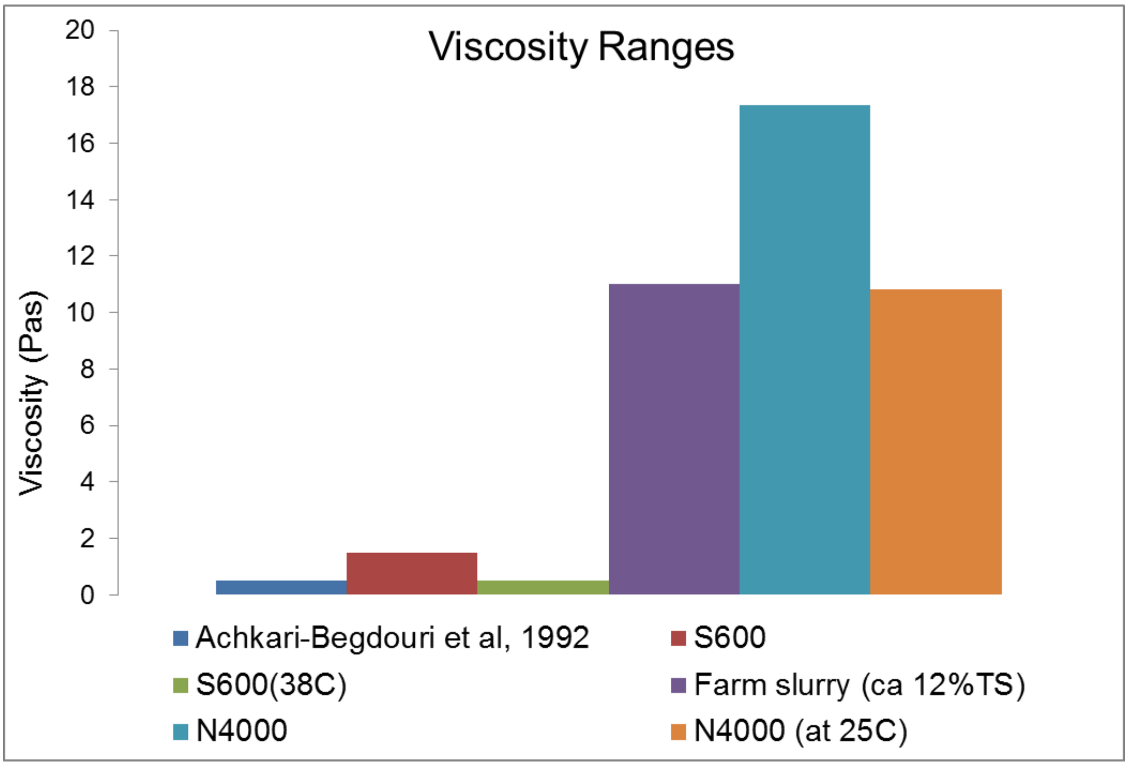


Figure 110 – Comparison of viscosity values of calibration fluids

The correlation procedure for the S600 fluid was repeated using N4000 fluid (Figure 111). The standard error associated with shear stress and viscosity measurements at fluid temperatures between 20 and 60˚C were again consistently high when a shear rate greater than 60s^{-1} was applied. Indeed, as rotational velocities increased, a vortex was seen to form around the rotor which affected shear stress readings. Hence, there was a limiting shear rate associated with the rotor/cup configuration above which readings would be unrepresentative. So, once again shear rate profiles were limited to 0-60s^{-1}, reducing the standard error to less than 5 percent. Profiles achieved using the geometries followed a similar trend to that guaranteed by the fluid although the values were lower.

