Novel Approach to Pre-treatment of Agricultural Products and Food Waste to Improve Biogas Production

A thesis submitted for the degree of

Doctor of Philosophy

by

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Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Doctor of Philosophy is entirely my own work, that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

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(Ayad K. M. Aboderheeba)

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Abstract

Biogas technology and the use of biogas are ever increasing in the agricultural sector. Organic waste to produce renewable energy and minimise environmental emissions, both resulting in reduction in greenhouse gas (GHG) emissions and reduce the dependency on the fossil fuel is one way of achieving this. Anaerobic Digestion (AD) is one of the most common biomass conversion technologies currently deployed for power and heat. The most suitable substrates for the digestion in agricultural biogas plants are: energy crops, organic wastes, and animal manures, these materials considered are lignocellulosic materials. In order to improve degradation of these kinds of materials and enhancing biogas yield, pre-treatments are necessary.

One of the aims of this research is to introduce the new mechanical pre-treatment technique by employing a Hollander Beater device to treat cellulosic and lignocellulosic materials. This method is called the "Beating treatment". Maize silage, fresh grass and potato waste were selected as main substrates. Three levels of beating treatment were identified for each of them. Each substrate was anaerobically co-digested with sludge in batch laboratory scale reactors at mesophilic condition (37 ^{o}C), with Hydraulic Retention Time (HRT) of 21 days. The highest efficiency of increment in comparison with untreated samples of maize silage was 27.35% achieved after 20 minutes beating treatment, while fresh grass was 38.48% after 5 minutes of beating treatment, and 31.34% efficiency for potato waste (potato skin) was obtained after 5 minutes beating treatment. The relationship between beating time, degree of beating and biogas production were analysed and discussed.

The second aim of this research was to predict and optimise the AD process after beating treatment for maize silage and waste of potato through applying Response Surface Methodology (RSM) via Design Expert software to develop mathematical models that relate the process input parameters to the output features (responses). The two main input parameters of AD process considered are beating time and temperature. The output features investigated are production of biogas, CH_4 concentration, CO_2 concentration and energy consumption. For each material, mathematical models were developed to predict the required responses. Moreover, the main effects of the process parameters on the responses were discussed and presented graphically. Furthermore, the developed models were optimised by determining the best combinations of input process parameters in order to reach an excellent output.

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Nomenclature

PITF	Program Implementation Task Force
GDP	Gross Domestic Product
DFID	Department for International Development
FAO	the Food and Agriculture Organization of the United Nations
GNP	the Gross National Product
OFMSW	Organic Fraction of Municipal Solid Waste
AD	anaerobic digestion
DP	degree of polymerization
VFA	volatile fatty acids
C/N	Carbon to nitrogen ratio
TOC	Total organic carbon
OLR	organic loading rate
COD	Chemical oxygen demand
HAc	Acetic
HPa	Propionate
Het	Ethanol
LA	Lactate
HBu	Butyric
NH_3	Ammonia
H_2S	Hydrogen sulphide
VS	Volatile solid
HRT	Hydraulic Retention Time
CH_4	Methane
CO_2	Carbon dioxide
H_2	Hydrogen
GD	Grubben Deflaker
KD	Krima Disperser
WAS	Waste Activated Sludge

OVAT	One-Variable-At-a-Time
DOE	Design of Experiments
RSM	Responses surface methodology
CCD	central composite design
BBD	Box-Behnken design
ANOVA	An analysis of variance
DA	Desirability Function Approach
NNFCC	National Non-Food Crops Centre
UCD	University College Dublin
SEM	Scanning Electron Microscope
MC	Moisture Content
P	Number of coefficients in the model.
N	Total number of runs.
n_0	Number of centre points.
df	Degree of freedom.
MS	Mean square.
DA	The Desirability Function Approach
ME	Metabolisable Energy
CP	Crude Protein
NDF	Neutral Detergent fibre
ADF	Acid Detergent fibre
DMD	Digestibility of DM
DM	Dry Matter
TS	Total Solid
^{o}C	Degree Celsius
K	Kelvin

Chapter 1

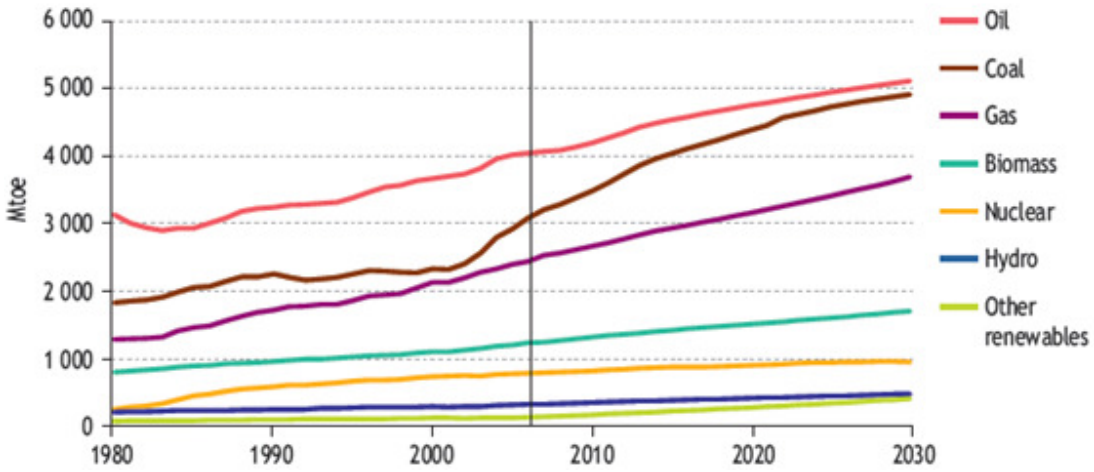
INTRODUCTION

1.1 Introduction

The world in the 21st century faces problems due to growing energy consumption and diminishing supply of fossil fuels. This has led to greater interests in the use of renewable energy sources and consequently the development of new energy production technologies [1]. Figure 1.1 shows that world energy demand is expected to double by 2050.

The demand for energy, as currently proposed and analysed, will exceeding the local supply sources at the rate that is considered exponentially unimaginable. This is based on the fact that fossil fuels will not be able to support this economic growth and energy security in the long term. This has been brought about through volatile instability in the Middle East coupled with other factors, such as uncertainty of supply availability of the vast reservoirs. This has resulted and has to a greater extent, shown some risk factors environmentally through fossil fuel exploitation.

Globally, energy security and its economics have become one of the most challenging issues that need to be quickly addressed. The developmental need and quick expansion of population has further impacted this necessity. Also, a suitable replacement is needed so as to sustain and improve the living standard of people. For there to be the possibility in attaining these goals, new technologies need to be developed as well as the modification of the existing ones. Development of alternative energies on a continual basis will also need to be considered.



Mtoe = million tonnes oil equivalent

Figure 1.1: Projected world energy demand [2]

On the reverse side to this issue, waste production is growing with significant increases in both developed and developing countries. According to World Bank projections, low middle-income countries are projected to generate 956 million tons of solid waste per day with the population predicted to reach 2.08 billion by 2025. In the EU-27 + Norway and Switzerland the generation of municipal waste is projected to be approximately 279 million tonnes per day in 2020 [3].

In 1992 the United Nations "Earth Summit" established the need to control greenhouse gases, recognising the growing concerns of rising levels of global warming and pollution [4]. The Kyoto Protocol, drawn up in 1997, aimed to reduce the emissions of greenhouse gases from developed countries and led to widespread policy support and encouragement for the generation of electricity from renewable sources.

In response to the concerns raised above, the world has seen interest in renewable energy and related conversion technologies over the last two decades. One of the possible solutions is biomass, which can deliver large quantities of energy at low net CO2 emission levels [5]. Biomass has been defined as contemporary plant matter formed by photosynthetic capture of solar energy and stored as chemical energy [6]. Anaerobic digestion (AD) is one of the biomass conversion technologies which has gained popularity in the last few decades as a solution to environmental and energy issues. [7]. AD is a natural process of decomposition and decay that takes place in

the absence of oxygen and by which organic matter is broken down to its simpler chemical components [8, 9, 10]. It is a process found in many naturally occurring anoxic environments including watercourses, sediments, waterlogged soils and the mammalian gut. It can also be applied to a wide range of feedstocks including industrial and municipal wastewaters, agricultural, municipal, food industry wastes, and plant residues [11, 12]. The most suitable substrates for the digestion in agricultural biogas plants are: energy crops, organic wastes, and animal manures. Maize, herbage, clover maize silage, Sudan maize silage, fodder and others may serve as energy crops [13, 14]. These materials are considered as lignocellulosic materials [15, 16], they consist of three main types of polymers, namely cellulose, hemicellulose and lignin, which are associated with each other, and smaller amounts of pectin, protein, extractives and ash. Cellulose, hemicelluloses and lignin are present in varying amounts in the different parts of the plant and they are intimately associated to form the structural framework of the plant cell wall. The composition of lignocellulose depends on the plant species, age and growth conditions. Distribution of cellulose, hemicelluloses and lignin varies significantly between different plants [17, 18]. Several researchers have concluded that the barrier to the production and recovery of lignocellulosic material is the structure of lignocelluloses. Lin and Tanaka [19], Xiao et al. [20], and O-thong et al. [21] indicate that the structure of lignocelluloses resist degradation due to cross-linking between the polysaccharides (cellulose and hemicellulose) and the lignin via ester and ether linkages. Hendriks and Zeeman [22] in their review conclude that the crystallinity of cellulose is just one of the factors that make hydrolysis of lignocellulose limited, and supported other factors reported in [23, 24, 25, 26] (1) degree of polymerization (DP), (2) moisture content, (3) available surface area and (4) lignin content. Therefore pre-treatments are necessary to improve degradation of cellulosic materials and enhance overall methane yield these treatments can be biological, mechanical or physico-chemical [27, 28]. Biogas production usually contains 55% to 65% methane, 35% to 45% carbon dioxide and <1% nitrogen from sewage digesters, biogas from organic waste digesters usually contains 60% to 70% methane, 30% to 40% carbon dioxide and <1% nitrogen while in landfills the methane content is usually 45% to 55%, 30% to 40% carbon dioxide and 5% to 15% nitrogen. Typically, biogas also contains hydrogen sulphide and other sulphur

compounds, compounds such as siloxanes and aromatic and halogenated compounds [29].

Mechanical pre-treatment methods such as chipping, grinding and milling (often referred to as physical method) reduce crystallinity but more importantly give reduction of particle size, make material handling easier and increase surface/volume ratio [30]. Significant research effort has been dedicated focusing on mechanical treatment to improving the performance of digesters treating different biomass resources. Carrère et al [28] and Alfarjani et al [31], in their review papers, classified the mechanical treatment as: ultrasonic treatment, lysis-centrifuge,liquid shear, and grinding.

In this work, a new mechanical pre-treatment technique has been presented by employing a Hollander Beater device to treat lignocellulosic materials. Attributed to the Beater device, the name "*Beating Treatment"* has been given to this method. Beating lignocellulosic materials will result in decrease particle size and increase surface area; also will damage and change its structure of component, this will improve hydrolysis and methane yield. The anaerobic co-digestion of the treated and the untreated sets of cellulosic and lignocellulosic materials with digester sludge were carried out.

In addition, in order to optimise anaerobic digestion after beating treatment optimization work was carried out using Design of Experiment (DOE) and Response Surface Methodology (RSM). In this part Central Composed Design (CCD) was used to develop the experimental design (design matrix). Once a study of this kind has been done, the optimum combinations of anaerobic digestion parameters can be selected and then used to produce the desired specifications.

1.2 Thesis Objective

The first aim of this research is to introduce the new mechanical pre-treatment technique by employing a Hollander Beater device to treat cellulosic and lignocellulosic materials. Attributed to the Beater device calling this method the *"Beating treatment"*. This aim can be achieved through the investigation similar to the treatment on the structure of the material, the effect of treatment on the productivity of biogas and the effect of treatment on CH_4 concentration. Energy

analysis will also take place to approve the economic visibility of new treatment technique.

The second aim of this research is to predict and optimise the AD process after beating treatment for maize silage and waste of potato through applying Response Surface Methodology (RSM) via Design Expert software to develop mathematical models that relate the process input parameters to the output features (responses). The two most important input parameters of the AD process considered are beating time and temperature. The output features investigated are production of biogas, CH_4 concentration, and energy consumption.

The following points summarise the second objective of this research:

(a) Appling Response Surface Methodology to develop mathematical models for the above mentioned materials using Design Expert V7 statistical software to predict and optimize the following process responses:

• Production of biogas (productivity);

• CH_4 concentration;

• Energy consumption.

(b) Presenting the developed models graphically to illustrate the effect of each AD parameter selected on the above-mentioned responses.

(c) Applying the analysis of variances (ANOVA) to test adequacy of the developed models and examine each term in the developed models using statistical significance tools.

(d) Determining the optimal combinations of input AD factors, using the developed models with numerical optimization and graphical optimisation, to achieve the desired criterion for the responses listed above.

1.3 Organisation of Thesis

The thesis is organised as follows;

- Chapter 1: provides an introduction to the work and also includes the thesis objective and thesis structure.
- Chapter 2: is a literature review chapter containing a background about agriculture, waste, lignocellulosic materials and its structure, also a review about AD techniques and mechanical pre-treatment methods.
- Chapter 3: introduces the new mechanical treatment (beating treatment) with details about a Hollander beater device and how it works which reflect the mechanism of the technique. This chapter will also explain how the DOE and RSM were used for optimisation for the AD of lignocellulosic materials after beating treatment.
- Chapter 4: details the lignocellulosic materials and its composition used in this work, with some previous study related. Chapter 4 also details the equipment and instrumentation used along with experimental procedures applied in this research work.
- Chapter 5: details experimental work applying beating treatment with results and discussion using one-variable at time approach.
- Chapter 6: contents the optimisation experimental work using DOE.
- Chapter 7: summarize the conclusions and further work.

Following this, references used in this thesis, appendices and publications arising from this work are listed.

Chapter 2

LITERATURE REVIEW

2.1 Background

2.1.1 Agriculture

The word agriculture refers to the science, art, and business of cultivating soil in the ground. It also refers to the production of crops, the raising of livestock, and farming in general [32]. A Program Implementation Task Force (PITF), consisting of representatives from the European Union and every country in the Baltic Sea drainage basin as well as international financing institutions and governmental and non-governmental organizations in their meeting 2001 have defined Agriculture as: The use of land for production of food, fodder, fibre, energy, medicine, etc. and for grazing (landscape preservation) [33].

2.1.1.1 Economic importance of Agriculture

Agriculture usually plays a vital role in the economy of every nation that exists. Not only for that reason that it tends to feed the entire population of a country but also in the respect that agriculture correlates and interacts with all the related industries of that country. A country is usually considered to be a social and politically stable nation if it possesses a very stable agricultural basis [34]. Theodore Schultz began his acceptance speech for the 1979 Nobel Prize in Economics observing:

“Most of the people in the world are poor, so if we knew the economics of being poor we would know much of the economics that really matters. Most of the world's poor people earn their living from agriculture, so if we knew the economics of agriculture we would know much of the economics of being poor” [35].

2.1.1.2 How Agriculture contribute to economic growth

Meijerink & Pim Roza from Wageningen University and Research Centre, indicate that there is a paradox in the role of agriculture in economic development. They show that the share of agriculture contributing to Gross Domestic Product (GDP) is declining over the years (see Figure 2-1). At the same time, the productivity of, for instance, cereal yields has been increasing (see Figure 2-2) [36]. Byerlee et al., justified the declining share of agriculture in GDP to an inevitable consequence of economic progress [37].

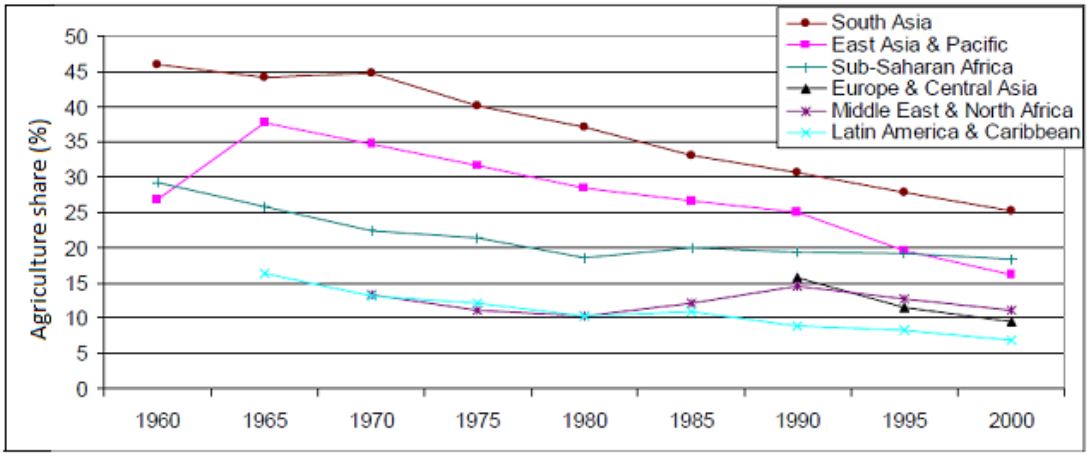


Figure 2-1: Share of agriculture (value added) in GDP

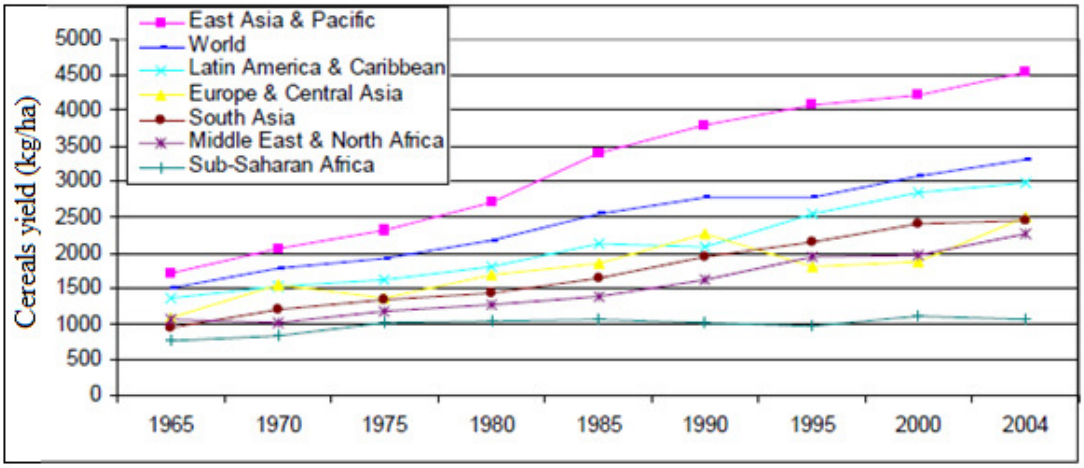


Figure 2-2: Average yield of cereals (kg per ha).

Despite the decline of GDP over years, in agricultural-based countries, it generates on average 29% of the GDP and employs 65% of the labour force. The industries and services linked to agriculture in value chains, often account for more than 30% of GDP in transforming urbanised countries [38].

In Africa, agriculture accounts for 17% of Africa's GDP, 57% of its employment and 11% of its exports. Its population will reach 2 billion in 2050. Agriculture and related industries are essential to economic growth in Africa and will cause a reduction in poverty and food insecurity [39]. The Food and Fertilizer Technology Centre FFTC for the Asian and Pacific Region shows that agriculture in 2007 accounts for 19% of Bangladesh's GDP, 32% of Cambodia's GDP, 11% of China's GDP, 18% of India's GDP, 14% of Indonesia's GDP, 1.6% of Japan's GDP, 10% of Malaysia's GDP, 50% of Myanmar's GDP, 20% of Pakistan's GDP, 11% of Thailand's GDP, 20% of Vietnam's GDP, 6% of New Zealand's GDP, and 3% of Australia's GDP [40].

2.1.1.3 Agriculture and poverty

In an article published by the Department for International Development (DFID) [41] the paper indicates that history has shown that different rates of poverty reduction over the past 40 years have been closely related to differences in agricultural performance – particularly the rate of growth of agricultural productivity. In the same paper they pointed out that statistics from the Food and Agriculture Organization of the United Nations (FAO, 2004) indicate that between 1961 and 2001, global cereal production more than doubled (from 900 to 2,100 million tonnes), far outstripping the rate of growth of population, the paper also mentions that 78% fall in food prices overall from 1950 to 1992. Globally, the percentage rate of poverty has declined steadily over the past four decades. Between 1981 and 2001, the percentage of the world's population living on less than a dollar (€0.74) a day fell from 40.4% to 21.1%. Even though world population grew by an estimated 1.5 billion over the same period, the number of people living in absolute poverty fell by almost 400 million (see table 2.1)[41].

Table 2-1: Percentage and numbers of population living below the US $1 per day poverty line, 1981–2001

% of population living below US $1 per day				Number of people living on less than US $1 per day (million)		
Region or country	**1981**	**1990**	**2001**	**1981**	**1990**	**2001**
East Asia and Pacific	57.7	29.6	14.9	795.6	472.2	271.3
China	63.8	33.0	16.6	633.7	374.8	211.6
Europe and Central Asia	0.7	0.5	3.7	3.1	2.3	17.6
Latin America & Caribbean	9.7	11.3	9.5	35.6	49.3	49.8
Middle East & North Africa	5.1	2.3	2.4	9.1	5.5	7.1
South Asia	51.5	41.3	31.3	474.8	462.3	428.4
India	54.4	42.1	34.7	382.4	357.4	358.6
Sub-Saharan Africa	41.6	44.6	46.9	163.6	226.8	315.8
Global Fig.	40.4	27.9	21.1	1481.8	1218.5	1092.7

Statistics from the World Bank indicate that the poverty forecast for 2015 is 15.5% of the population living on less than $1.25 per day (see Table 2-2) [42].

At the macro-economic level, growth in agriculture has been consistently shown to be more beneficial to the poor than growth in other sectors, Peter Warr [43] confirmed that in a number of South East Asian countries, poverty reduction was related to growth of agriculture and services but not to growth of industry. Datt and Ravallion [44] showed that rural sector growth in India reduced poverty in both rural and urban areas, while economic growth in urban areas did little to reduce rural poverty. In terms of the role of agricultural productivity in reducing poverty, Thirtle et al. (2001) showed a very strong correlation between productivity gains and poverty reduction, they conclude that, on average, every 1% increase in labour productivity in agriculture reduced the number of people living on less than a dollar a day by between 0.6 and 1.2% [45].

Table 2-2: Poverty in developing countries by region.

Number of people living on less than $1.25/day (millions)				Percentage of the population living on less than $1.25/day		
Region or country	1990	2005	2015	1990	2005	2015
East Asia and the Pacific	873.3	316.2	137.6	54.7	16.8	6.8
China	683.2	207.7	84.3	60.2	15.9	6.1
Europe and Central Asia	9.1	17.3	9.8	2	3.7	2.2
Latin America & the Caribbean	49.6	45.1	30.6	11.3	8.2	5
Middle East and North Africa	9.7	11	8.8	4.3	3.6	2.5
South Asia	579.2	595.6	403.9	51.7	40.3	23.8
India	435.5	455.8	313.2	51.3	41.6	25.4
Sub-Saharan Africa	297.5	388.4	356.4	57.6	50.9	37.1
Total	1,818 .50	1,373 .50	947.2	41.7	25.2	15.5

2.1.1.4 Agriculture and energy

Global energy consumption is increasing dramatically due to our quest for higher living standards and an increasing world population, Figure 2-3 showing the evaluation of world total primary energy supply from 1971 to 2009. At the same time, particularly in the 90s the issue of global climate change is gaining greater interest in the scientific community. This led to the Kyoto Protocol in 1997 being issued.

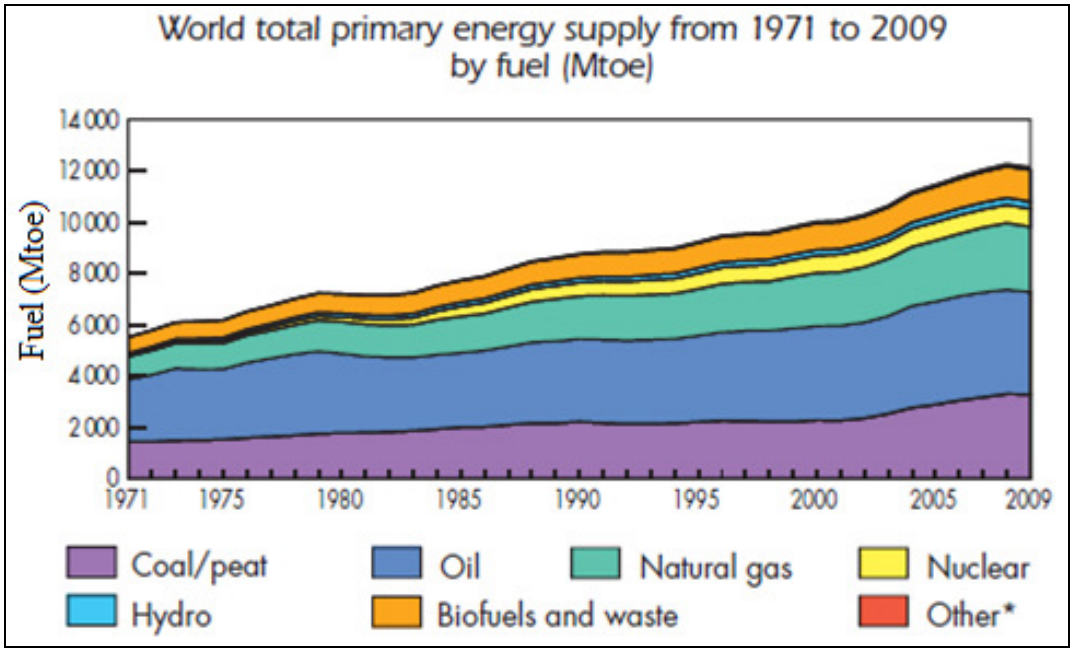


Figure 2-3: The total of primary energy supply [46]

The purpose of the Kyoto Protocol was to reduce the total greenhouse gas emissions of developed countries (and countries with economies in transition) to 5% below the level they were in 1990. The protocol sets targets for greenhouse gas emissions of developed countries for the period 2008 to 2012 [47]. In addition, the EU energy and climate change policy defines targets of 20% greenhouse gas reduction, 20% and a 20% share of renewable energy by 2020 [48]. Bioenergy is promoted as key in reaching these targets as biomass can replace fossil fuels in stationary applications, such as heating utilities or electricity production, as well as in the transport sector [49].

Globally 140 billion metric tonnes of biomass is generated every year from agriculture. This volume of biomass can be converted to an enormous amount of energy and raw materials, equivalent to approximately 50 billion tonnes of oil. Agricultural biomass waste converted to energy can substantially displace fossil fuel, reduce emissions of greenhouse gases and provide renewable energy to some 1.6 billion people in developing countries, which still lack access to electricity. As raw materials, biomass wastes have attractive potentials for large-scale industries and community-level enterprises [46].

The production and use of biomass as energy sources are linked to many issues, including agriculture and food security, land use and rural development, sustainable

forest management and biodiversity conservation, and mitigation of climate change [50].

Land availability is often seen as a constraint to the production of energy crops. With many people in developing countries still undernourished, it is a justified concern that there should be sufficient land for food production and that food should be the priority. However, food production is a complex socio-economic, political and cultural issue that goes beyond the earth's carrying capacity to grow food crops. If farmers are given the opportunity through economic incentives, land tenure rights and capital investment, they will be able to produce more food than has been the case so far [50].

In parallel with the prospects of increased food production, several studies have focussed on the potential ability of biomass to improve energy production in lieu of fossil fuels. A study published by the FAO in 1999 indicated that there are large areas of deforested and degraded land that would benefit from the establishment of biomass plantations, with estimates ranging up to over 300 Mha available for reforestation and agro-forestry. While other studies of the potential cropland resources in developing countries have also indicated that these countries will be using only 40% of their potential cropland in 2025 [50]. In the United States, statically 8% of energy came from a renewable source and was consumed in the year 2010 (see Figure 2-4) [51]. In a further study to determine whether the land resources are in a position to produce a sustainable supply of biomass sufficient as a replacement of the current 30 % or more of the country's petroleum consumption confirmed that 1.3 billion dry tonnes per year of biomass potential could be produce and will be enough in meeting more than one-third of the current demand for transportation fuels through the biofuel production (see Figure 2-5) [52].

The balance between higher yields in good lands and the benefits of bringing back into production, degraded lands is an important issue.

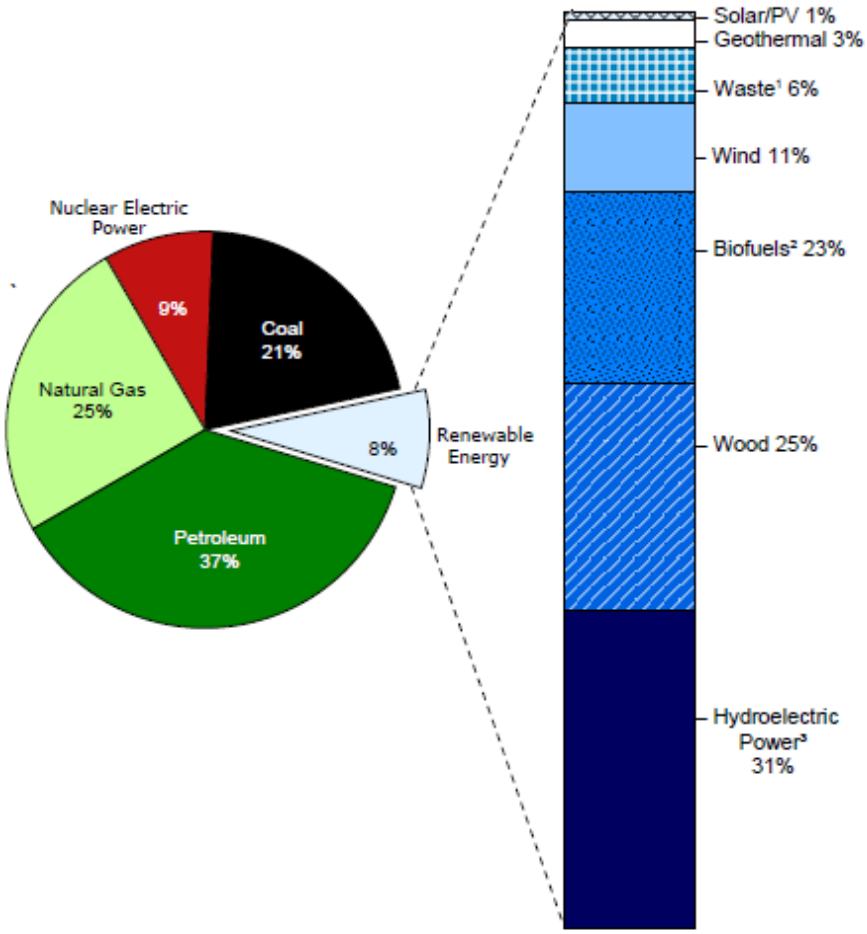


Figure 2-4: Renewable energy as share of total primary energy consumption in US.

Bioenergy programmes, when coupled with agro-forestry and integrated farming, have the potential to improve food production by making energy, crops and income available. Increasing agricultural production of biomass can be achieved by substituting for other agricultural crops that are in surplus, intermixing energy crops with food or forage crops in an agro-forestry approach, and incorporating into land conservation systems such as windbreaks and shelter-belts [50].

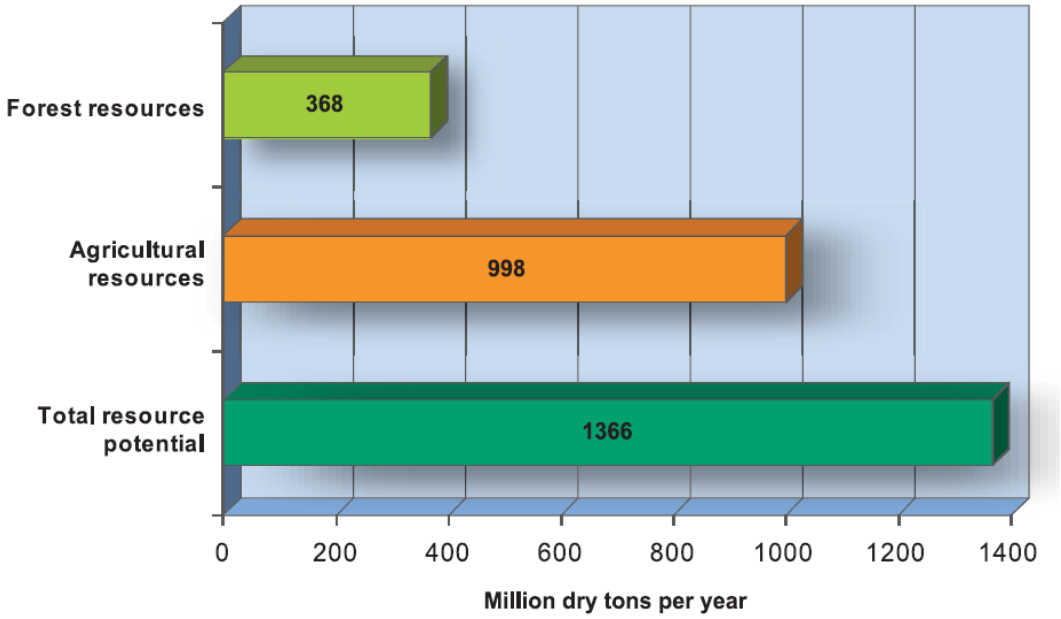


Figure 2-5: Annual biomass resources potential from forest and agriculture resources in US [52].

2.1.2 Waste produce and management

Worldwide, waste production is growing with significant increases in both developed and developing countries. According to World Bank projections, the low income countries are expected to generate 213 million tonnes of solid waste a day with an overall population increase by 676 million by 2025. Lower middle countries' incomes are also projected to generate 956 million tonnes of solid waste per day. Its population is predicted to reach 2.08 billion. Waste generation will hit 360 million tonnes per day by 2025 in upper middle income countries with expected population increases of 619 million. For High Income nations, waste generation a day by 2025 will reach 686 million tonnes and population increases of 912 million.[53]. From an analytical study, solid waste can be classified as nonorganic and organic waste. The majority of this waste (~70%) is organic [54]. Organic waste defines as any waste that is capable of undergoing anaerobic or aerobic decomposition through a biological treatment process, such as food and garden waste [55].

2.1.2.1 Waste management hierarchy

Due to the environmental problems caused by solid waste generation, during the last 30 years its management has become a major concern around the world. The waste hierarchy is a useful framework that has become a cornerstone of waste

management. It sets out the order in which options for refuse management should be considered based on environmental impacts. The hierarchy states that the most preferred option for waste management is prevention and minimisation of waste, followed by re-use and recycling, energy recovery and, least favoured of all, disposal (Figure 2-6). The overall intent of the hierarchy is to highlight the different levels and to one day move waste management away from landfill into those options in the upper tiers.

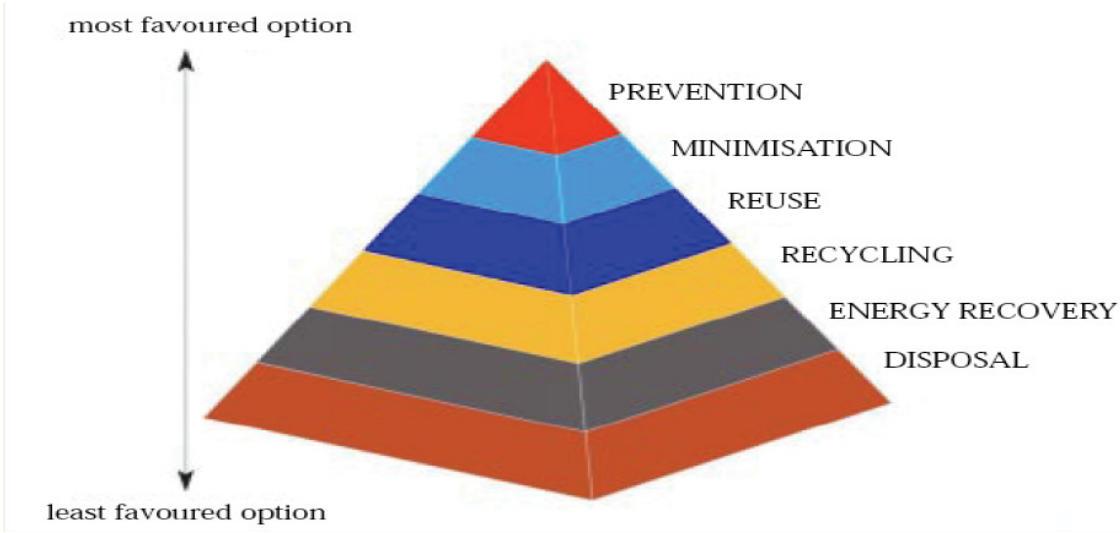


Figure 2-6: Waste Management Hierarchy

Collection, treatment, and disposal of waste are expensive processes. Cointreau-Levine, 1999 expressed the cost of solid waste management as a percentage of the Gross National Product (GNP) of a country and reported that effective waste management in middle income countries would cost about 0.5-1.3 % of their per capita GNP. It takes about US$100 per tonne to collect and dispose of solid waste in Jamaica. A large part of the cost is related to the distances transportation trucks have to travel [56]. George Goldman and Aya Ogishi, 2001[57] pointed out that, Platt and Morris (1993) [58], who studied 15 different communities throughout the United States, estimated that the collection and disposal costs of residential solid waste fell in the range of $40 and $170 per tonne, while the net costs of source-separated curb side recycling and composting were between $35 and $120 per tonne. Net recycling costs include costs of collection and processing minus revenues from the sales of recyclables.

2.1.2.2 Organic waste recovery options

Since organic material forms a large proportion of urban refuse, ways can be sought to use this resource more effectively. According to Inge Lardinois, 1993 [59], organic material can be reused in three ways:

1. To feed animals (fodder);

2. To improve the soil (compost);

3. To produce energy (biogas or briquettes).

The first two options are already very common in economically less developed countries. In Lahore, Pakistan, for example, 40% of urban refuse is collected by farmers and used as animal feed and soil amendment. Compost is the end product of basically two processes: composting and anaerobic digestion. Both refer to the biological degradation of organic material, but via different processes. Composting, which is probably the oldest method of waste treatment, occurs in the presence of oxygen, whereas anaerobic digestion occurs in the absence of oxygen.

Compost is the stable end product derived from the biological degradation of organic material, which can vary from dead leaves and roots to kitchen waste and vegetable remains. If well decomposed, the odourless and pathogen-free black brown mixture can be used as a soil conditioner.

2.1.2.3 Rationale of anaerobic digestion of solid waste

Due to its simplicity and financial reasons, solid waste disposal on sanitary landfill has been the common practice for many decades. However, many studies show that reducing landfilling in favour of increasing recycling of energy and materials lead to a lower environmental impact, a lower consumption of energy resources, and lower economic cost. According to the European Landfill Directive (ES, 1999), member states of European Union have to reduce the amount of biodegradable solid waste that is deposited on sanitary landfills to be less than 35% of the total biodegradable solid waste that were produced in 1995 being deposited on sanitary landfills. Separation of municipal waste into a recyclable fraction, residual waste and a source-sorted organic fraction is a common practice option of waste management adopted

by the European Union in order to meet the obligations of the Landfill Directive. In Germany, for instance, in 2006 about 8.45 million tonnes of Organic Fraction of Municipal Solid Waste (OFMSW) were collected and separated. It consisted of 4.15 million tonnes of source-sorted organic household residues and the remaining is compostable solid waste from gardens and parks. Due to high moisture content and low caloric values of organic waste, incineration would not be an economical option. Thus, the treatment of OFMSW can be realised alternatively by anaerobic digestion or aerobic composting [60].

2.1.2.4 Food waste

Food waste, composing a large proportion of bio-waste, is waste composed of raw or cooked food materials and includes food materials discarded at any time between farm and fork; in households relating to food waste generated before, during or after food preparation, such as fruit and vegetable peelings, meat trimmings, and spoiled or excess ingredients or prepared food [61]. Roughly one-third of the edible parts of food produced for human consumption gets lost or wasted globally, which is about 1.3 billion tonnes per year [62]. In United Kingdom household's, waste contributes to some 6.7 million tonnes of food every year, the largest quantity is potato; 359,000 tonnes of potato goes uneaten every year, including 177,400 tonnes of potatoes thrown away whole and untouched (49%) [63]. In the United States, 34 million tonnes of food waste is generated each year, 97% ending up in landfills or incinerators, food represents nearly 14% of the total municipal solid waste stream in US [64]

In light of rapidly rising costs associated with energy supply and waste disposal, increasing public concern for environmental quality, successful application of anaerobic digestion (AD) technology could provide an economical and an environmentally friendly means for bioenergy recovery from food wastes with simultaneous remediation of waste [65]. In England, India and Taiwan, for example, methane generating units as well as plants using cow manure and municipal waste have been in operation for a number of years [66]. In the United States there has been considerable interest in the process of anaerobic digestion as an approach to generating a safe clear fuel as well as source of fertilizer [67]

2.1.3 Lignocellulosic material

Liginocellusic materials is a broad term that can be applied to a wide range of materials generally derived from plants or other organic sources [68] They consist of three main types of polymers, namely cellulose, hemicellulose and lignin, which are associated with each other, and smaller amounts of pectin, protein, extractives and ash. Cellulose, hemicelluloses and lignin are present in varying amounts in the different parts of the plant and they are intimately associated to form the structural framework of the plant cell wall. The composition of lignocellulose depends on plant species, age and growth conditions. Distribution of cellulose, hemicelluloses and lignin varies significantly between different plants [17, 18]. A primary example of such material is wood. An impression of the structure of lignocellulosic biomass illustrating its complexity is presented in Figure 2-7 for wood [69].