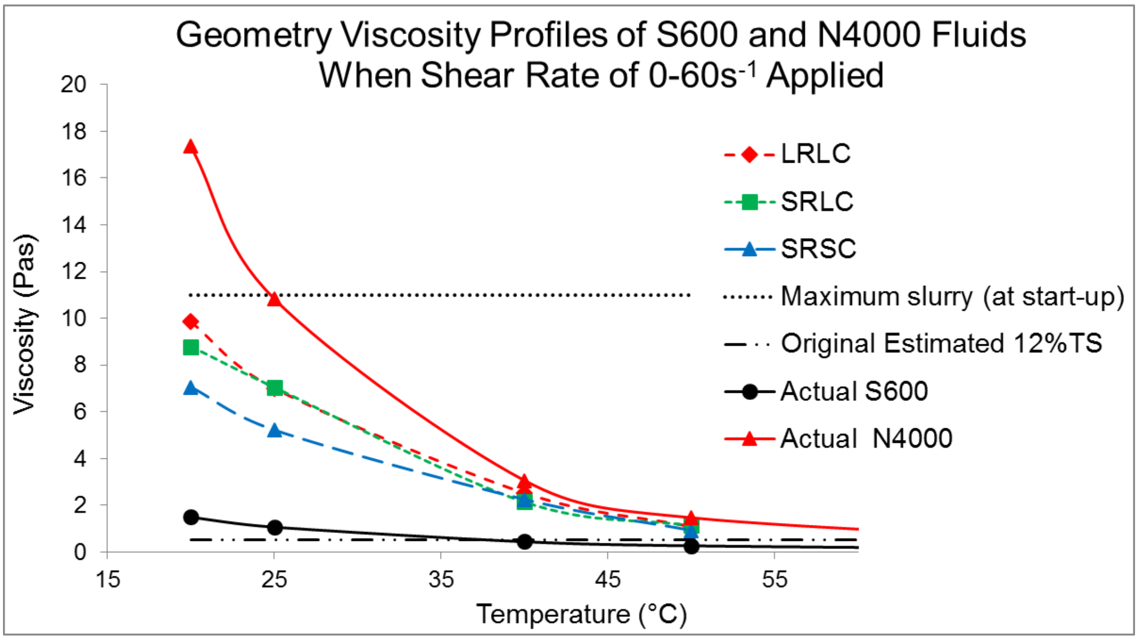


Figure 111 – Comparison of viscosity profiles of different geometries using the S600 and N4000 calibration fluids

Detailed calibration profiling between at 20, 25, 40, 50 and 80˚C produced a distinct viscosity correlation profile when measured and actual viscosity values were compared (Figure 112). The LRLC configuration produced a single second order polynomial relationship that captured all viscosity values within a R^2 correlation value of 0.9993:

$$\text{Actual viscosity value} = 0.1384x^2 + 0.7483x + 0.3014 \qquad \text{Equation 12}$$

where x is the measured rheometer value. This was closely followed by the SRSC ($R^2 = 0.9992$) and the SRLC ($R^2 = 0.9918$). As a result, the LRLC was adopted as the geometry of choice for the remainder of the research. However, the minor difference in R_2 values achieved using the LRLC and SRSC geometries indicated that increasing the gap by using a smaller rotor had a minimal effect on measurements. This suggests that the research could inform the design of an in-line rheometer.

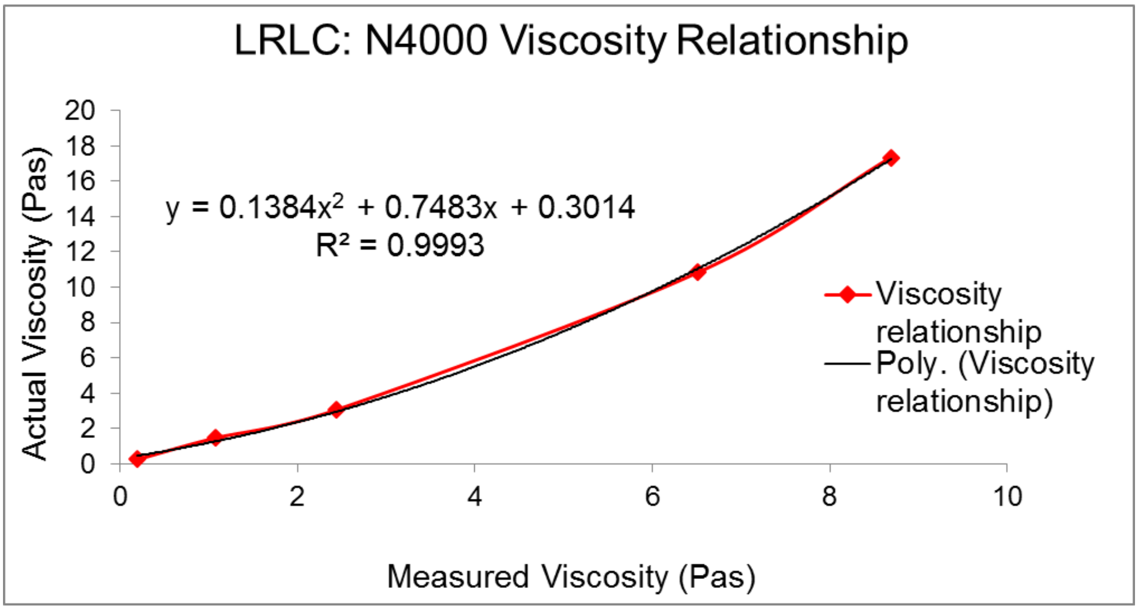


Figure 112 – Viscosity correlation at different temperatures using N4000 calibration fluid and a LRLC configuration

When actual and measured shear stress values where compared calibration profiling produced 5 distinct linear shear stress correlations exhibiting high R^2 values (Figure 113). However, the similarity of the correlation profiles of the higher temperatures allowed the same linear correction formula to be used for all 3, leaving the lower temperatures to be determined by a different formula:

Actual shear stress at 20˚C = 2.0547x – 3.3059 Equation 13
($R^2 = 0.9996$)

Actual shear stress at 25˚C = 1.7005x – 0.4749 Equation 14
($R^2 = 0.9998$)

Actual shear stress at 40/50/80˚C = 1.2573x + 1.4886 Equation 15
($R^2 = 0.9999$)

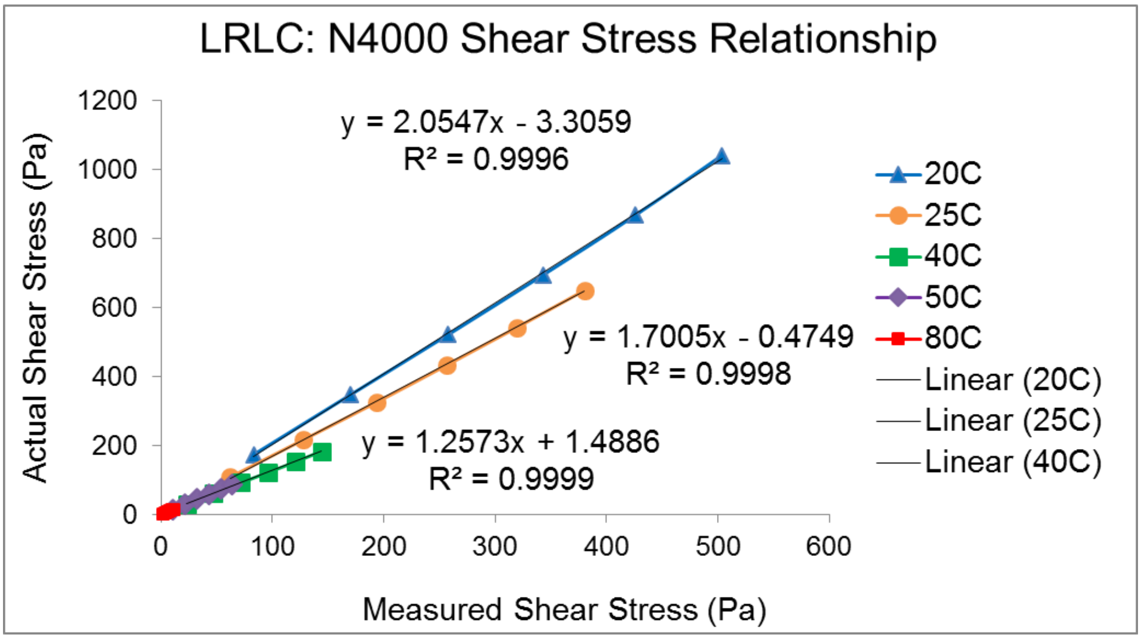


Figure 113 – Shear stress correlation at different temperatures using Rheotek N4000 calibration fluid and a LRLC configuration

Although the viscosity range of the N4000 fluid better reflected actual slurry values, as the experiments progressed viscosity values of high %TS samples at low temperatures were observed outside the guaranteed accuracy range of the fluid. This limitation was noted and accepted.