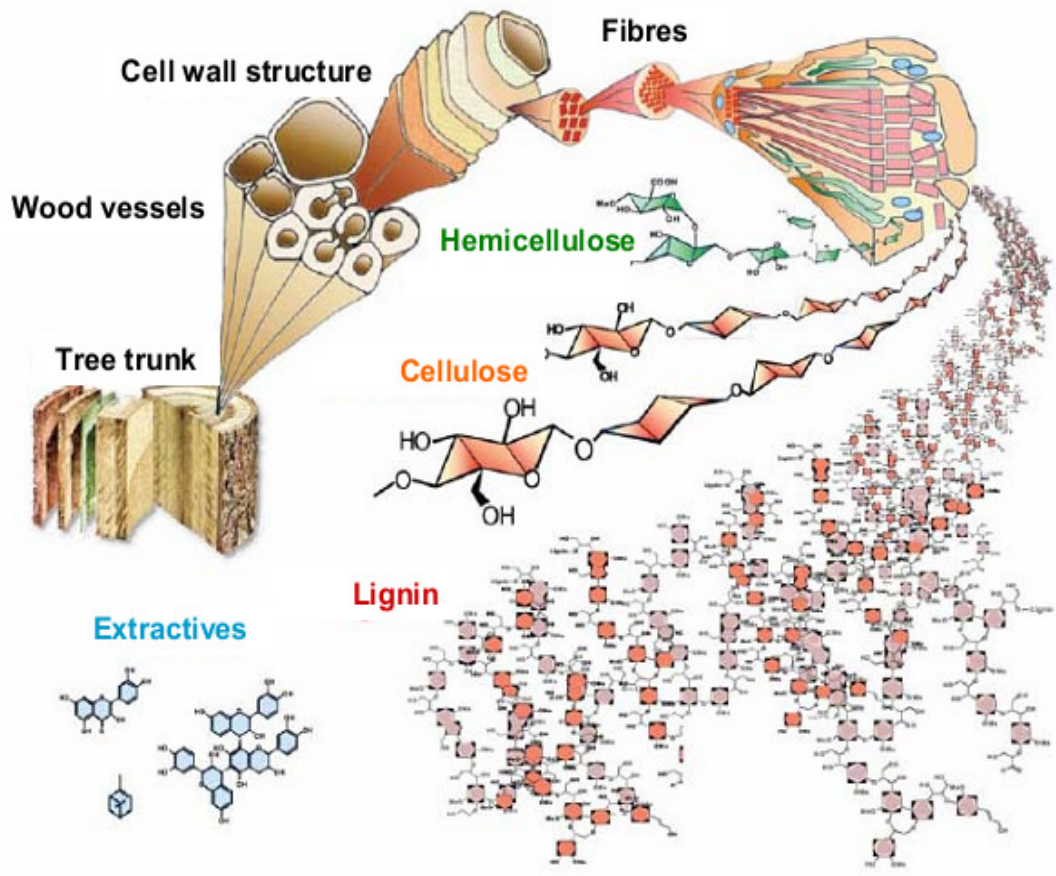


Figure 2-7: The composition of wood, illustrating the structure of lignocellulosic biomass.

Depending on the plant species, lignocellulose biomass typically contains 35-38% cellulose (consisting of D-glucose units), 22-30% hemicellulose, 15-27% lignin (see Figure 2-8) [70], and smaller amounts of (organic and inorganic) extractives and other inorganic compounds as mentioned above.

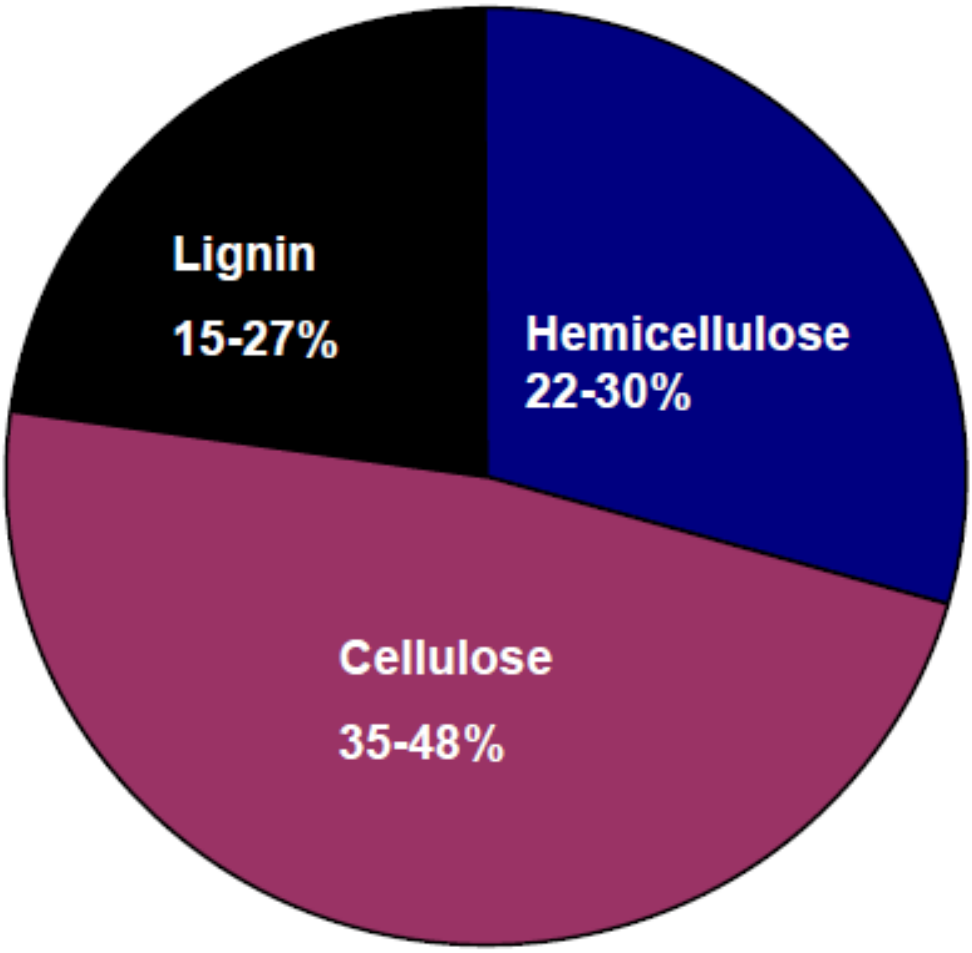


Figure 2-8: Typical lignocellulosic material composition

2.1.3.1 Cellulose

Cellulose is the major polymer in lignocellulosic biomass (35– 48%) [70], and exists of D-glucose subunits, linked by B-1,4 glycosidic bonds [17, 71, 72]. Cellulose in biomass is present in both crystalline and amorphous forms. Crystalline cellulose comprises the major proportion of cellulose, whereas a small percentage of

unorganized cellulose chains form amorphous cellulose. Cellulose is more susceptible to enzymatic degradation in its amorphous form [73]. Cellulose fibres are embedded in a lignin-hemicellulose matrix and this property contributes to the recalcitrance of lignocellulosic biomass to hydrolysis. Therefore, pre-treatment of lignocellulosic biomass before enzymatic hydrolysis is a vital step [70]

2.1.3.2 Hemicellulose,

The second major constituent of lignocellulosic biomass (22–30%) [70]. Hemicelluloses are heterogeneous polymers of pentose (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids. Unlike cellulose, hemicelluloses are not chemically homogeneous and easily hydrolysed to its constituent [74]. Hemicellulose is considered a weak compound in lignocellulose, but it plays a fundamental role in strengthening the structure: hemicellulose is linked to the other polysaccharides, to lignin and to proteins, forming a network [11]

2.1.3.3 Lignin

The third largest polymer composition of lignocellulosic biomass is lignin (15-27%) [70]. It is present in the cell wall, conferring structural support, impermeable, and resist against microbial attack and oxidative stress. Structurally, lignin is an amorphous heteropolymer, non-water soluble and optically inactive; it consists of phenylpropane units joined together by different types of linkages [75].

2.2 Anaerobic digestion

Nature has a natural provision in destroying and disposing of wastes in the form of dead plants and animals. Tiny microorganisms called bacteria carry out this decay or decomposition. Manure and compost can also be obtained through the decomposition of organic matter. AD is defined as the biological breakdown of organic material by the microorganisms in an airtight environment with no oxygen present [76]. The AD process can be used to turn residues from livestock farming, food processing industries, waste water treatment sludge, water treatment plant sludge among other organic wastes into biogas and digestate. The biogas can be used to generate heat and/or electricity; fibre. The biogas produced in AD plants is comprised largely of methane (60-80%) and carbon dioxide (20-40%) but also

contains a small amount of hydrogen sulphide (H_2S) and ammonia (NH_3), as well as traces of other gases [77].

2.2.1 History of anaerobic digestion

The process of breakdown of organic material by microorganisms in the absence of oxygen is commonly known as AD resulting in biogas (methane and carbon dioxide). This can then be used as chemical feedstock or as a fuel. AD has long been exploited by human beings for brewing alcoholic drinks, bread making and food preservation [78] however, anecdotal evidence indicates that biogas was used for heating bath water in Assyria 3,000 years ago [79]."Marsh gas" was discovered by Shirley in 1667. In 1630, Van Helmont pointed out the existence of an inflammable gas in putrefying waste and in the rumen of animals by examining 15 different gases. For the first time, it was only in 1776 that Volta recognized the presence of methane gas in the marsh or swampy place. Pristely discussed this gas in 1790 and Dalton tried to find out its chemical formula in 1804. In 1808, Humphrey Davy studied the fermentation of the mixture of water and cow dung and collected a one-litre volume of gas. This gas contained 60 % carbon dioxide and the rest comprised of a mixture of gas, which was rich in methane and nitrogen [80]. In 1860, Louis Pasteur discovered all fermentation processes are resultant from microbial activity. Louis Pasteur also defined the process of fermentation as life without oxygen [81]. In 1808, Sir Humphrey Davy concluded that methane was present in gases produced during the anaerobic digestion of animal manure [82]. The first anaerobic digestion plant occurred in 1859 in Bombay, India. In 1895, anaerobic digestion was introduced in England; biogas released from the sewage treatment plant was used to light street lamps in Exeter [83]. Buswell (1936) and Boyle (1977) developed a scientific model describing the composition of biogas (CH_4, CO_2, H_2S and NH_3) following anaerobic digestion and the chemical composition of organic substrates: C, H, N and S the chemical formula illustrates the biodegradability and the composition of methane yielding after anaerobic digestion [84]. The Buswell and Boyle scientific chemical formula [85]:

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3.d}{4} + \frac{e}{2}\right) H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} + \frac{3.d}{8} + \frac{e}{4}\right) CH_4 +$$

$$\left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3.d}{8} + \frac{e}{4}\right) CO_2 + d\ NH_3 + e\ H_2S \qquad (2.1)$$

2.2.2 General Process Description AD

The process of AD can be further divided into four steps: pre-treatment, digestion, gas upgrading and digestate treatment (see Figure 2-9).

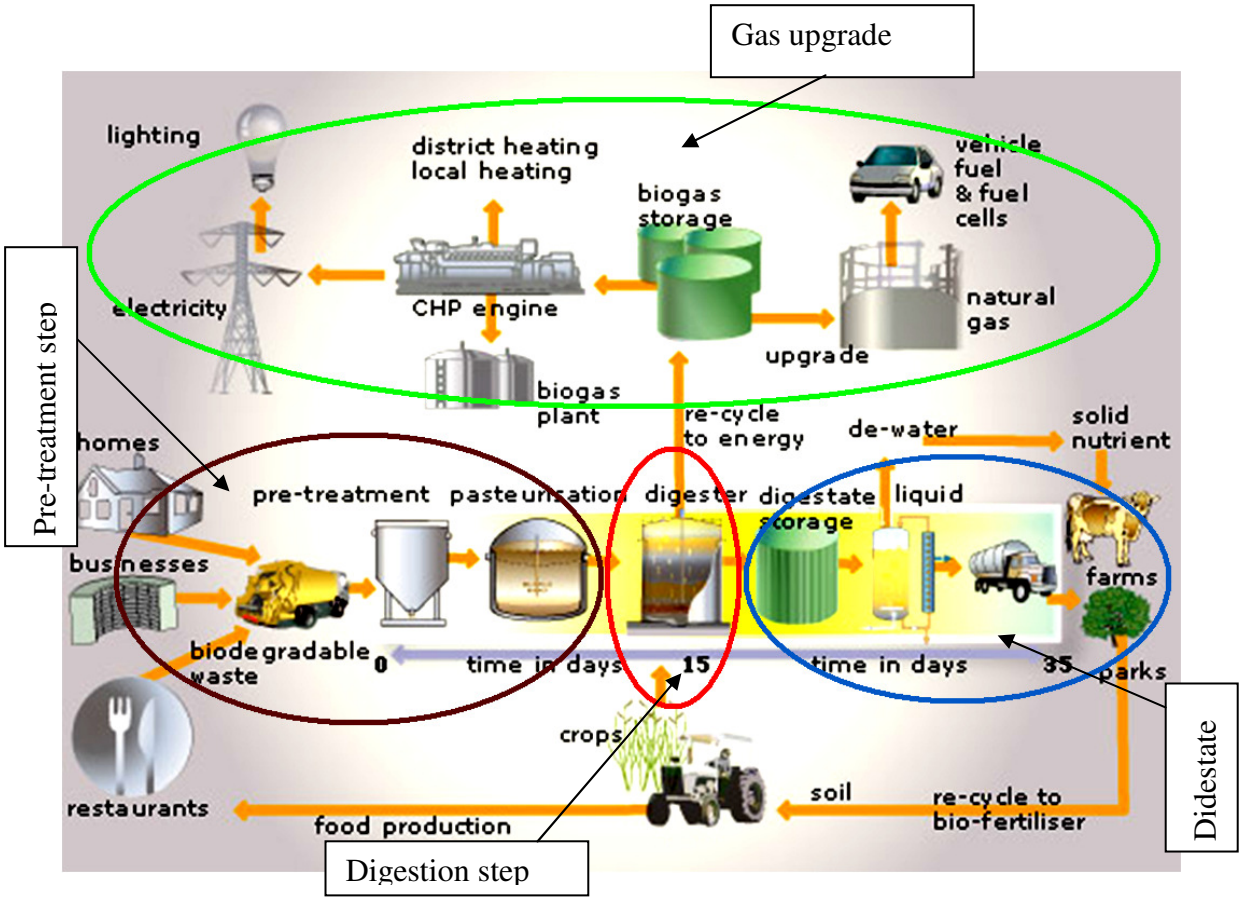


Figure 2-9: General process steps of AD **[86].**

2.2.2.1 Pre-treatment

Pre-treatment is used extensively to improve degradability and the rate of hydrolysis of the material being fed into digesters to increase the methane yield in the anaerobic digestion process [87]. Several researchers have concluded that the barrier to the

production and recovery of lignocellulosic material is the structure of lignocelluloses. Lin and Tanaka [19], Xiao et al. [20], and O-thong et al. [21] indicate that the structure of lignocelluloses resist degradation due to cross-linking between the polysaccharides (cellulose and hemicellulose) and the lignin via ester and ether linkages. Hendriks and Zeeman [22] in their review conclude that the crystallinity of cellulose is just one of the factors that make hydrolysis of lignocellulose limited, and supported other factors reported in [23, 24, 25, 26] (1) degree of polymerization (DP), (2) moisture content, (3) available surface area and (4) lignin content. Pre-treatment therefore is needed to alter or remove structural and compositional impediments to the hydrolysis process and subsequent degradation processes in order to enhance digestibility, improve the rate of enzyme hydrolysis and increase yields of intended products [88] (see Figure 2-10 [71]).

Carrere *et al.*, pointed out that pre-treatment could be done in any of the following ways [28]:

- Biological treatment methods;
- Chemical treatment methods;
- Thermal hydrolysis;
- Mechanical treatment.

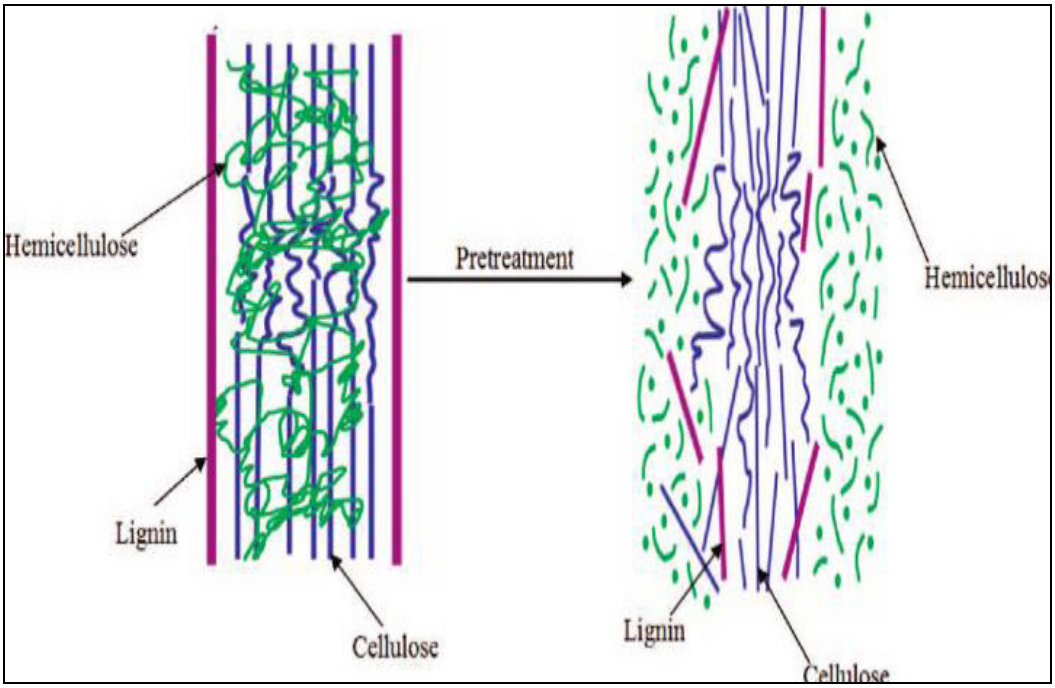


Figure 2-10: Schematic of the role of pre-treatment in the conversion of biomass to fuel.

2.2.2.2 Digestion

The digestion stage takes place in a digester (reactor). The organic material breakdown to its simpler chemical components, through a set of biochemical reactions in the absence of oxygen results in the formation of biogas (the following sections will cover the biochemical reaction in more details). There are many types of digesters that can operate within two temperature ranges, either at 35 °C (mesophilic) or 55 °C (thermophilic). The digestion can be either dry or wet depending on the solid content [89]. Thus, the feedstock can be mixed with water and other appropriate liquid wastes such as sewage sludge or re-circulated liquid from the digester effluent [90].

2.2.2.3 Gas upgrading

The biogas produced during the digestion stage has to be upgraded because it contains impurities such as hydrogen sulphide, oxygen, nitrogen, water and particulates. The main reason for doing this is to prevent corrosion and mechanical wear of the equipment in which the biogas is used. Removal of carbon dioxide for instance will be required if the gas is to be used as natural gas or vehicle fuel [91]. Upgrading biogas has gained increased attention due to rising oil and natural gas

prices and increasing targets for renewable fuel quotes in many countries. New plants are also continually being built. The number of upgrading plants in EU countries was around 100 in 2009 (Figure 2-11) [92], an overview of anaerobic digestion process, biogas upgrade and its use is shown in Figure 2-12.

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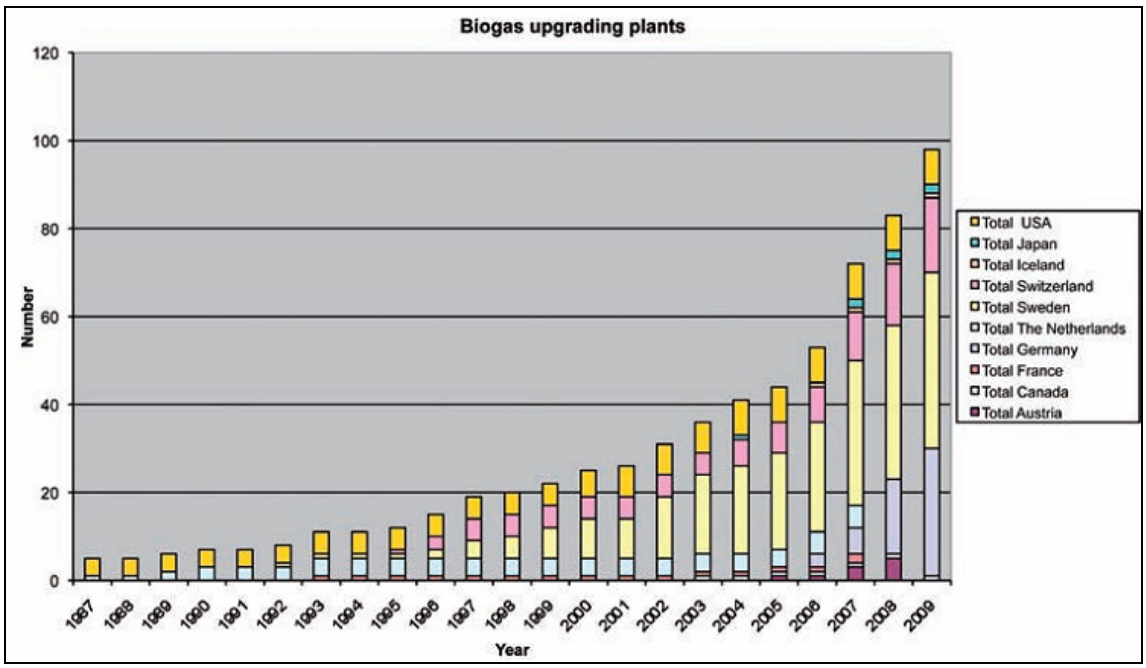


Figure 2-11: Total number of upgrading plants from 1987 to 2009.

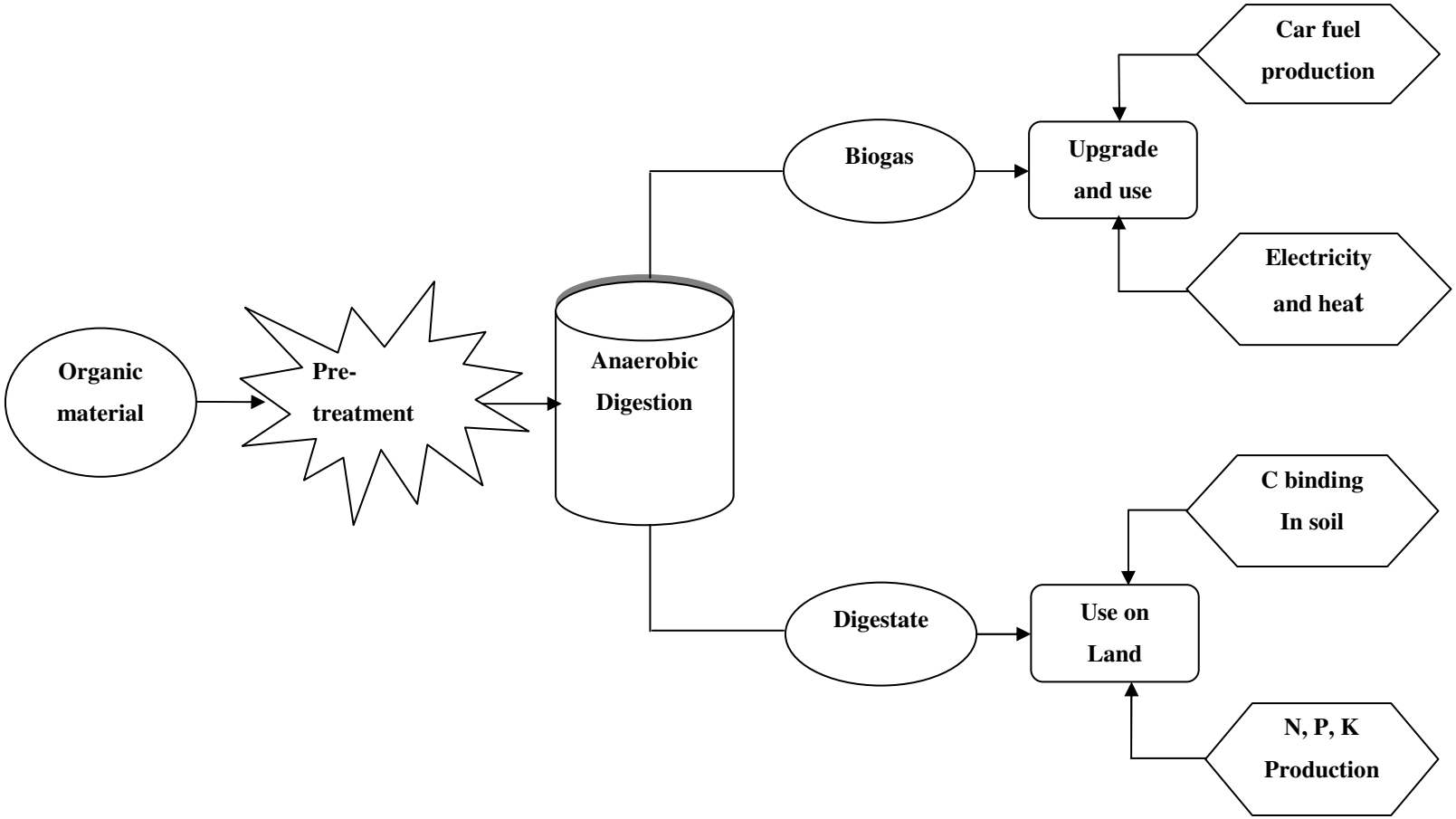


Figure 2-12: Over view of AD process, upgrading gas with its use and digestate with its used.

2.2.2.4 Digestate

In addition to biogas, AD also produces solid and liquid by-products; these by-products are termed the digestate. Digestate consists of a mix of microbial biomass (produced by the digestion process) and undigested material; the volume of digestate produced will be approximately the same as the feedstock volume, although the mass will typically be reduced by approximately 15%. Digestate contains all the nitrogen, phosphorus and potassium present in the original feedstock and as a consequence has value as an organic fertiliser. Typical nutrient values for digestate are: Nitrogen (2.3 - 4.2 kg/tonne), Phosphorous (0.2 - 1.5 kg/tonne) and Potassium (1.3 - 5.2 kg/tonne) [93]. Digestate has values as fertilizer or soil amendment. Digestate quality and nature will depend on the quality of the feedstock, the method of digestion (wet or dry) and the extent of the post treatment refining processes. The main product at dry digestion process is as solid digestate that can be matured into a compost product. The flow chart in Figure 2-12 depicts the digestate as an end product from AD process and its use.

2.2.3 Biochemical Reactions in anaerobic digestion

AD is a series of chemical reactions during which organic material is decomposed through the metabolic pathways of naturally occurring microorganisms in an oxygen- depleted environment [94]. AD can be used to process any carbon-containing material, including food, paper, sewage, yard trimmings and solid waste, with varying degrees of degradation. The organic fraction of municipal solid waste, for example, is a complex substrate that requires an intricate series of metabolic reactions to be degraded [95]. This section describes the reactions pertaining to AD and the reactions detailing the intermediary products formed.

In the anaerobic digestion process different types of bacteria degrade the organic matter successively in a multistep process and parallel reactions [94]. The anaerobic digestion process and production of methane is divided into stages. Four stages with four different types of microorganisms: hydrolysis (hydrolytic bacteria), acidogenesis (acidogens), acetogenesis (acetogens), and methanogenesis (methanogens) are used to illustrate the sequence of microbial events that occur during the digestion process [96, 97]. The mechanisms and conditions for digestion

will be discussed for each of the four stages. The critical biochemical reactions within these stages are presented in Figure 2-13 [98].

The revenues of the anaerobic digestion process are efficiently if the degradation rates of all four stages are equal. If the first stage is inhibited, then the substrates for the second, third and fourth stages will be limited and methane production decreases [97].

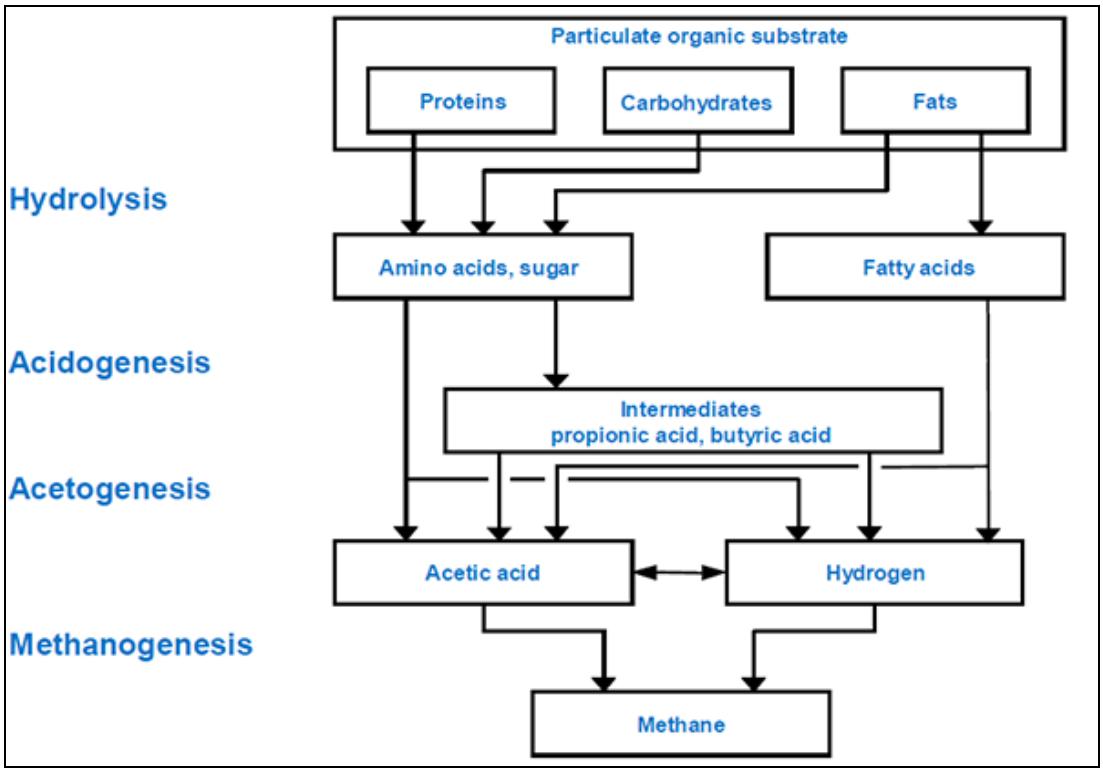
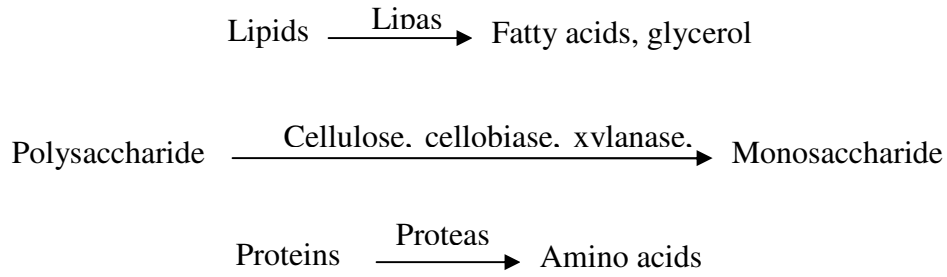


Figure 2-13: The anaerobic digestion biochemical conversion pathways.

2.2.3.1 Hydrolysis

In the first stage of hydrolysis, complex organic materials are broken down into their constituent monomers, Fermentative bacteria are responsible for the creation of monomers: proteins are converted to amino acids; fats to fatty acids, glycerol and triglycerides; complex carbohydrates such as polysaccharides, cellulose, lignin, starch and fibre converted to simple sugars, such as glucose. [99, 100]. Hydrolysis is catalysed by enzymes excreted from the bacteria, such as cellulase, protease, and lipase, etc.



The hydrolytic activity is of a significant importance in the high organic content waste and may become rate limiting [100, 101]. The rate of the hydrolysis process depends on parameters such as: size of particles, pH, and production of enzymes, diffusion and adsorption of enzymes on the particles of wastes subjected to the digestion process [102]. If the feedstock is complex such as raw cellulolytic waste, which contains lignin, the hydrolytic phase is relatively slow. For this reason, woody waste is not an ideal feedstock for the AD process without pre-treatment. Carbohydrates, on the other hand, are known to be more rapidly converted via hydrolysis to simple sugars and subsequently fermented to volatile fatty acids (VFA) [96]. An approximate chemical formula for the mixture of organic waste is $C_6H_{10}O_4$. A hydrolysis reaction where organic waste is broken down into a simple sugar, in this case glucose, can be represented by the following [96]:

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2 \quad (2.2)$$

2.2.3.2 Acidogenesis

In this process, acid forming (fermentative) bacteria known as acidogens turn the solubilised monomers produced by hydrolysis process into simple organic compounds, mostly short-chain organic acids (formic, acetic, propionic, butyric, pentanoic), alcohols (methanol, ethanol), aldehydes, carbon dioxide and hydrogen [102]. The specific concentrations of products formed in this stage vary with the type of bacteria as well being influenced by the culture conditions, such as temperature and pH. The most important of the organic acids is acetate since it can be used directly as a substrate by methanogenic bacteria [94, 102].

Amino acids, sugars, Fatty acids —*Acidogens*→ Intermediary products (propionate, butyrate)

Typical reactions in these stages are shown below. In equation 2, glucose is converted to ethanol and equation 3 shows glucose is transformed to propionate [96].

$C_6H_{12}O_6 \leftrightarrow 2\ CH_3CH_2OH + 2CO_2$ (2.3)

$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2\ H_2O$ (2.4)

2.2.3.3 Acetogenesis

The acetogenesis is often considered with acidoenesis to be part of a single acid forming stage. In this step low molecular weight volatile fatty acids are converted into acetate, hydrogen gas and carbon dioxide by acetogenic bacteria. These bacteria require a low H2 partial pressure in order to conserve energy for growth. The end products are also formed during the acidogenesis phase, but complete acid breakdown is achieved during acetogenesis in preparation for the formation of biogas through methanogenesis [94, 103]. The main product of acetogenesis, acetate, is the most important compound produced during the fermentation stage of the digestion process, because approximately 70% of methane arises in the process of acetates reduction. Consequently, acetates are a key intermediate product of the process of methane digestion. In the acetogenesis phase approximately 25% of acetates are formed where approximately 11% of hydrogen, produced in the wastes degradation process [102, 103]. The following equations shows the breakdown of propionic and butyric acids to form methane. The first step represents the actions of acetogenic bacteria, while the second step is seen during methanogenesis [103].

Breakdown of propionic acid:

Step 1 - acetogenesis

$CH_3CH_2COOH + 2\ H_2O \longrightarrow CH_3COOH + CO_2 + 3\ H_2$ (2.5)

Step 2 - methanogenesis

$CH_3COOH \longrightarrow CO_2 + CH_4$ (2.6)

Breakdown of butyric acid:

Step 1 - acetogenesis

$CH_3CH2CH_2COOH + 2\ H_2O \longrightarrow 2\ CH_3COOH + 2\ H_2$ (2.7)

Step 2 - methanogenesis

$CH_3COOH \longrightarrow CO_2 + CH_4$ (2.8)

2.2.3.4 Methanogenesis

Methanogenesis is also known as methane/methanogenic phase is the last stage of anaerobic digestion. During this stage, the end products of acetogenesis are converted to methane and carbon dioxide by methanogenic microorganisms [80, 90] . Methanogenic microorganisms are the most sensitive to oxygen among known bacteria, and are therefore the most strictly anaerobic [103]. There are several types of methanogenic bacteria. These bacteria are classified according to their structure, substrate utilisation, types of enzymes produced, and the temperature range associated with growth [97].

Methane in this stage can be produced in two ways: either by means of cleavage of acetic acid molecules to generate 70 % of methane and carbon dioxide, or by reduction of carbon dioxide with hydrogen to yield 27-30 % methane and water [104]. The reaction that takes place in this process of methane production is called methanisation and expressed by the following equation [99]:

Acetate conversion:

$$2CH_3CH_2OH + CO_2 \leftrightarrow 2CH_3COOH + CH_4 \quad (2.9)$$

Followed by: $CH_3COOH\ CH_4 + CO_2$

Methanol conversion:

$$CH_3OH + H_2 \leftrightarrow CH_4 + H_2O \quad (2.10)$$

Carbon dioxide reduction by hydrogen

$$CO_2 + 4H_2 \leftrightarrow CH4 + H_2O \quad (2.11)$$

2.2.4 Conditions and variables influencing AD

For an optimum operation of the anaerobic digestion, numerous parameters must be taken into consideration and be controlled. Consequently, a rapid change in one parameter of an anaerobic digestion system can initiate a chain reaction of effects that may eventually lead to inhibition of the digestion process. For instance, when methanogenic bacteria are not operating properly, acid build-up is seen in the digester [103]. The complete microbial metabolism processes requires a complex interaction of several varieties of bacteria that must be in equilibrium in order for the digester to remain stable [105]. In anaerobic digestion, the acid forming and the methane forming microorganisms differ widely in terms of physiology, nutritional needs, growth kinetics, and sensitivity to environmental conditions. Failure to maintain the balance between these two groups of microorganisms is the primary cause of reactor instability [106, 107, 108].

To enhance the microbial activity and thus increase the anaerobic degradation efficiency of the system, the following must be monitored and maintained within acceptable ranges: pH, temperature, C/N ratio, retention time, volatile fatty acids VFA**,** bacterial competition, nutrient content, the presence of toxicants and solids content. The optimal ranges and importance of these parameters are discussed below.

2.2.4.1 Operating Temperature

Operating temperatures are an important factor determining the performances of the AD reactors because it is an essential condition for the survival and optimum thriving of the microbial consortia**.** There is a linear relationship between the temperature and the rate of metabolic reaction during AD [109]. It is well known that there are three ranges of anaerobic degradation temperatures: degradation at ambient temperature (psychrophilic range) at 0-20 °C, mesophile degradation at 33-40 °C and

thermophilic degradation at 50-60 °C. Typically, temperature ranges that are at a higher temperature, decomposition will take place quickly. Technically, only the mesophilic and thermophilic range is interesting with optimum at 35 °C and 55 °C, respectively, since at the ambient temperature the anaerobic degradation is extremely slow [110, 111]. It has been observed that higher temperatures in the thermophilic range reduce the required retention time. In fact, the greater gas production can be obtained if a digester operates in thermophilic conditions as shown in Figure 2-14 [112]. However, this is rarely performed because the energy requirement in maintaining the temperature is more expensive than the biogas yields. Moreover, the thermophile bacteria are more sensitive than that of mesospheric bacteria, so higher costs are needed to control the temperature in the thermophilic range [113,114]. Bolzonella, *et al.* [115] reported that all digestion plants were initially operated at mesophilic temperatures. Therefore, it was recommended to preserve digestion system at mesophilic level, in order to maintain the feasibility of utilising AD to produce alternative source of renewable fuel [116].

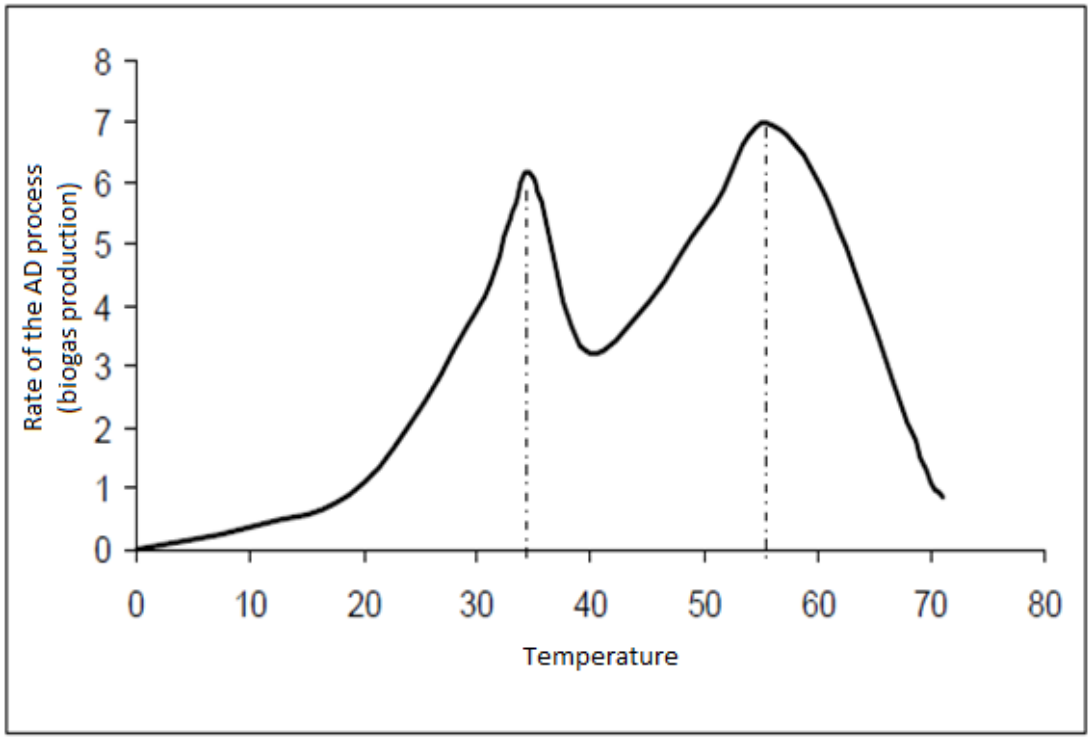


Figure 2-14: Temperature range for anaerobic digestion.

2.2.4.2 pH value

The pH value of the digester content is an important parameter and again must be monitored and maintained for success and the stability of an anaerobic digestion process. A falling pH can point toward acid accumulation (VFA) and digester instability [105]. The pH and VFA are linked to each other but their relation depends on the waste composition that may differ from the type of waste and the environmental conditions of anaerobic digestion process [117]. Different microorganisms within the digest have different optimum pH values, but the most important of these are the methanogens. The methanogenic bacteria are extremely sensitive to pH in the reaction. When the pH value deviates from the optimum range for the methanogens, this results in a greater decrease in methanogenic activity, which leads to a build-up of acetogenesis end products [118]. It has been determined that an optimum pH value for AD lies between 5.5 and 8.5 [96]. Lay et al (1998) mention that most anaerobic bacteria including methane_forming bacteria function in a pH range of 6.5 to 7.5, but optimally at a pH of 6.8 to 7.6, and the rate of methane production may decrease if the pH is lower than 6.3 or higher than 7.8 [119]. Zhang et al, (2005) [120] reported that an anaerobic digestion of kitchen wastes with controlled pH value at 7.0 resulted in a relatively high rate of hydrolysis and acidogenesis with about 86 % of total organic carbon TOC and 82 % of chemical oxygen demand COD were solubilized.