1:3:7 Independent Validation of Rheometer Values

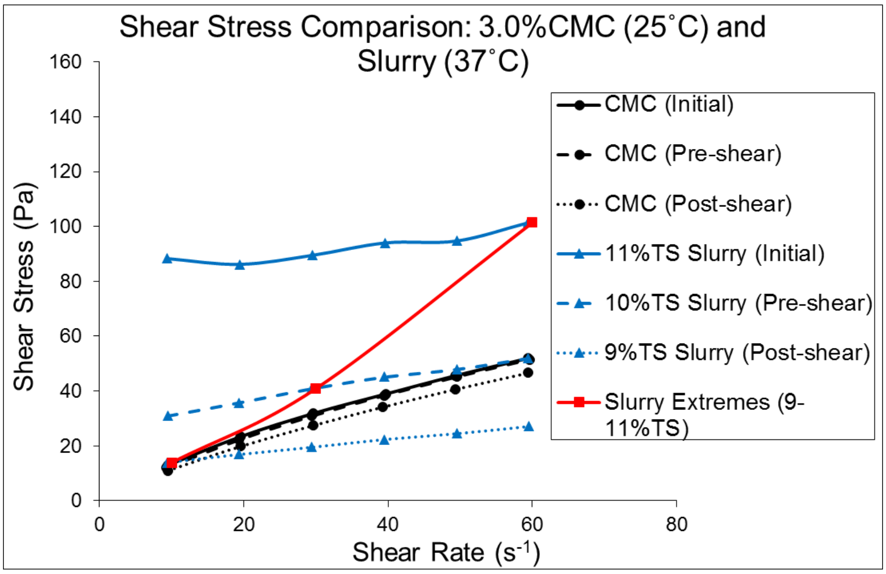
Independent validation was not required as known viscosity Newtonian calibration fluids without particulates were used to provide shear stress values.

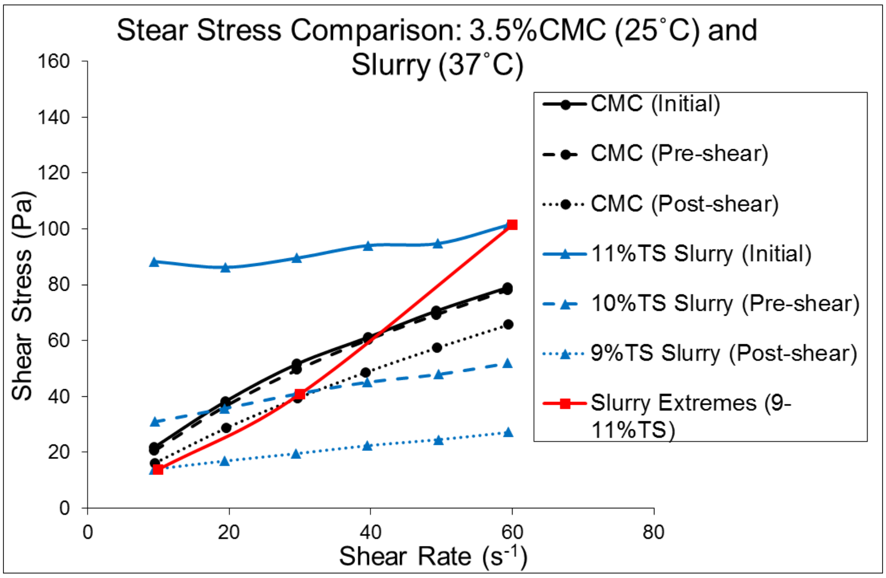
1:3:8 CMC Analysis

To compare the non-Newtonian characteristics of CMC with that of cow slurry, rheological analysis of a range of concentrations was performed. Concentrations of 3, 3.5 and 4.0 percent were found to be the most appropriate to determine predicted shear stress and apparent viscosity values associated with the cow slurry to be analysed. However, to simplify the application of CMC to support all experiments a single CMC substitute that captured all predicted values was identified.

1:3:9 Shear Stress Values

The 3 CMC concentrations were used to obtain a wide range of shear stress values and profiles when using the SSRP and conditioning as indicated by the black profiles (Figure 114). However, to be suitable the substitute also had to represent predicted variations in the non-Newtonian properties of cow slurry as solids content changed due to bio-degradation during both batch and fed-batch processes. Apparent viscosity was expected to gradually reduce during the batch process as volatile solids were consumed over time and the %VS gradually reduced. Conversely, feeding would periodically introduce new feedstock with a higher solids content and embedded VS as the digester contents gradually bio-degraded resulting in a gentle sinusoidal solids content value. Also, the CMC substitute had to capture the characteristics of a slurry experiencing shear-thinning due to changing shear stress associated with mixing intensity as well as that caused by thixotropy during prolonged mixing. The extreme range of shear stress values associated with the TS range, shear rates and states of conditioning to be captured are represented by the red line with the actual values achieved represented in blue.





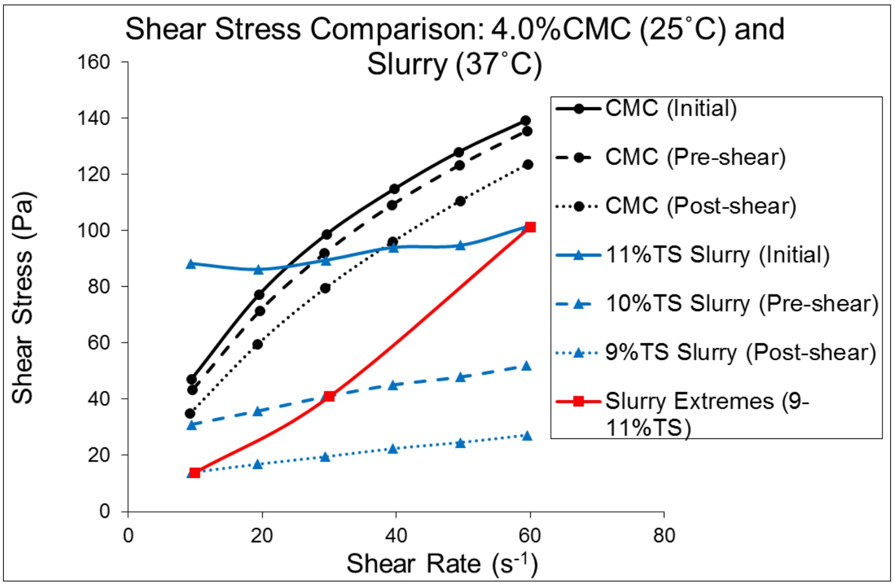


Figure 114 – Comparison of shear stress values of different CMC concentrations and key %TS slurries

A more detailed graphical representation of the range of shear stress values (Figure 115) indicates that 3.5%CMC was the most suitable substitute. Despite not quite capturing the extremes of shear stress values produced by 11%TS slurry when initially mixed or 9%TS after prolonged mixing the concentration provided better coverage than the alternatives, particularly in the mid-region.

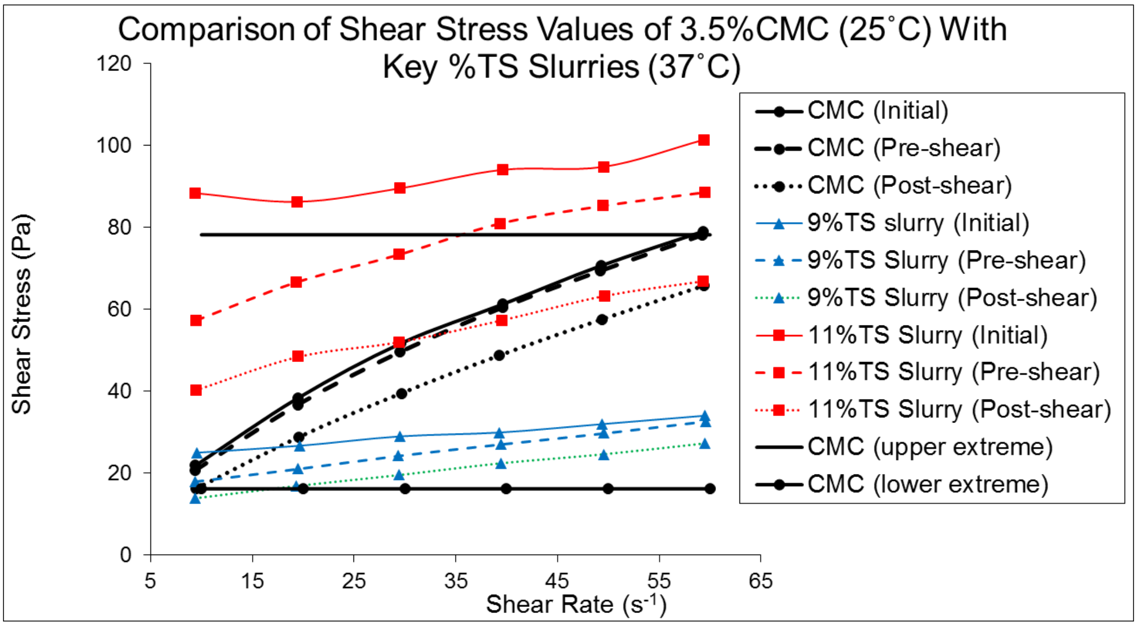


Figure 115 – Comparison of shear stress values of a 3.5% CMC concentration and key %TS slurries

1:3:10 Apparent Viscosity Values

The suitability of CMC substitution was less clear when shear stress values were translated into apparent viscosity and extreme values (represented in red) were considered (Figure 116). However, 3.5%CMC (black) did provide a mid-range substitute capturing the majority of expected conditions.