2.2.4.3 Volatile fatty acids (VFA)

VFA are intermediate compounds (acetic HAc, propionate HPa, ethanol Het, lactate LA and butyric HBu) that are produced during acidogenesis. Volatile fatty acids can be inhibitory to the production of methane. The increased concentration of acid exhibits the effect of fermentation digestion [121, 122]. Hydrogen plays a significant role in preventing the formation of methane if the accumulation of acids is uncontrolled. The high concentration of VFA will decrease the overall pH value and indirectly disrupt the fermentation process. AD processes will not work below a certain pH value as mentioned above [123,124]. It has been shown that fermentation of glucose is inhibited at total VFA concentrations above 4 g l−1 [125]. Acetic acid is usually present in higher concentrations than other fatty acids during anaerobic digestion [121]. As shown in many studies, the conversion rates of VFAs to methane

vary in the order of acetic acid HAc > ethanol (HEt) > butyric acid (HBu) > propionic acid (HPa) [126]. Lactic acid, which has the potential to be converted to HPa, is an undesirable terminal fermentation product. Therefore, accumulation of HPa always results in failure of methanogenesis [127]. Y. Wang *et al.* [122] mention that when the highest concentrations of ethanol, acetic acid and butyric acid were 2400, 2400 and 1800 mg L^{-1}, respectively, there was no significant inhibition of the activity of methanogenic bacteria. However, when the propionic acid concentration was increased to 900 mgL^{-1}, significant inhibition appeared, the bacteria concentration decreased from 6 x 10^7 to 0.6–1 x 10^7 mL^{-1}.

2.2.4.4 Carbon to Nitrogen Ratio (C/N).

The relationship between the amount of carbon and nitrogen present in organic materials is represented by the C/N ratio. A high C/N ratio is an indication of rapid consumption of nitrogen by methanogens and results in lower gas production. On the other hand, a lower C/N ratio causes ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogenic bacteria [128]. Optimum C/N ratios in anaerobic digesters are between 20 – 30 in order to ensure sufficient nitrogen supply for cell production and the degradation of the carbon present in the process, and in order to avoid at the same time excess nitrogen, which could lead to toxic ammonium concentrations [129]. Thus, the optimum C/N ratios of the digester materials can be achieved by mixing materials of high and low C/N ratios, such as organic solid waste mixed with sewage or animal manure [105].

2.2.4.5 Effect of toxicity on digestion

Toxic compounds affect digestion by slowing the rate of metabolism at low concentration, or by poisoning or killing the organisms at high concentration. The methanogenic bacteria are generally the more sensitive, although all groups involved in digestion can be affected. In order to control and adjust operation, to minimise toxic effects, it is important to identify inhibition in its early stages. The two main indicators of inhibition are [130 ,131]:

- Reduction in methane yield, indicated by two or more consecutive decreases of more than 10% in daily yield at a constant loading rate;

- Increase in volatile acids concentration, generally occurring when the total volatile acid (expressed as acetic acid) exceed the normal range of about 250 to 500 ppm (mg/L).

The major toxicants usually encountered with natural feedstock are ammonia, Hydrogen sulphide, volatile acids, and heavy metals.

Ammonia (NH3) is derived from digestion of protein during the hydrolysis step in AD process. NH3 is an important source of nutrients for growing plants, thus this compound can be used as fertilizers [109]. High concentration of ammonia is toxic or inhibitory to anaerobic microbial populations, methanogens [132].

Hydrogen sulphide (H2S) originates from the primary raw materials such as silage and sewage sludge, in which high concentration of sulphide is present. If sulphide concentration is the dominant composition during the AD process, it may avoid biomethanization in favour of sulphide production. Sulphide is important in the production of sulfur amino acids in bacteria and it also acts as a chemical reducing agent allowing growth of anaerobic microorganisms [109].

Heavy metals can be present in significant concentrations in municipal sewage and sludge. The heavy metals identified to be of particular concern include chromium, iron, cobalt, copper, zinc, cadmium, and nickel. Advantages of heavy metals are that, unlike many other toxic substances, they are not biodegradable and can accumulate to potentially toxic concentrations. The concentration of these heavy metal ions must be kept low, in order to maintain the growth of certain bacteria and to support methanogenesis [106,109].

Nutrients are also essential for the growth of bacteria. Municipal wastewater sludge usually contains all the nutrient quantities that is require for optimal growth. These macronutrients are carbon, nitrogen, phosphor and sulphur. The optimal ratio for (C:N:P:S) is considered 600:15:5:1. Nutrients must be sufficient to maintain the growth of bacteria. Insufficient elements and nutrients may lead to inhibition effect and cause disruption to AD process [109].

2.2.4.6 Organic loading rate (OLR).

The organic loading rate (OLR) is the quantity of organic matter fed per unit volume of the digester per unit time, (e.g., Kg VS m-3 d-1). OLR plays an important role in anaerobic wastewater treatment in continuous systems and is a useful criterion for assessing performance of the reactors. A higher OLR feed rate may cause crashing of anaerobic digestion if the acidogenic bacteria multiply and produce acids rapidly. Many industrial plants have reported system failures due to overloading. Maximum OLR for an anaerobic digester depends on a number of parameters, such as reactor design, wastewater characteristics, the ability of the biomass to settle, and activity among others [133].

2.2.4.7 Retention time

The Hydraulic Retention Time (HRT) is the time needed to achieve the complete degradation of the organic matter. The retention time varies with process parameters, such as process temperature and waste composition. The retention time for waste treated in a mesophilic digester ranges from 15 to 30 days and 12-14 days for thermophilic digester [90 and 128]. Reducing HRT reduces the size of the digester, resulting in cost savings. Therefore, there is an active incentive to design a system that can achieve a complete digestion in shorter HRT. A shorter HRT will lead to a higher production rate per reactor volume unit, but a lower overall degradation. These two effects have to be balanced in the design of the full-scale anaerobic digester [96].

2.2.4.8 Mixing

The objective of mixing in a digester is to improve the contact between the microorganisms and substrate. Mixing distributes the heat and bacteria uniformly in the digester; furthermore, mixing prevents scum formation and avoids temperature gradients within the digester. However, excessive mixing can disrupt the microbes thus slow mixing is preferred [128], also Alastair et al., [11] noted that evidence suggests that minimal mixing in the digester is preferable unless there is some form of microbial support material used which prevents the loss of active microbial biomass. However, the optimal mixing pattern is still a topic of debate. Mixing can be achieved through several methods, including mechanical mixers, recirculation of

digester contents, or by recirculation the produced biogas to the bottom of the digester using pumps [134].

2.2.5 Improvement of the biogas process

Biogas process optimisation through better monitoring and control is one way of improving process efficiency [135]. Other ways or strategies can be through pre-treatment of the substrate to release more biodegradable compounds (see section 2.2.2.1), co-digestion strategy, or combined pre-treatment and co-digestion strategies. This will limit the inhibition from the substrate and enhance the biogas production.

2.2.5.1 Co- digestion strategy

In general, co-digestion refers to the anaerobic digestion (AD) of multiple biodegradable substrates (feedstock) in an AD system. The idea of co-digestion offers several possible ecological, technological and economic advantages, so it can improve organic waste treatment through anaerobic digestion [136]. Co-digestion with other wastes, whether industrial (glycerin), agricultural (fruit and vegetable wastes) or domestic (municipal solid waste) has been successfully option for improving biogas production [137] and [138].

Co-digestion can therefore improve the profitability of biogas plants. In addition, co-digestion of animal manure and slurry with suitable organic wastes from food industries utilise the huge amounts of organic wastes that are produced annually and in many places otherwise dumped into landfills [139]. In some countries, such residues are spread to land without any further treatment. Examples of direct land spreading of organic residues from sugar refining, drinks manufacture, fruit and vegetable processing etc. are given by Davis and Rudd (1999) [140], Gendebien, et al. (2001)[141]. However, when these residues are digested in a biogas plant they will yield not only their fertiliser value but also renewable energy

2.2.5.2 Combined pre-treatment and co-digestion

Besides adding co-substrates, pre-treating substrates using various pre-treatment methods prior to anaerobic digestion has also been reported as a potential approach to improve biogas production efficiency [142]. Neves et al., found out that when the

waste was subjected to alkaline hydrolysis pre-treatment before co-digestion with activated sludge, the methane production increased 67%, while, if co-digested with kitchen waste, the methane production increased 61% [143]. In this work the new mechanical pre-treatment (Beating treatment) will be used to treat the main substrates (maize silage, fresh grass, and potato waste) then will be co-digested with digested sludge.

2.2.6 Biogas properties

Biogas is regarded as the most important product of fermentation digestion. Biogas is a flammable gas and the quality of which is defined by its composition. Biogas consisting of primarily of CH4 and CO2. Additionally, small traces of other gases Nitrogen (N2), Hydrogen (H2), Hydrogen sulphide (H2S), ammonia (NH3), Oxygen (O2) and water vapour (H2O). Jönsson et al 2003 [29], pointed out that once biogas is produced it usually contains 55% to 65% methane, 35% to 45% carbon dioxide and <1% nitrogen from sewage digesters, biogas from organic waste digesters usually contains 60% to 70% methane, 30% to 40% carbon dioxide and <1% nitrogen while in landfills the methane content is usually 45% to 55%, 30% to 40% carbon dioxide and 5% to 15% nitrogen. Table 2-3 contains some average biogas composition values, found in most of the literature conducted by T. A. Seadi et al 2008 [101].

Table 2-3: Composition of biogas

Compound	Chemical symbol	Content (Vol.-%)
Methane	CH4	50-75
Carbon dioxide	CO2	25-45
Water vapour	H2O	2 (20°C) – 7 (40°C)
Oxygen	O2	<2
Nitrogen	N2	<2
Ammonia	NH3	<1
Hydrogen	H2	<1
Hydrogen sulphide	H2S	<1

2.2.7 Current application of AD technology on an industrial scale

There has been interest in recent years in biological treatment of Municipal solid waste. In the year of 2009 it has been estimated that about 240 anaerobic digestion plants around the world operating of capacity over 2,500 metric tonnes of organic waste per year. The total installed capacity of these plants is over 11 million metric tonnes per year [144]

In Europe, and due to waste and energy policies, (e.g., The Landfill Directive) the anaerobic digestion technology is well established and increased in the last decade. By the end of 2006, there were some 124 anaerobic digester plants with capacity greater than 3,900,000 tonnes per year. While the first assessment carried out in 1999 indicates that there were about 53 AD plants have been identified which meet the criteria, with a total installed capacity of 1,037,000 tonne per year up to the year 2000. In essence, this means doubling of the number of plants and almost quadrupling of the capacity installed over a period of 6 years [145]. This excludes thousands of manure and sludge digesters that co-digest smaller amounts of food and household wastes or energy crops, for instance in Germany, the number of digesters using energy crops has increased from about 100 in 1990 to nearly 4,000 in 2008 (Figure 2-15) [144]

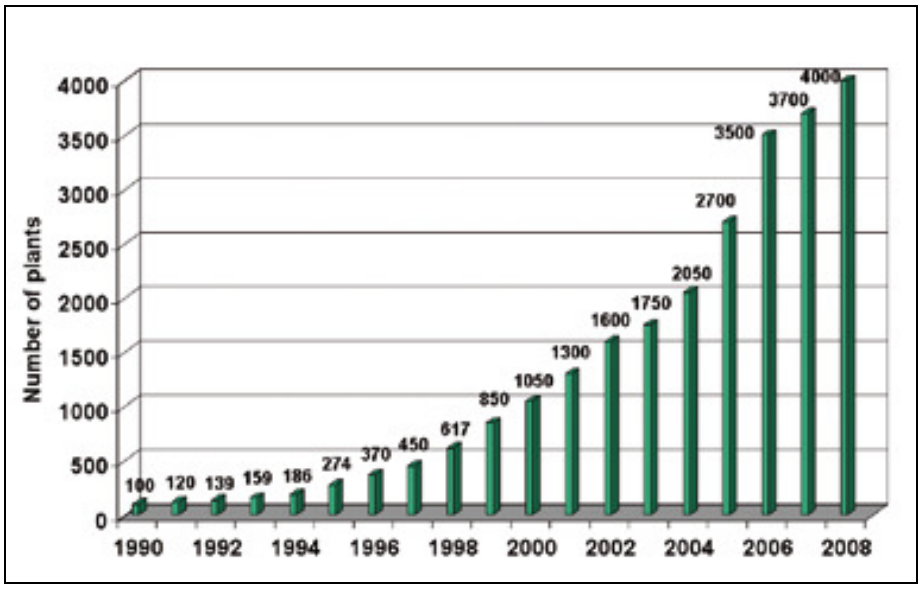


Figure 2-15: Number of biogas plants in Germany.

2.2.8 Advantages of anaerobic digestion process.

Some advantages of the AD process can be summarised in the following:

- AD contributes to reducing the greenhouse gases. A well-managed AD system will aim to maximise methane production without release any gases to the atmosphere, thereby reducing overall emissions [90];
- The feedstock for AD is a renewable source, and therefore does not deplete finite fossil fuels [90];
- The slurry produced (digestate) is an improved fertiliser in terms of both its availability to plants [11]
- AD leads to a reduction up to 80% of the odour associated with animal slurries, included volatile compounds that are oxidatively decomposed upon combustion, e.g. H_2S forms SO_2 [90].
- On a financial aspect, the advantage of AD is to convert residues into potentially saleable products: biogas, soil conditioner, liquid fertilizer [90].
- Successful in treating wet wastes of less than 40% dry matter [146].
- AD destroys a wide range of pathogenic and faecal micro-organisms [147].

2.3 Mechanical pre-treatment

Mechanical pre-treatment is aimed at reducing the particle size and crystallinity of the substrate thus increasing the digestibility of cellulose and hemicellulose in the biomass material. This increases the digestion performance and biogas yield [148]. Mechanical pre-treatment methods are included grinding, ultrasonic treatment, high pressure homogeniser, collision plate and lysis-centrifuge.

2.3.1 Grinding

The predominantly used pre-treatment technique is milling, or more specifically a grinding technique. The aim of milling is to improve susceptibility of enzymatic hydrolysis by reduction of particle size and crystallinity of lignocelluloses in the material, These parameters lead to the increase of the total hydrolysis yield by 5–25 %, but also reduce the digestion time by 23–59%, thus increasing the digestion efficiency and biogas yield [149, 150, 22]. Several milling technologies were experimented with ranging from, mechanical chopping, hammer milling, roll

milling, colloid mill, vibratory milling and ball milling [148, 150]. All these techniques have increased surface area and confirm successes as a low cost pre-treatment strategy [148,151], It has been reported that the ball mill is the best performing and the most common form of milling treatment, though many disadvantages make it not economically feasible for large-scale applications, especially due to high energy requirements, long process times, and feed rate of material [152].

Ball mills consist of a cylindrical chamber (vertical or horizontal) which is almost completely filled with grinding beads by diameter (0.2–0.25 mm) into the agitator disc that generate kinetic energy to small beads in the chamber, this energy creates shear forces and compression loading between the grinding agents to break the cell walls (see Figure 2-16) [166, 153, 154 , 155].

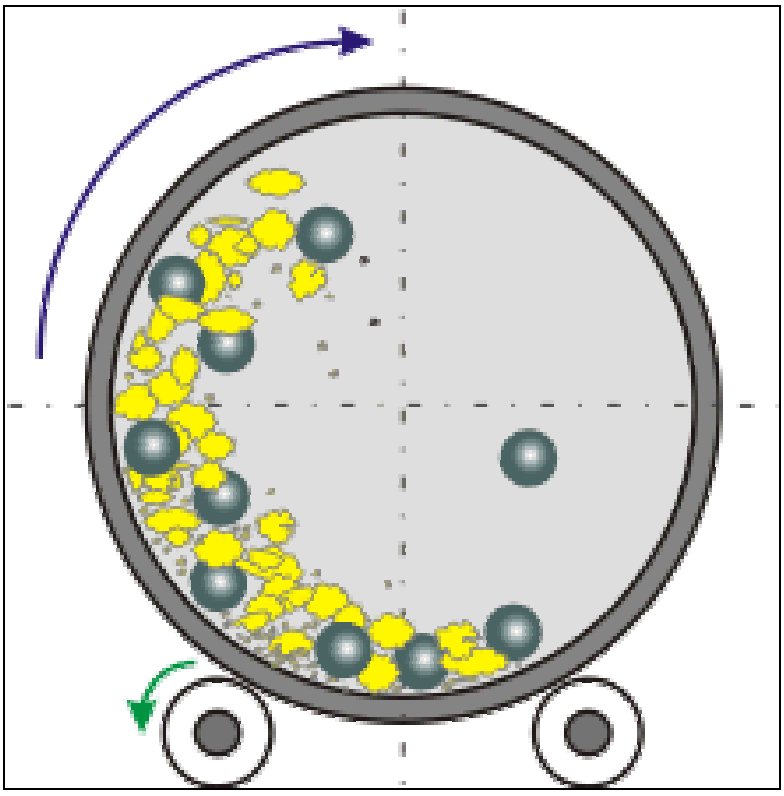


Figure 2-16: Horizontal section of ball mill [156].

The size of the substrate is usually 0.2-2 mm after milling or grinding [157], while extremely reducing the size of the substrate this has little effect on the hydrolysis rate of the biomass. It is caused by the accumulation of volatile fatty acid (VFA),

resulting in decreased methane production and decreased solubility in the anaerobic digestion process [158, 23]. The energy requirement for mechanical commination depends on the final particle size and materials characteristics and can be one of the most important parameters describing the economical side of this physical pre-treatment [152 , 159].

Mshandete *et al.* [160] used sisal fibre waste and found a reduction in grinding to 2 mm particle size using a laboratory mill with 2 mm sieve and demonstrated that smaller particles increased the surface area available to the microorganisms. This resulted in increased food availability to bacteria; thus, anaerobic biodegradability increases and mentioned that the methane yield increased by 23% with decreasing particle size from 100 mm to 2 mm and the fibre degradation increased from 31% to 70%. Izumi *et al.* [158] studied grinding pre-treatments on food waste by a bead mill process and found that particle size of the substrates decreased from 0.843 to 0.391 mm, respectively, at 20,000 total revolutions where methane production increased by 28% when the particle size was decreased from 0.888 to 0.718 mm. Kratky *et al.* [152] pointed out that Koullas reported the dependence of process time on the hydrolysis effectiveness for wheat straw. The results of this work demonstrated that the conversion of saccharides for untreated straw was 17.7% and after ball milling with a process time of 2 h there was an increase in conversion up to 61.6%. Baier *et al.* [161] reported that during anaerobic digestion of sludge, which had been disintegrated by stirred ball mills by diameter 0.25 mm, grinding was more beneficial on digested sludge (increase of batch biogas production by 60%).

J. Lindmark et al [162] explore the use of two types of mechanical treatment equipment originally built for the pulp and paper industry, the Grubben Deflaker (GD) and the Krima Disperser (KD), for pre-treatment of ley crop silage, and the effect of these treatments on the biogas potential. They describe the full-scale pre-treatment and the laboratory experiments used to evaluate the results. They found that methane production increased by 59% and 43% respectively after grinding with GD and KD. They indicate that in both treatments, 90% of the ley crop was ground to particles of less than 2 mm and more than 50% of the sample was reduced to particles smaller than 0.125 mm. also they pointed out that the energy balance was positive for GD and around the break-even point for KD.

2.3.2 Ultrasonic treatment.

The major effect of ultrasonic treatment is in the disruption of the physical, chemical and biological properties of sludge, reduction of floc size, and biodegradability improvement. So, an ultrasonic pre-treatment of sludge could increase sludge biodegradability through enhancing the hydrolysis stages and thus leads to enhanced anaerobic digestion [163,164]. The ultrasound treatment is cyclic sound pressure (compression and rarefactions) with low frequencies (20–40 kHz); these frequencies are common and extremely efficient in generating high-frequency waves. When these ultrasound waves propagate in sludge medium, it generates a repeated pattern of compressions and rarefactions in the medium. The compressions cycle makes positive pressure on the liquid by pushing the molecules together and the rarefaction cycle makes a negative pressure by pulling the molecules from one another. Micro bubbles (cavitations) are generated from large negative pressure in a rarefaction region. As a result of alternating expansion and compression cycles, these bubbles expand and implode, at very extreme conditions of temperature (5000 K) and pressure (500 bar) (see Figure 2-17) and produces hydro mechanical shear forces, rupturing the cell wall and membranes [163, 165 , 166, 167].