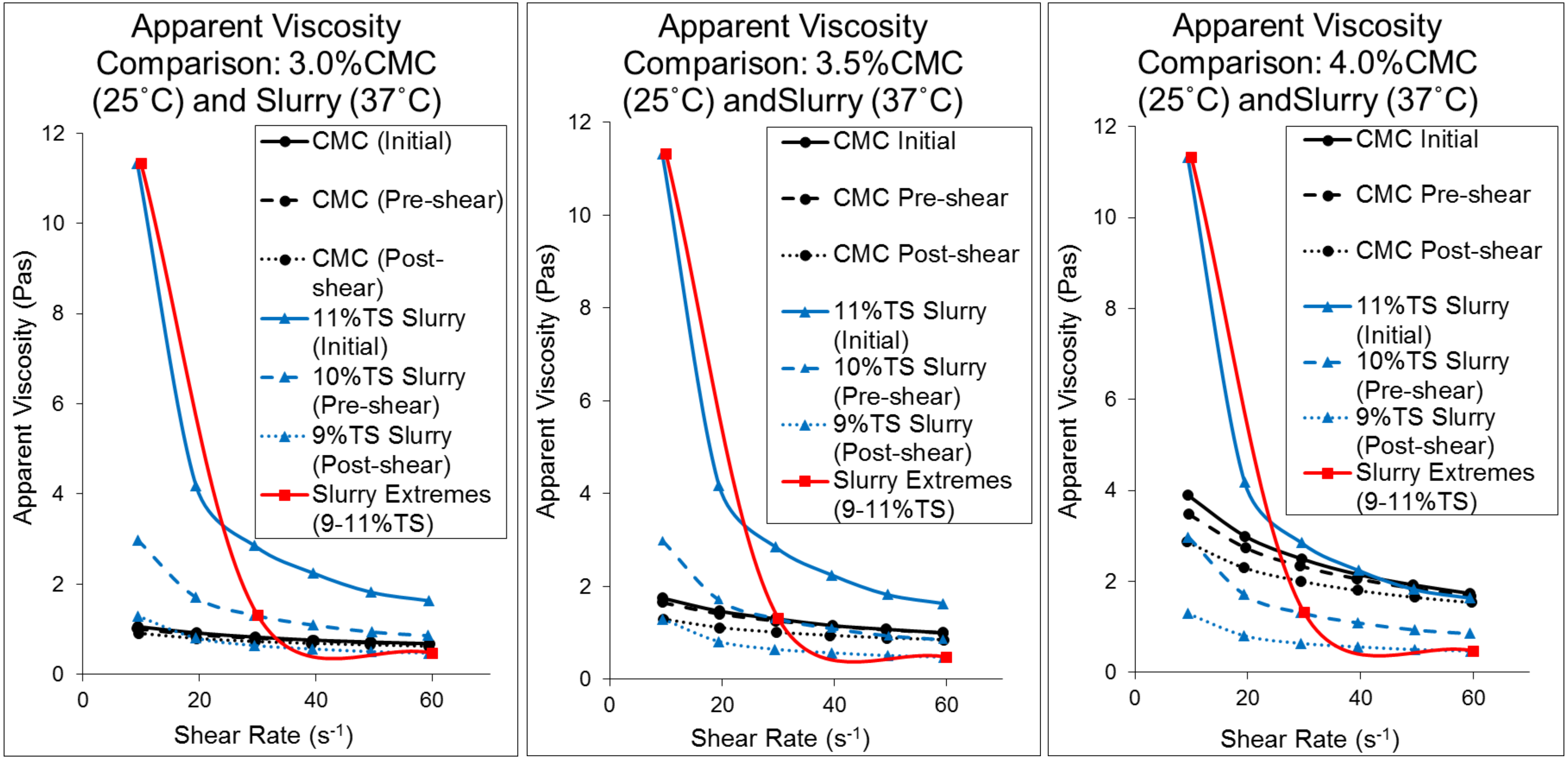


Figure 116 – Comparison of apparent viscosity values of different CMC concentrations at key %TS slurries

1:3:11 Recovery After Resting

The ability of CMC to regain original non-Newtonian characteristics after resting was determined. Solutions of 3, 3.5 and 4%CMC were again measured using the SSRP at 25˚C although some data was invalidated due to corruption. Of the samples measured (Figure 117) partial recovery was always achieved after 1 hour of resting. At 3.5% CMC concentration, values of shear stress after 12 hours resting were higher than when shear force was first applied. This may have been due to evaporation of the water in the solution during the 12 hour rest period despite the beaker being covered with foil. Pinho & Whitelaw (1990) observed the opposite effects of CMC degradation when apparent viscosity values decreased over time. However, lower concentrations were used and the degree of degradation reported to be inversely proportional to concentration. When 4.0% CMC concentration was tested in the current study no distinct pattern was recognisable as the rest period increased. Indeed, the partial recovery experienced after 1 hour of rest was reversed and further thinning observed when the solution was rested for 3 and 6 hours. The reasons for this erratic outcome are unknown although diurnal variations in the ambient laboratory temperature over the rest period may have been a factor. Pinho & Whitelaw (1990) suggested that samples should be used within 6 hours of preparation which may have been to avoid such anomalies.

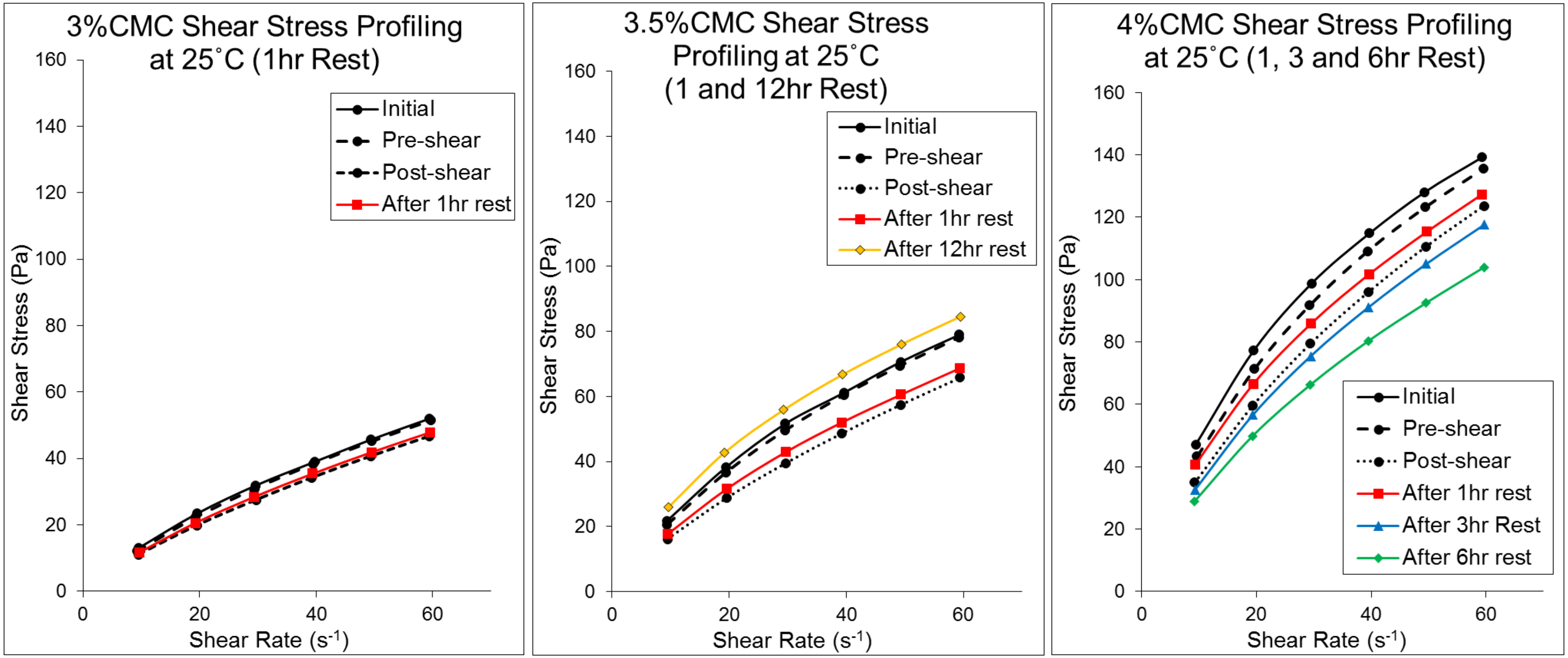


Figure 117 – Comparison of shear stress profiles of different CMC concentrations after resting

As apparent viscosity is directly related to shear stress there was no surprise when, apart from the partial recovery of the samples after 1 hour of rest, outcomes provided no clear pattern (Figure 118).