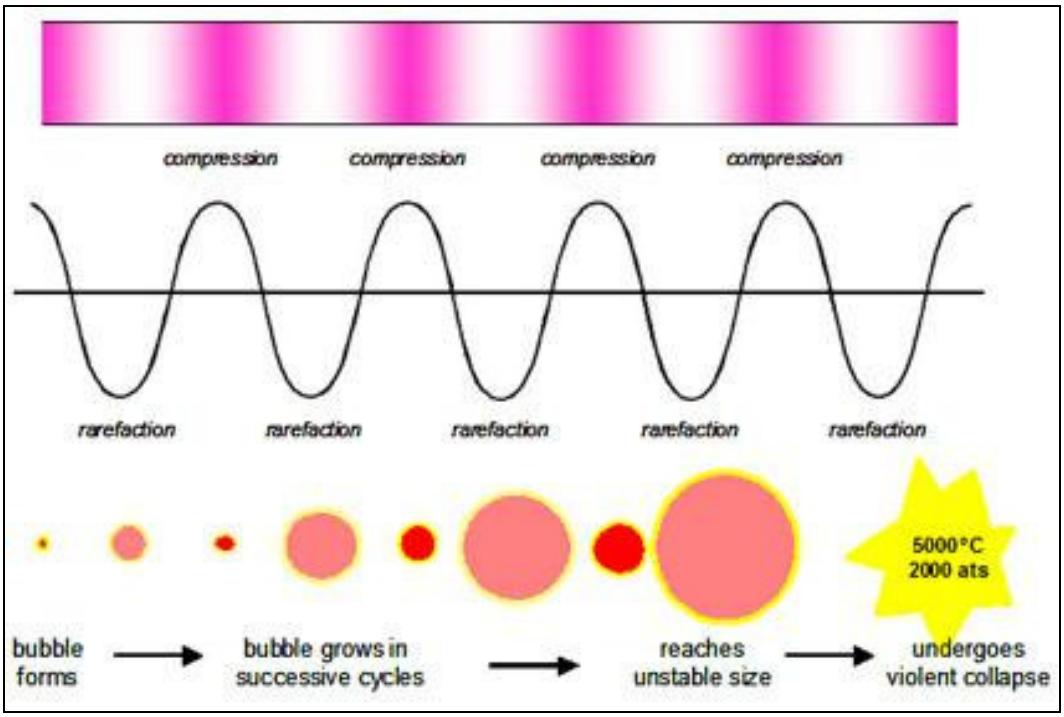


Figure 2-17: The illustration shows how a cavity builds up successively until it implodes [168].

Kameswari *et al*., observed that during the optimum contact times of 2 and 1 min, increases in the soluble chemical oxygen demand COD of 85 and 97% were observed for the primary and the secondary sludge samples using ultrasonication where it was observed that, during 6 weeks of residence time The increase in biogas generation was observed for ultrasonicated pre-treated primary and secondary sludge along with fleshings was 53% [167].

2.3.3 High pressure homogeniser

A high pressure homogenizer is one of most widely used methods in large-scale operations; disruption in this method is worked out through pumping the sludge under high pressure (400-900 bar) through a homogenising valve at high velocity against an impaction ring with a decrease in pressure, (See Figure 2-18) this will generate intense energy which lead to the formation of cavitation bubbles [166, 155, 169, 170] . Rai *et al.* [171] studied the disintegration of sewage sludge by employing high-pressure homogenisers with disk valves from 150 to 750 bar, they found out that the degree of disintegration increased to 29% and increasing in particle size reduction was observed. Engelhart *et al.* [172] studied the effects of mechanical disintegration (by a high-pressure homogenizer) on anaerobic biodegradability of sewage sludge. A 25% increase in volatile solids where a reduction was achieved, also resulting in a higher specific biogas production. Onyeche *et al.,* [173] conducted mechanical disruption by using a high-pressure homogeniser for sewage sludge at 500 bar where it was demonstrated after 20 days, improved anaerobic digestion could be realised thereby increasing the biogas production.

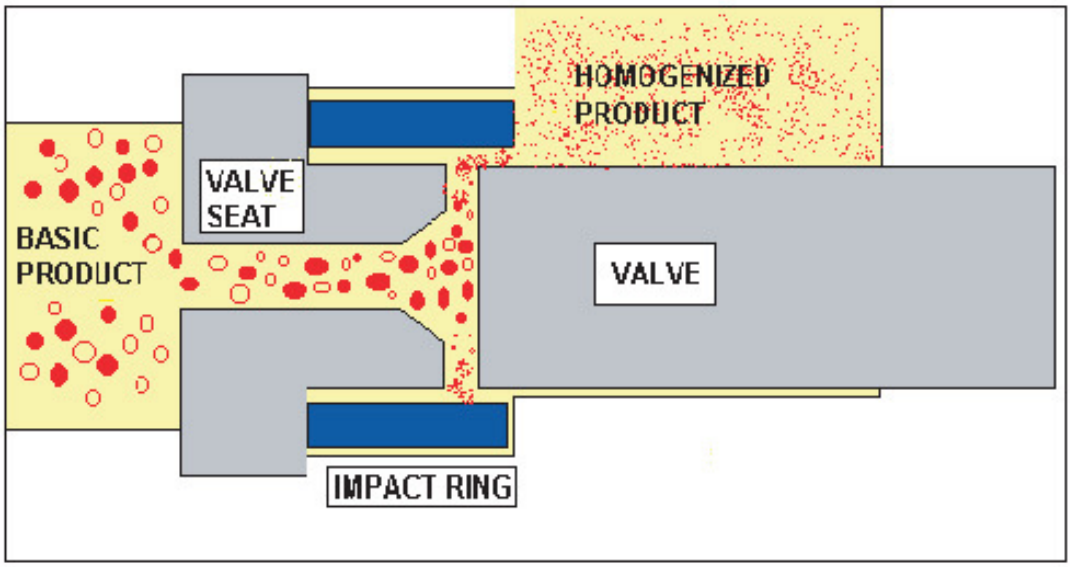


Figure 2-18: Cross-section of high pressure homogeniser [170].

2.3.4 Collision plate

This technique is commonly used in the treatment process of wastewater, where sludge is pressurised to 30–50 bar by a high pressure pump and jetted to the collision plate after going through a nozzle (see Figure 2-19). Thus, sludge undergoes a rapid depressurisation and then jetted on to a plate with velocities of 30–100 ms-1. This process has only been applied at laboratory scale and allowed to decrease in Hydraulic Retention Time (HRT) from 14 to 6 days without affecting anaerobic digestion performance [28]. Nah *et al.* [174] examined the mechanical pre-treatment of Waste Activated Sludge (WAS) and determined that jetting to and colliding with a collision plate at 30 bar to solubilize the sludge, thus enhanced volatile mass reduction to 30% and unit gas production and decrease the anaerobic digester SRT from 13 to 6 days.

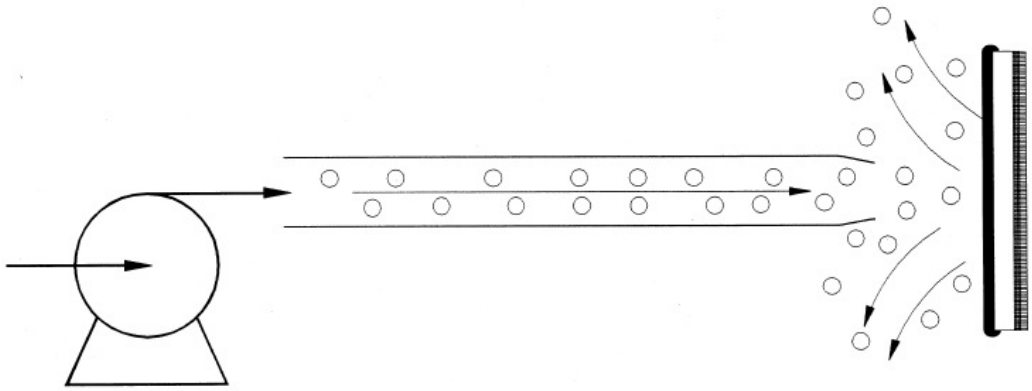


Figure 2-19: Schematic diagram of the Collision plate mechanical pre-treatment of WAS [174].

2.3.5 Lysis-centrifuge.

Lysis-centrifuge works by directly operating on the thickened sludge stream in a dewatering centrifuge. The goal of this method is the partial disintegration of cells during the thickening with the centrifuge through kinetic energy generated by the centrifuge without any additional energy [154] (see Figure 2-20). Zabranska *et al.* [175] proved that anaerobic digestion of sewage sludge could be improved by this process, organic matter in digested sludge significantly decreased to 48-49% and an increase in biogas production by 15–26%. In similar studies, Delgenés *et al.* [154] mentioned that Dohanyos *et al.* [176] reported the improvement of methane yield from thickened activated sludge, in comparison with untreated activated sludge, was 84.6%. The extent of increase in methane production was found to depend on sludge age and the content and type of organic material in mixed raw sludge, and the hydraulic retention time in digesters [175,177].

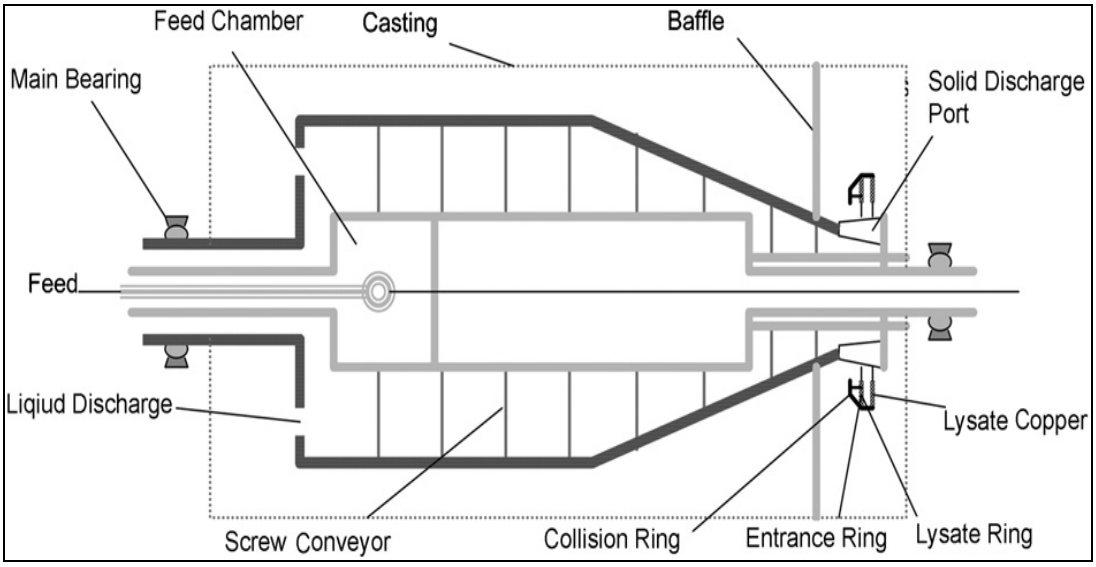


Figure 2-20: Schematic of a lysate-thickening centrifuge [166].

Chapter 3

HOLLANDER BEATER AND DESIGN OF EXPERIMENT

3.1 The new mechanical treatment (beating treatment)

In Chapter 2, the most up to date, mechanical, pre-treatment techniques used to treat substrates to enhance anaerobic digestion processes were discussed. The work in this project, based on this idea, introduces a new mechanical treatment technique by employing a Hollander Beater device to treat cellulosic and lignocellulosic material. This in turn has been designed to improve biogas production through the anaerobic digestion process. This device was invented in the 1860s, and until now has been used for paper manufacturing processes. To the best of our knowledge, no literature covers the Hollander beater used as a tool for mechanical treatment to enhance biogas production. Contributing to this device (Hollander beater) we call this method the "Beating Treatment" method. Beating lignocellulosic materials will result in decreases in particle size of the lignocellulosic materials and increase the surface area; this will damage and change their structural components, thus improving rate of hydrolysis and methane yield

3.1.1 Hollander beater device (Reina beater)

The Reina beater is a traditional style beater whose harks back to the paper beaters made in Holland in the 1860s. The beater (see Figure 3-1) consists of an ovoid raceway with a beater wheel placed at a single point along the raceway. The beater wheel is made up of a number of paddles mounted on a shaft. The beater wheel is similar in appearance to a water wheel. The model used in this work is 2lb. Reina beating which is the most popular model has been in production for 29 years. The ideal capacity of a beater for a paper manufacturing purpose equates to 2 lb of dry pulp running with 14 gallons (about 53 L) of water. For this propose, treating biomass to enhance biogas production to the dry substrate can be increased depending on the type of required digestion.

The motor of the beater is single phase, 1 h.per 60 cycle and 220 V, (Table 3.1 illustrates the technical specification of the beater).

Table 3.1: Technical specification of the Hollander Beater

Motor	1hp (746 watts)
	220v
	6.9 Amps
	1 Phase
	1450 rpm
V- Belt drive:	2.5: 1 Reduction
Drum Speed:	580 rpm
Tub Volume:	Maximum Capacity =90 litres
	working capacity = 40 litres
Drum diameter	200mm
Drum paddles	24 paddles

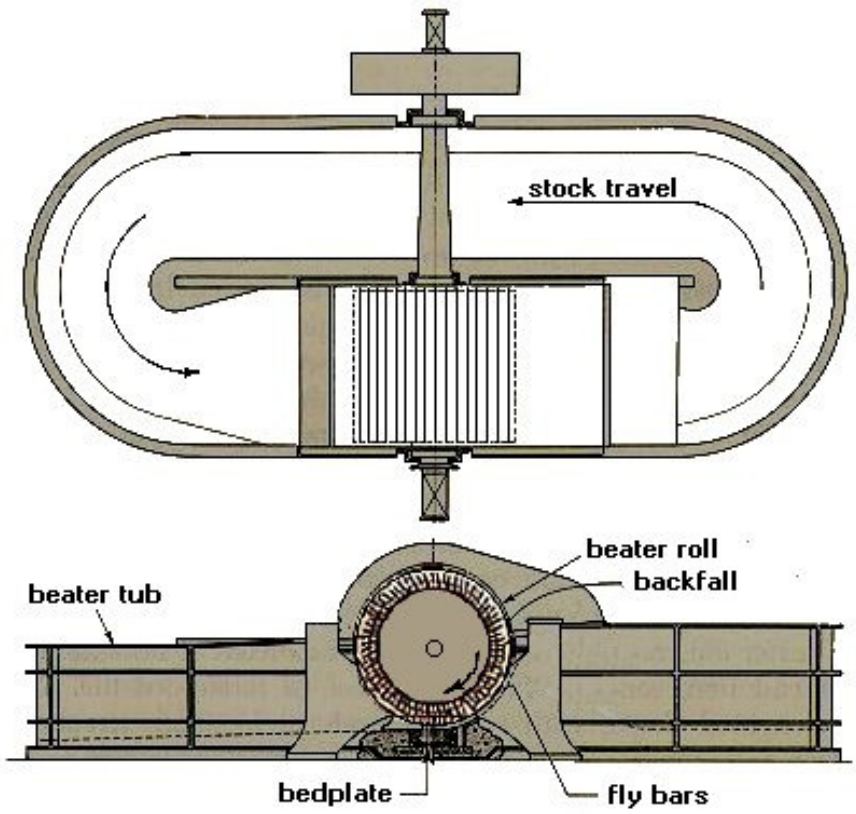


Figure 3-1: Hollander beater with the main parts illustrated and named [178].

3.1.2 The mechanism of technique

The beater has an adjustable beater roll with digital height indicator; by turning a hand wheel, the roll is raised and lowered. For precision, beating and the optimum distance between the roll and bedplate are determined. The digital height used in this beating treatment is “1”. The dial gauge has been used to determine digit 1 in terms of distance between beater roll (drum) and bedplate that was 75.00 micrometres (µm). By operating the beater, substrate (maize, maize silage, grass, grass silage, potato waste or any cellulosic material) will pass through the gap with water (see Figure 3-2), this results in decrease particle size of the substrate and increased surface area; the process also damages and changes the structural components of the substrate in terms of reduced cellulose crystallinity.

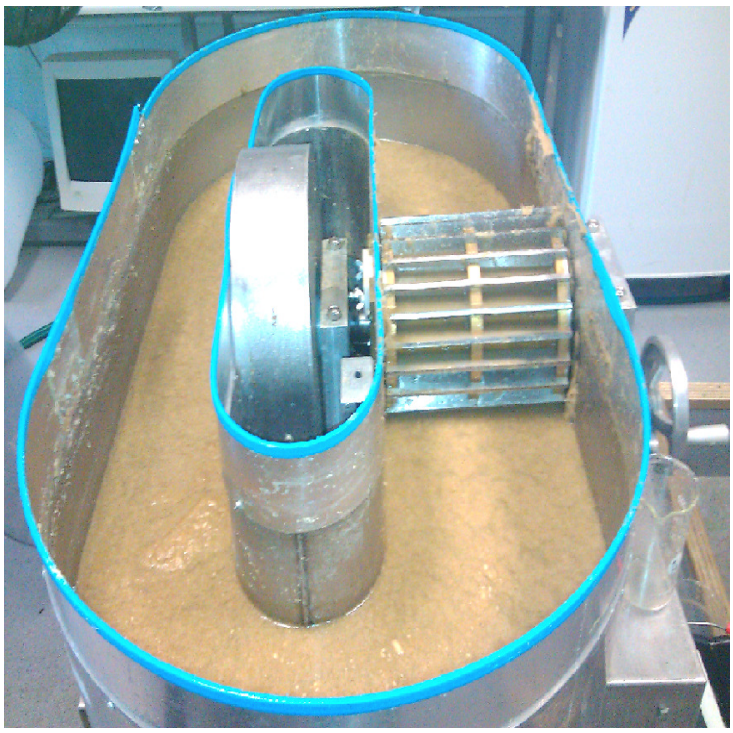


Figure 3-2 Beating treatment of lignocellulosic material

3.1.3 Dial gauge measurement

The dial gauge (also be known as a dial) is a device used to measure small, linear distances with accuracy and (or) to indicate linear movement [179]. The dial gauge is used to measure the gap between the steel bedplate and the blades (drum) where the real action happens. Figure 3-3 depicts the measurement process.

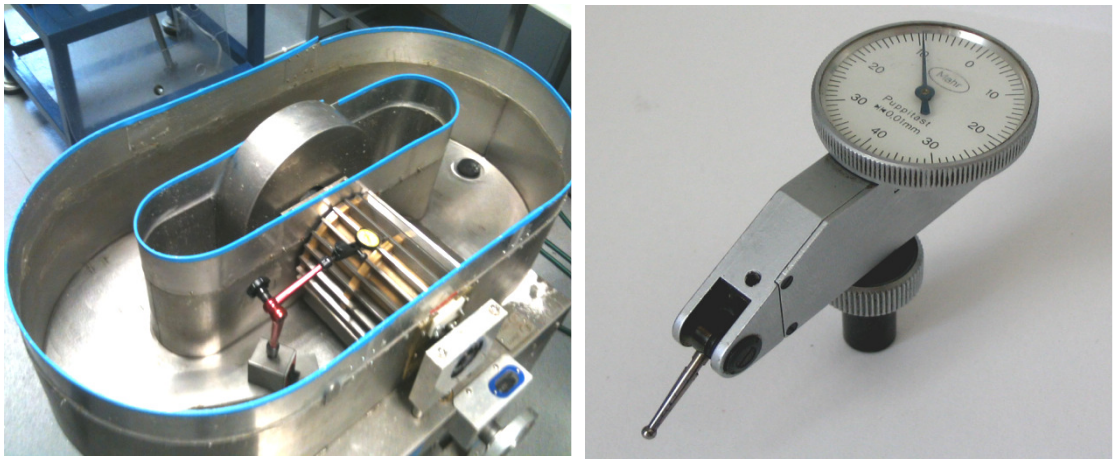


Figure 3-3 Dial gauge device used to calculate the gap between the drum and the bedplate.

3.2 Design of experiment DOE

The most common approach employed by engineers in many manufacturing companies is a One-Variable-At-a-Time (OVAT) approach, where they vary one variable at a time keeping all other variables in the experiment fixed. This approach depends upon guesswork, luck, experience and intuition for its success. Moreover, this type of experimentation requires large resources to obtain a limited amount of information about the process. Thus OVAT experiments are often considered as unreliable, inefficient, time consuming and may yield false optimum conditions in the process.

Design of Experiments (DOE) was developed in the early 1920s by Sir Ronald Fisher at the Rothamsted Agricultural Field Research Station in London, England. His initial experiments were concerned with determining the effect of various fertilizers on different plots of land. The final condition of the crop was not only dependent on the fertilizer but also on a number of other factors (such as underlying soil condition, moisture content of the soil, etc.) of each of the respective plots. Fisher used DOE that could differentiate the effect of fertilizer and the effect of other factors. Since then DOE has been widely accepted and applied in biological and agricultural fields [180]. DOE can be used to find answers in situations such as

"what is the main contributing factor to a system/process?", "what is the relationship between input (factors) and output (responses)?", "what is the best combination of factors values to minimise or maximise multi responses?" etc.

Design of Experiments (DOE) techniques enable designers to determine simultaneously the individual and interactive effects of many factors that could affect the output results in any design. DOE also provides a full insight of interaction between design elements; therefore, helping turn any standard design into a robust one. Simply put, DOE helps to pin point the sensitive parts and sensitive areas in your designs that cause problems in Yield. Designers then are able to fix them and produce robust and higher yield designs prior to any production stages.

3.2.1 Response surface methodology

Responses surface methodology (RSM) is the best-known type of DOE designs; the concept of RSM was introduced in the early 1950's by Box and Wilson [181]. RSM is a collection of statistical and mathematical techniques that can be used for developing, improving, and optimizing processes, products, and systems [182]. RSM also specifies the relationships among one or more measured responses and the essential controllable input factors [183]. Among the RSM designs, the two most popular types of experimental designs exist for developing second-order models: central composite design (CCD) and Box-Behnken design (BBD). In this work, CCD is used to build a mathematical model to predict and optimise the performance of anaerobic digestion of lignicellulosic material after beating treatment. The application of RSM in such case, where several input variables (factors) influence some performance measure or quality characteristic (response) of a process, can represent the relationship as:

$$y = f(x_1, x_2, \ldots x_k) \tag{3.1}$$

Where: k is the number of independent variables

To optimise the response "y", it is necessary to find an appropriate approximation for the true functional relationship between the independent variables and the response surface. Usually, a second order polynomial Eq.3.2 is used in RSM.

$$y = b_o + \sum b_i \chi_i + \sum b_{ij} \chi_i \chi_j + \sum b_{ii} \chi_{ii}^2 + \varepsilon \qquad (3.2)$$

Where b_o is the intercept or the free term, $b_i \chi_i$ are the linear terms, $b_{ii} \chi_{ii}^2$ are the quadratic terms, and $b_{ij}\ \chi_i \chi_j$ are the interaction terms of the polynomial model.

3.2.2 Central composite design (CCD).

The most popular RSM design is CCD; CCD has three associated groups of design points: two-level factorial or fractional factorial design points, axial points (sometimes called star points) and centre points. CCD's are designed to estimate the coefficients of a quadratic model. All point descriptions will be in terms of coded values of the factors [182, 184].

3.2.2.1 Factorial points.

The two-level factorial design part consists of all possible combinations of the +1 and -1 levels of the factors. In the two factor case there are four design points: (-1, -1) (+1, -1) (-1, +1) (+1, +1). In general, the number of factorial points equal to 2^k.

3.2.2.2 Star or axial points.

The star or axial points all have factors set to 0, the midpoint, except one factor, which has the value +/-α. For a case with two factors, the star points are: (-α, 0) (α, 0) (0, -α) (0, α). The value for α is calculated in each design for both rotatability and orthogonality of blocks. A design is rotatable if the variance of the predicted response, at any point x, depends only on the distance of x from the design centre points and a design is orthogonal if the effects of any factor balance out (sum to zero) across the effects of the other factors. The experimenter can choose values between these or enter different ones. The default value is set to the rotatable value and can be calculated by: $\alpha = (2^k)^{1/4}$. The number of star points is equal to 2k.

3.2.2.3 Centre points.

Centre points, as implied by the name, are points with all levels set to coded level (0) the midpoint of each factor range: (0, 0). Centre points are usually repeated 4-6 times

to get a good estimate of experimental error (pure error). These points are shown in Figure 3-4.

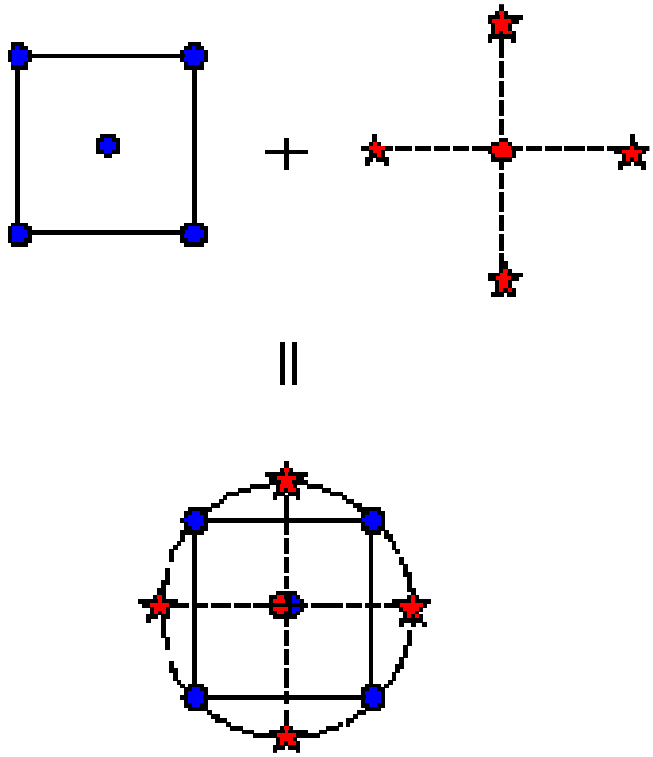


Figure 3-4 Generation of CCD for two factors [185].

3.2.3 Analysis for the design

The sum of squares of the model and each term is given by Eqs. 3.3- 3.9

Sum of Squares –total = $SS_T = \sum_{i=1}^{n} (y_i - \bar{y})^2$ (3.3)

Sum of Squares- model = $SS_M = \sum_{i=1}^{n} (\hat{y}_i - \bar{y})^2$ (3.4)

Sum of Squares –Residuals = $SS_R = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2$ (3.5)

Sum of Squares-Pure error = $SS_{PE} = \sum_{i=1}^{n_o} (y_i - \hat{y}_i)^2$, for centre points only (3.6a)

$$SS_{lof} = SS_R - SS_{PE} \quad (3.6b)$$

$$SS_{b_i} = b_i \sum_{i=1}^{n} x_i y_i \quad (3.7)$$

$$SS_{b_{ij}} = b_{ij} \sum x_i x_j y_i \quad (3.8)$$

$$SS_{b_{ii}} = b_0 \sum_{i=1}^{n} y_i + b_{ii} \sum_{i=1}^{n} x_i^2 y_i - (\sum y_i)^2 / n \quad (3.9)$$

3.2.4 Advantage of Central Composite Design.

1. Created from a 2-level factorial design, improved with centre points and axial points.
2. Normally has 5 levels for each factor, this can be modified to a face-centred CCD by choosing α =1.0. The face-centred design has only three levels for each factor.
3. Created for estimating a quadratic model.
4. Replicated centre point provides excellent prediction capability near the centre of the design space.
5. Region of operability must be greater than region of interest to accommodate axial runs.

3.2.5 General steps in RSM.

RSM is usually carried out as a problem that is considered in sequential steps. The following steps are performed in order to develop a mathematical model in the case of anaerobic digestion of lignocellulosic materials:

3.2.5.1 Identifying the critical process variables (or factors).

These critical factors may be defined from past literature or by conducting a preliminary study (i.e. screening study) based on factorial design or partial factorial

design. In a present case, vital process factors are determined from historically published articles. As mention in chapter 2, the factors influencing the anaerobic digestion process are many. Most of these factors are studied and has minimal optimum ranges. In this work pre-treatment (beating treatment) as a first stage of process has been combined with second stage (digestion stage) in one process. The process input factors considered here are: beating time and temperature.

3.2.5.2 Finding the limits of each factor.

To find the limits of each factor, the trial beating of lignocellulosic materials as main substrates in our work was performed for different times. The particle size of lignocellulosic materials was a criterion of selecting the range of beating time factor.

As the anaerobic digestion process was at a mesophilic range (30 – 40 °C) [186], thus a range of temperatures were selected inside this range. Design-Expert V7 software (see Figure 3-5) was used to code the data, develop the design matrix and analyse the case, the limits for each factor were coded via the following relationship: $X_I = 2(2X - (X_{max} + X_{min}))/ (X_{max} - X_{min})$. Where: X_i is the required coded value, X is any value of the factor that requires coding and X_{max}, X_{min} are the upper and lower limit of the factor being coded respectively [182].

3.2.5.3 Design matrix development.

The matrix depends on the type of RSM design selected, for CCD the design matrixes in coded values are shown in Table 3.2. As previously stated in some of the most current work carried out experimentally, the matrix for each experiment was developed using the same statistical software.

Table 3.2: Design matrix for CCD, coded values.

			Factor 1	Factor 2
Std	Run	Block	A: beating time	B: temperature.
			hour	deg. C
1	4	{ 1 }	-1	-1
2	10	{ 1 }	1	-1
3	7	{ 1 }	-1	1
4	13	{ 1 }	1	1
5	3	{ 1 }	-1	0
6	9	{ 1 }	1	0
7	12	{ 1 }	0	-1
8	8	{ 1 }	0	1
9	11	{ 1 }	0	0
10	5	{ 1 }	0	0
11	1	{ 1 }	0	0
12	6	{ 1 }	0	0
13	2	{ 1 }	0	0

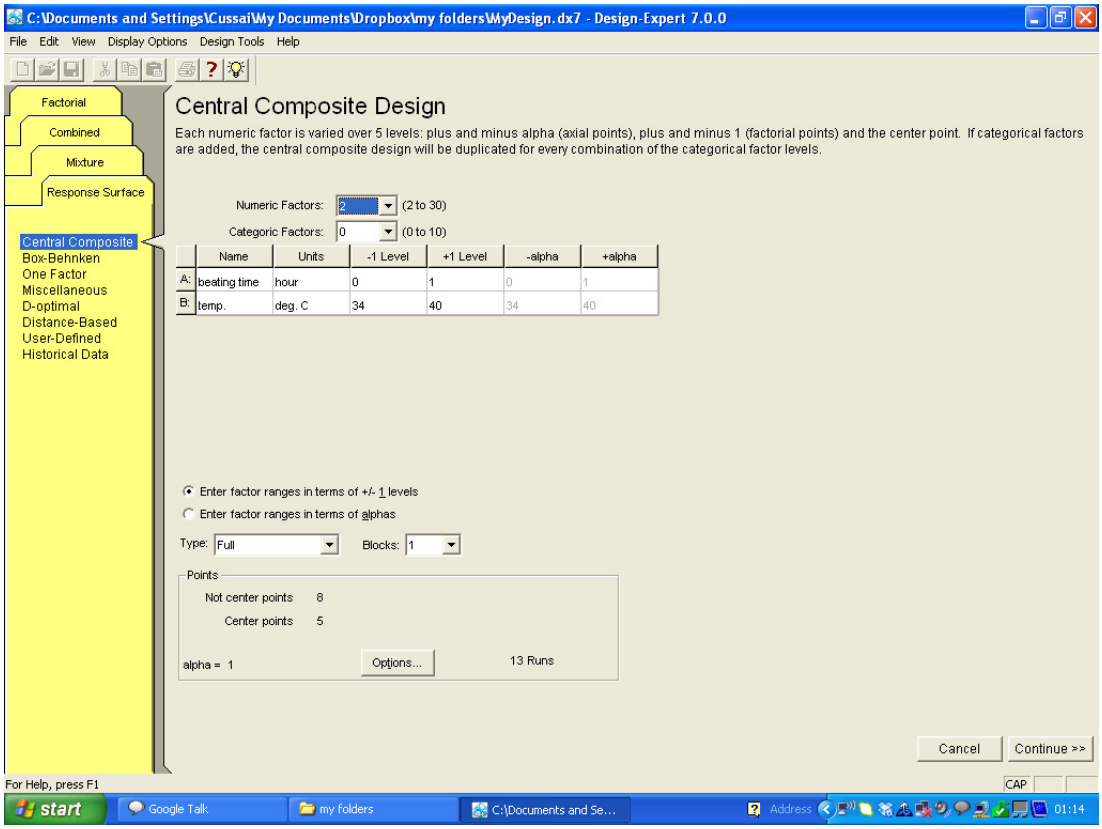


Figure 3-5 layout of Design Expert V7 software.

3.2.5.4 Performing the experiment.

The anaerobic digestion experiments were accomplished according to the design matrix, Table 3.1 and in a random order to avoid any systematic error in the experiment. All responses, mentioned earlier in chapter one, were measured and recorded for responses in all experiments and then used to develop the model.

3.2.5.5 Development of mathematical model.

The functional relationship representing any response of interest can be expressed as $y = f(t, T)$ and Eq. 3.2 becomes as follows:

$$Y = b_0 + b_1 t + b_2 T + b_{11} t^2 + b_{22} T^2 + b_{12} tT \qquad (3.10)$$

3.2.5.6 Estimation of the coefficients in the model.

Regression analysis is applied in order to specify the values of the coefficients in Eq. 3.10. Nevertheless, computer software was used to evaluate the coefficients for all responses of each experiment.

3.2.5.7 Testing the adequacy of the models developed.

An analysis of variance (ANOVA) was used to test the adequacy of the models developed. The statistical significance of the models developed and each term in the regression equation were examined using the sequential F-test, lack-of-fit test and other adequacy measures (i.e. R^2, Adj- R^2, Pred. R^2 and Adeq. Precision ratios) using the same software to obtain the best fit. The prob >F (is sometimes called the *p*-value) of the model and each of the terms used in the model can be computed by means of ANOVA. If the Prob > F of the model and of each term does not exceed the level of significance (say α= 0.05) then the model may be considered adequate within the confidence interval of (1- α). For the lack-of-fit test, the lack of fit could be considered insignificant if the Prob >F exceeds the level of significance. Table 3.3 below is a summary of the ANOVA table. The equations by which the adequacy measures can be calculated are shown below, Eqs. 3.11 to 3.15 [182,184].

Table 3.3: ANOVA table for full model.

Source	SS	df	MS	$F_{cal.}$- Value	p-value or Prob > F
Model	SS_M	p	Each SS divided by its df	Each MS divided by MS_R	From table or software library
A- Beating time	SS_1	1			
B- Temperature	SS_2	1			
AB	SS_{12}	1			
A^2	SS_{11}	1			
B^2	SS_{22}	1			
Residual	SS_R	N-p-1			-
Lack of Fit	SS_{lof}	$N - p - n_0$			From table
Pure Error	SS_E	n_{0-1}			-
Cor Total	SS_T	N - 1	-	-	-

Where:

P: Number of coefficients in the model.
N: Total number of runs.
n_0: Number of centre points.
df: Degree of freedom.
MS: Mean square.

$$R^2 = 1 - \left[\frac{SS_R}{SS_R + SS_M} \right] \tag{3.11}$$

$$AdjR^2 = 1 - \left[\left(\frac{SS_R}{df_R} \right) \times \left(\frac{SS_R + SS_M}{df_R + df_M} \right)^{-1} \right] \tag{3.12}$$

$$predR^2 = 1 - \left[\frac{PRESS}{SS_R + SS_M} \right] \tag{3.13}$$

$$PRESS = \sum_{i=1}^{n} (y_i - \hat{y}_{i,-i})^2 \tag{3.14}$$

$$Adeq.precision = \left[\frac{Max(\hat{Y}) - Min(\hat{Y})}{\sqrt{\frac{p \times MS_R}{n}}} \right] \tag{3.15}$$

Where:
p: Number of model parameters (including intercept b_0)
n = number of experiments

3.2.5.8 Model reduction.

Usually, the full model Eq. 3.10 consists of an insignificant model of terms that need to be eliminated (i.e. terms with p-value greater thanα). This elimination can be done manually or automatically by using one of the selection procedures provided by the Design Expert V7 (see Fig. 3.6). The three automatic procedures for evaluating all possible regression equations (or selection of variables) are [184,187]:

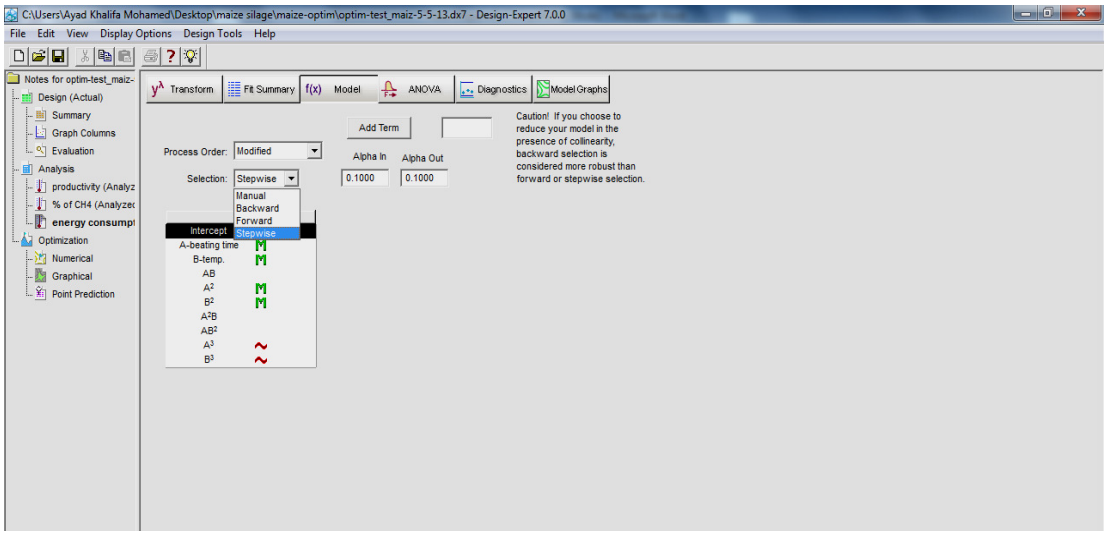


Figure 3-6 Model reduction methods in design expert software.

- **Forward selection procedure:**

This procedure begins with the constant term only; the first variable added is the one with the highest simple correlation with y. If the regression coefficient of this variable is significant, it remains in the equation and a new search for the second variable with the highest correlation with y commences. After y has been adjusted for the effect of the first variable and the significance of the regression coefficient, the second variable is then tested. If the regression coefficient is significant, a search for a third variable is made in the same manner, and so on. The procedure is completed when the last variable entered to the equation has insignificant regression coefficient or all the variables have been included. The test statistic for this selection procedure is the standard t or F-statistic, which is equal to t^2.

- **Backward elimination procedure:**

In this procedure, the full equation is fitted and sequentially eliminates one variable each time. The variable with the smallest contribution to the reduction of error is eliminated first, or the variable with the smallest t ratio (i.e. the ratio of the regression coefficient to its standard error) is eliminated and so on. In the case where more than one variable having insignificant t ratios, the procedure operates by dropping the variable with the smallest insignificance for t ratio and the equation with the remaining variable is then fitted where the ratios for the new regression coefficient are then tested. The procedure is stopped when all the t ratios are significant or all but one variable has been deleted.

- **Stepwise regression method:**

This method is a forward selection. However, the possibility of eliminating a variable that might be added in an earlier stage, as in backward procedure, is considered. The calculation made for inclusion and deletion of variables are the same as the forward and backward procedures. This procedure has the advantage of assuming different or similar levels of significance for inclusion or deletion of variables from the regression equation.

3.2.5.9 Development of the final reduced model.

At this stage, the final reduced model, as determined by applying the above steps, can be built upon. This model contains only the significant terms and the terms that are necessary to maintain hierarchy. Furthermore, a reduced quadratic ANOVA table can be produced.

3.2.5.10 Post analysis.

As the final model was tested and checked and was found to be adequate, then, predicting the response at any midpoints using this adequate model is possible at this stage. In addition, it is possible by using the model to produce plots such as 3D graphs, contours and perturbation plots in representing the factors that affect how they contribute in the response. Moreover, the possibility of employing the developed model for finding the optimal condition for optimised anaerobic digestion processes.

3.2.6 The Desirability Function Approach

The Desirability Function Approach (DA) is a simultaneous, optimisation of multiple responses and was a technique popularised by Derringer and Suich [188] in the 1980s. In this technique, an objective is set to each response: a target value, maxima or/and minima then, each estimated response (Y_i) are converted into a dimensionless measure of performance called the individual desirability function (d_i) which varies between 0 and 1. If the estimated response is at its goal or target value, then d_i=1, if it is within an acceptable limit, then ($0 < d_i < 1$), and if it is outside an acceptable limit, then $d_i = 0$. All individual desirability functions are then combined into an overall desirability function (D) by using the geometric mean. The

objective is to choose an optimum setting for the input variables in order to maximise the overall desirability as:

$$\max \quad D = (d_i * d_2 * \dots d_m)^{1/m} \tag{3- 16}$$

$$subject\ to: L(x_i) \leq x_i \leq U(x_i)$$

Where:

m is the number of responses and $L(x_i)$ and $U(x_i)$ are the Lower and Upper limits of the input variables x_i

The single value of D gives the overall assessment of the desirability of the combined response levels so, if any $d_i = 0$ (that is, if one of the response variables is unacceptable) then, $D = 0$ which indicates an unacceptable overall product regardless of how desirable the other response variables might be. For more details, refer to Derringer and Suich [188]. In this work and through the Design Expert software (see Figure 3-7), the individual desirability for each response d_i was calculated using Eqs.3.17 - 3.20. The shape of the desirability function can be changed for each goal by the weight field 'wt_i'. Weights are used to give added emphasis to the upper/lower bounds or to emphasise the target value. Weights can be ranged between 0.1 and 10; where weight greater than one gives more emphasis to the overall goal, while weight that is less than one gives less emphasis toward the goal. With a weight value of one, this will make the d_i's vary from zero to one in a linear mode. In the desirability objective function (D), each response can be assigned an importance (r), relative to other responses. Importance varies from the least important a value of 1(+), to the most important a value of 5(+++++). If the varying degrees of importance are assigned to the different responses, the overall objective function is shown below Eq.3.21. Where n is the number of responses in the measure and T_i is the target value of i^{th} response [184].