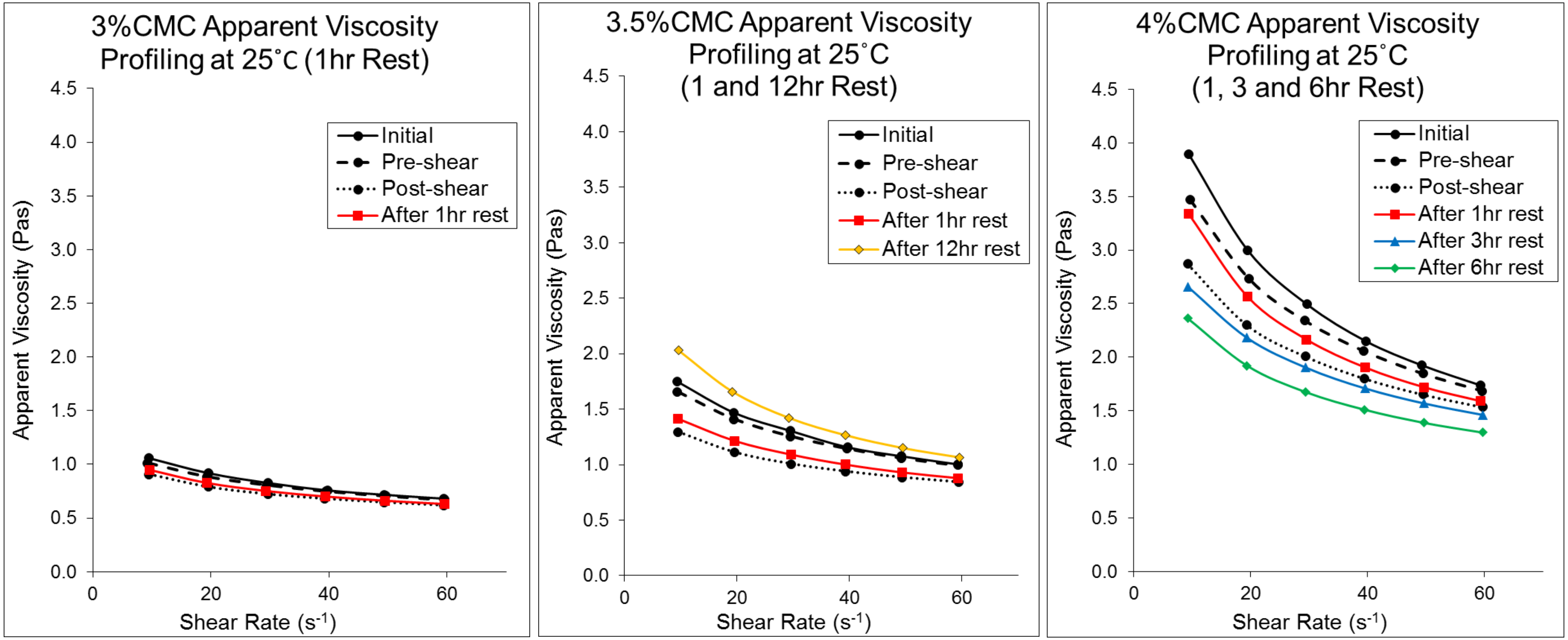


Figure 118 – Comparison of apparent viscosity profiles of different CMC concentrations after resting

1:4 Conclusions

From the extensive viability testing, calibration, rheological measurement of dairy farm slurry and numerical analysis, the following was concluded:

- The AR2000 Rheometer and rotor/cup geometry provided an effective means of measuring shear stress induced in a representative range of dairy farm cow slurries within a temperature-controlled environment of 10-70˚C using a pre-determined range of shear rate.
- Viability and accuracy depended upon:
    - Extensive calibration of the equipment with a calibration fluid.
    - Shear rate limited to 0-60s^{-1} to reduce standard errors to below 5 percent.
    - The use of static temperature environments to accommodate limitations associated with manual chilling.
- A 28mm diameter, 4-bladed rotor in a 44mm diameter cup provided the best correlation between viscosity values produced using the geometry and guaranteed values associated with calibration fluids at similar temperatures.
- The 14mm diameter rotor in a 44mm diameter cup (15mm gap) also provided excellent correlation, demonstrating that a rotor/wall gap greater than 8mm had a minimal effect on shear stress and viscosity measurements with this geometry.

The extensive testing of various concentrations of CMC solutions demonstrated that:

- A solution of 3.5% (w/w) CMC concentration may be used as a suitable substitute for cow slurry when simulating flow patterns in cow slurries of 9-11%TS (w/w) when applying shear rates of 0-60s^{-1} and under the conditions tested.
- Profiling using 3 and 4%CMC concentrations did not accurately replicate the values measured when analysing cow slurry so using CMC as a transparent flow modelling substitute has limitations.

- CMC did not accurately represent the effects of resting expected of a thixotropic fluid so may not be appropriate for simulating such properties should they be observed in cow slurry.

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