- For a goal of maximum, the desirability will defined as:

$$d_i = \begin{cases} 0 & , \quad Y_i \le L_i \\ \left(\dfrac{Y_i - L_i}{U_i - L_i} \right)^{wt_i} & , \quad L_i \langle Y_i \langle U_i \\ 1 & , \quad Y_i \ge U_i \end{cases} \tag{3.17}$$

- For a goal of minimum, the desirability will define by:

$$d_i = \begin{cases} 1 & , \quad Y_i \le L_i \\ \left(\dfrac{U_i - Y_i}{U_i - L_i} \right)^{wt_i} & , \quad L_i \langle Y_i \langle U_i \\ 0 & , \quad Y_i \ge U_i \end{cases} \tag{3.18}$$

- For a goal as a target (T), the desirability will defined by:

$$d_i = \begin{cases} \left(\dfrac{Y_i - L_i}{T_i - L_i} \right)^{wt_{1i}} & , \quad L_i \langle Y_i \langle T_i \\ \left(\dfrac{Y_i - U_i}{T_i - U_i} \right)^{wt_{2i}} & , \quad T_i \langle Y_i \langle U_i \\ 0 & , \quad Otherwise \end{cases} \tag{3.19}$$

- For a goal within range, the desirability will defined by:

$$d_i = \begin{cases} 1 & , \quad L_i \langle Y_i \langle U_i \\ 0 & , \quad Otherwise \end{cases} \tag{3.20}$$

$$D = \left(\prod_{i=1}^{n} d_i^{r_i} \right)^{\frac{1}{\sum r_i}} \tag{3.21}$$

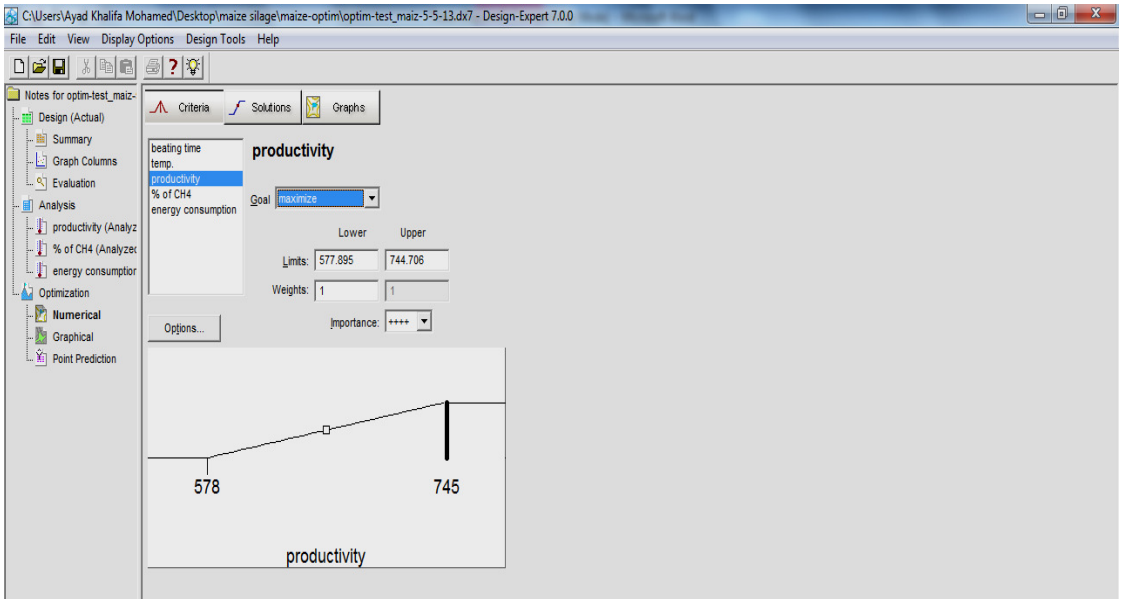


Figure 3-7 Optimization analysis using Design-Expert V7.

Chapter 4

MATERIALS AND METHODS

4.1 Materials.

In this work, three different materials were used as the main substrate. They were selected to be anaerobically co-digested with digester sludge as an inoculum. These materials can be considered as a sustainable resource for bioenergy. The chosen materials are: maize silage, fresh grass and waste of potato.

4.1.1 Maize silage.

Many different types of energy crops are suitable for anaerobic digestion. Maize is the most dominating crop for biogas production. Maize is considered to have the highest yield potential of field crops grown in Central Europe[84].

A recent evaluation of biogas-producing plants in Germany and Austria show that maize silage is the first most frequent crop used as feedstock (85.5%) [189, 190]. National Non-Food Crops Centre (NNFCC) and The Andersons Centre.[191] stated that the values of methane yield from maize silage was between 200 L/Kg VS and 220 L/Kg VS. Martin Závacký et al [192] experiments aimed at determination of optimal specific power in the ultrasonic chamber stated that biogas yield from untreated maize was approximately 400 $N/L/kg_{VS}$ taking the average of 347.4 $N/L/kg_{VS}$ and 408.9 $N/L/kg_{VS}$, in the same vein, the CH_4 yield was approximately 180 $N/L_{CH4}/kg_{VS}$ taking the average of 143.9 $N/L_{CH4}/kg_{VS}$ and 221 $N/L_{CH4}/kg_{VS}$. After combining a 'Grinding Treatment' and an 'Ultrasonic Treatment' with optimum specific power P_V of 252.8 kW/m^3, the biogas and methane yield were 529.4 Nl/kg VS and 286.2 Nl_{CH4}/kg_{VS} respectively. S. Schittenhelm 2008 [193], conducted a study to determine the influence of harvest date and hybrid maturity on the yield and quality of maize biomass for anaerobic methane production , it was found that the specific methane yields of 282–419 Nl_{CH4}/kg_{VS} was obtained. Thomas Amon et al,[194] demonstrated an optimised anaerobic digestion for maize, showing

that maize methane yield between 250 and 375 Nl CH4 (kg VS)$^{-1}$ could be achieved. Zaki-ul-Zaman Asam et al [7], assessed the biogas potential of energy crops (maize and grass silage) and solid manure fractions from manure separation units, and showing that the ultimate methane yield per kg VS maize silage has an average 236 ± 52 L/kg VS. Stewart DJ et al, demonstrated that with a loading rate of 2.5 Kg total solids/m³ digester daily and a retention time of 20 days, the mean volumes of biogas (in litres) and methane contents (% methane) obtained from each kilogram of total solids of maize added to the digester was 406 L/kg$_{TS}$ with 57% CH_4 .[195].

Maize silage (see Figure 4-1) with its characteristics was obtained from UCD Lyons Research Farm. The farm consists of approximately 580 acres of land. It is used for teaching and research field activities by the School of Agriculture, Food Science and Veterinary Medicine in University College Dublin (UCD) [196]. Characteristics of the maize silage are reported in table 4.1.

Table 4.1: Characteristics of Maize silage

Parameters (%)	Value
Metabolisable Energy (ME)	11.9
Crude Protein (CP)	7.7
Neutral Detergent fibre (NDF)	38.0
Acid Detergent fibre (ADF)	24.0
Starch	28.9
Digestibility of DM (DMD)	71.0

Figure 4-1 Maize silage.

4.1.2 Grass

Grass is one of the most abundant renewable energy sources in Europe. Grass biomethane has been shown to be a sustainable gaseous transport biofuel [197]. It has an excellent energy balance; superior to first generation liquid biofuels from temperate climates and similar to tropical biofuel systems [198]. It is also shown to allow economic viability both to the producer and the consumer [199]. IEA bioenergy [200] stated that the energy value from grass can vary from 298 L CH_4/Kg VS to 467 L CH_4/kg VS. Nizami et al. [201] pointed that at stable and optimized performance of the system, the average methane production was 341 L CH_4/kg VS added. Murphy et al. [202] reported that the values of methane yield from grass silage varied from 290 to 467 L CH_4/kg VS added. Stewart et al. [195] stated 310 L CH_4/kg VS added from a single stage CSTR using ryegrass plus clover at an organic loading rate of 2.25 kg VS m^{-3} d^{-1}. A range of methane yields from 320 to 510 L CH_4/kg VS added for grass was documented in a review by Nizami and Murphy [203]. A methane yield of 0.165 and 0.27 m^3/ kg VS of grass added was observed by Yu et al. [204] and Cirne et al. [205] respectively using lab scale leach beds connected with an anaerobic filter. Nizami et al. [201] documented that batch

labscale experiments conducted by [206] produced biogas of 280 L – 330 L /Kg VS with 55% methane content. Also the author documented that higher ranges of methane yields (423–627 L CH_4/kg VS added) was observed from ryegrass at various stages of maturity by Pouech et al. [207]. Murphya et al. [208], documented that a study Ma¨hnert et al. [209]on fresh and ensiled grass pecies measured methane yields of between 310 and 360 m^3 CH_4/tVS for fresh cut meadow foxtail and perennial rye grass during batch experiments.

Fresh grass or pasture (see Figure 4-2) was obtained from UCD Lyons Research Farm. The chemical composition was provided by Lyons research farm laboratory. Characteristics of the maize silage are reported in Table 4.2.

Table 4.2: Chemical composition of pasture.

	Pasture
DM *(g kg^{-1})*	207
Energy *(MJ kg DM^{-1})*	10.9
Chemical composition (g kg DM^{-1})	
CP	17.2
NDF	438
ADF	219
ADL	63
Ash	73

DM = dry matter, ME = metabolisable energy, CP = crude protein (N * 6.25), NDF = neutral detergent fibre, ADF = acid detergent fibre, DMD = digestibility of DM

Figure 4-2 Fresh grass.

4.1.3 Waste of Potato

The problem with the management of potato waste causes considerable concern to the potato industries, thus implying the need to identify an integrated, environmental-friendly solution. Potato waste is a zero value waste from potato processing plants [210]. Successful application of anaerobic digestion (AD) technology could provide an economical and an environmental-friendly means for bioenergy recovery from potato waste with a simultaneous remediation of the waste. By this solution the material can be value added instead of a zero value.

Anaerobic batch digestion of potato waste and co-digestion of potato waste with sugar beet was investigated in lab-scale work by Parawira et al [211]The authors reported that the co-digestion of potato waste with sugar beet leaves resulted in a higher methane yield between 31 and 62%, as compared with digestion of potato waste alone. For the potato waste, the highest methane yield was determined to be 0.32 litres CH_4/g VS added, which is comparable to the methane yield of 0.43 l/g VS added of potato waste reported by Stewart et al [195], while for co-digestion of potato waste and sugar beet leaves, the highest methane production was 1.63 L (for 24% potato waste + 16% beet + 60% TS inoculum) [211]. Stewart DJ et al, stated that with a loading rate of 2.5 Kg total solids/m³ digester daily and a retention time of 20 days, the mean volumes of biogas (in litres) and methane contents (% methane) obtained from each kilogram of total solids potato waste (peelings plus rejects)

added to the digester was 820 L/Kg_{TS} with 50% CH_4 .[195]. B. Linke, in his work on potato processing wastes anaerobically digested to produce biogas, using thermophilic Continuous Stirred-Tank Reactors CSTRs, with an organic loading rate OLR range from 0.8 to 3.4 g/L/d, biogas yields and methane composition were determined to be 0.85–0.65 L/g, and 58–50%, respectively. Both biogas yield and methane percentages decreased with an increase in OLR [212].

Waste of potato (Figure 4-3) as main substrate was obtained from Coles Catering Company which is a wholesaler of fresh fruit and fresh prepared vegetable located in the main vegetable market in Dublin. Chemical analysis of potato waste which is achieved by A. Mahmood et al, [213] reported in Table 4.3.

Table 4.3: Characteristics of potato waste.

Component (%)	Potato waste (peel & trimmings)
Dry matter	17.82
Total soluble sugars	1.40
Reducing sugars	0.91
Pectin	3.39
Cellulose	2.20
Starch	66.78
Crude protein	14.70
Ash	7.65
Volatile solids	92.32
pH	5.99

Figure 4-3 Potato waste.

4.1.4 Sludge

As previously discussed, the co-digestion strategy is one of way to improve the efficiency of the anaerobic digestion process. The sewage sludge will act as a biological catalyst to digest the lignocelulosic material during the fermentation process. The sewage sludge is a brown/dark, heavy, viscous fluid with an unpleasant odour (see Figure 4-4) In general, the species of the micro-organisms and types of materials inside the sludge has the potential to react with the substrate and release the biogas. Fresh sludge with its composition analysis was obtained from the Dublin water sewage treatment plant located in Ringsend, Dublin2. The characteristic of sludge depends on the sewage (which is the mix of water and whatever wastes from domestic and industrial life flushed into the sewer), therefore the characteristic of sludge of each experiment is diver to other [214]. Table 4.4 showing the average composition of sludge.

Figure 4-4 Sewage sludge.

Table 4.4: Characteristic of sludge.

Parameters	Value
Total Solids	4.61%
Volatile Solids	70.48%
COD	57.780 mg/l
Ammonia	2.15275 mg/l
alkalinity	12.315 mg/l
VFA	42 mg/l
pH	7.42

4.2 Equipment

The main machine in this work is the Hollander Beater which has been described in chapter 3. There are other pieces of equipment used in the lab for the project which includes; electric equipment, glassware, machines, sieves and plastic materials.

4.2.1 Electronic Equipment.

4.2.1.1 Portable Gas Analyser.

One of key objectives of this work is to investigate the chemical composition of biogas produced from lignocellulosic material after beating treatments. The portable gas analyser in the department of physics research laboratory in DCU has been used for this purpose. The analyser is manufactured by Drager Medical UK Ltd and the model series is Drager X-am 7000. The gas analyser used in the laboratory can be

seen in Figure 4-5 below. The analyser monitors methane (CH_4), oxygen (O_2), carbon dioxide (CO_2) and carbon monoxide (CO) as standard.

Figure 4-5 Biogas analyser.

By connecting the plastic bag which stored the biogas produced to the Drager X-am 7000 device, the gas goes through the device. The sensors will detect the elements of biogas.

4.2.1.2 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. In this work the scanning electron microscope (EVO LS 15 developed by Carl Zeiss, Germany) shown in Figure 4-6 was used to estimate the effect of beating treatment on the lignocellulosic materials in terms of particle size reduction and the change in the microstructure of the materials,

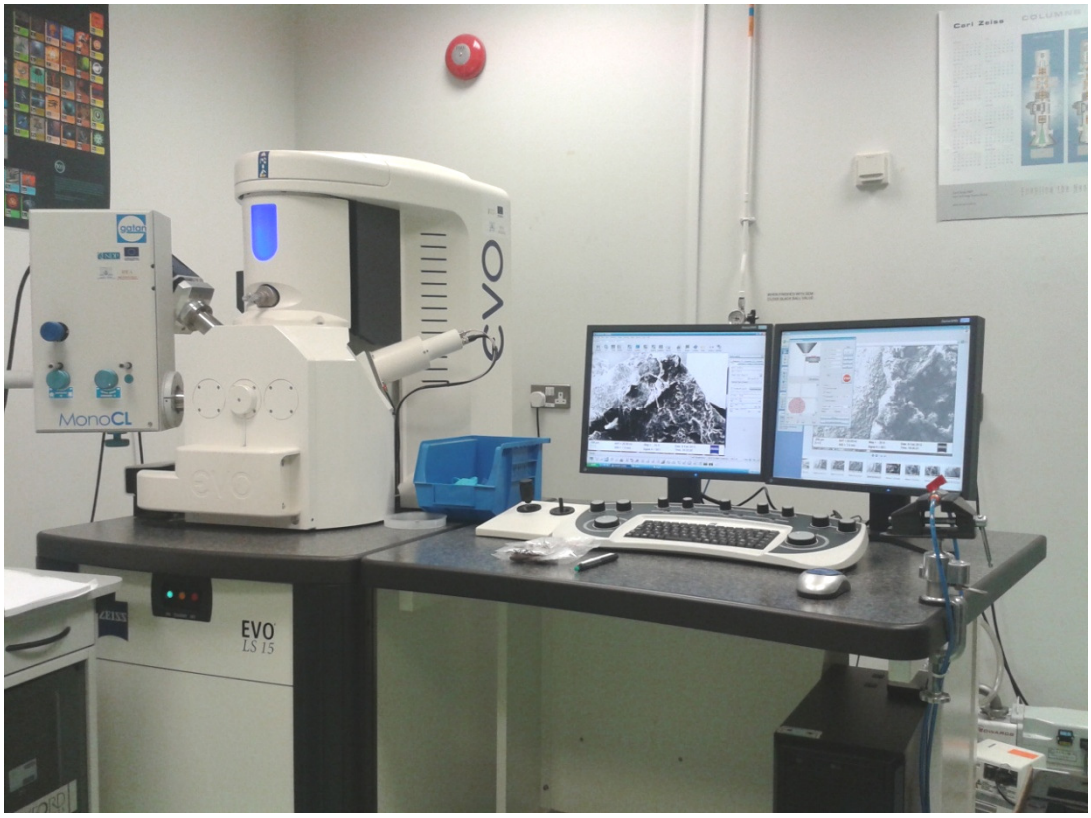


Figure 4-6 Scanning Electron Microscope (SEM).

4.2.1.3 PH meter.

The pH meter used in this research work was developed by HANNA instruments, USA. The device contains an electrode, temperature probe and electronic control unit. The electrode responds to the concentration of hydrogen ions in the sample solution to produce a chemical signal. This signal is then converted into pH values which are displayed on the control unit. pH of each of the samples has been investigated both before and after the digestion process.

4.2.1.4 Laboratory Ovens

The main function of the laboratory oven shown in the Figure 4-7.A is to extract moisture contents of the substrates (lignocellulosic materials) to calculate the dry matter of the samples (all details of procedure to calculate dry matter of substrate will be covered later). The laboratory high temperature furnace with maximum temperature 1600 ^{o}C shown in Figure 4-7.B is used to calculate the Volatile Solid (VS) in samples (all details of procedure to estimate ash and VS of substrate will be covered later) the instrument is designed to operate overnight and has automatic

safety operation. The temperature adjustment mechanism is located on the laboratory oven and temperature can be adjusted from the 10- over 100 0C. The thermometer located on the top of the oven represents the actual temperature of the oven.

Figure 4-7: [A] Laboratory ovens and [B] high temperature furnace.

4.2.1.5 Electronic Pump

The electronic pump is shown in the Figure 4-8. The main function of this pump is to prepare the anaerobic condition by removing any gas, especially oxygen, from the fermentation vessels and aluminium bags (bioreactor). Nitrogen gas which is an inert gas is used in this experiment to clear the presence of any gas in the fermentation vessels and the aluminium bags by electronic pump. Overall the electronic pump helps to maintain an air tight environment for this experiment.

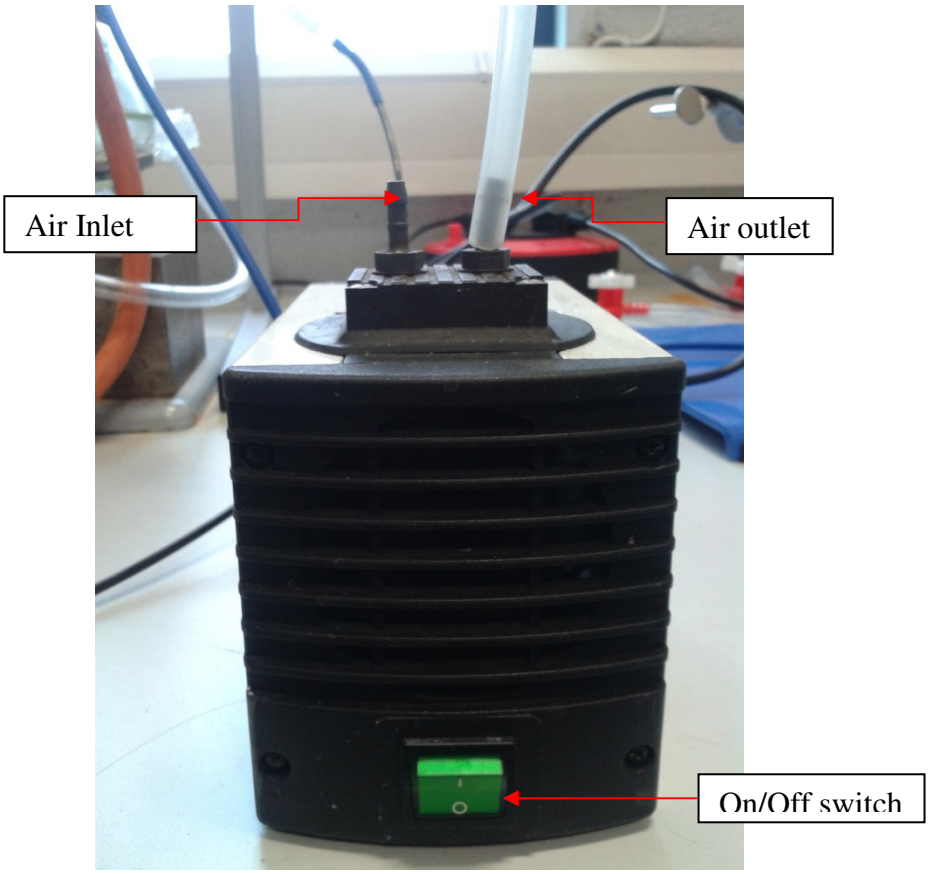


Figure 4-8: Electronic pump.

4.2.1.6 Waterbaths

The main function of the waterbath in this work is to maintain mesophilic conditioning for all the samples during the anaerobic digestion process. All samples were submerged in the waterbath. The temperature of the waterbath was maintained at 37 ^{0}C for those experiments which are curried out to prove the effect of the beating treatment as a new technique to enhance anaerobic digestion of lignocellulosic materials and to maintain the temperature of optimisation experiments according to the design matrix developed by RSM. The water level in the bath was checked daily for this experiment. Low water levels can cause serious effects either on the samples or on the tank due to overheating if no water is present. By maintaining the water level in the tank, an even heat distribution can be maintained, which is a requirement of the anaerobic process.

4.2.1.7 Energy meter.

Energy metering is the process of measuring the amount of electric energy consumed by a residence, business, or an electrically powered device. The energy meter used to measure the energy consumed in terms of electricity for the beating treatment and mesophilic conditioning. It has a displayed screen that allows the consumption to be displayed, which are indicated in fraction of kilowatt per hour. This is since its use for this purpose last between minutes and 21 days during the retention time of anaerobic digestion process.

4.2.1.8 Electronic Weighing Scale

The function of the electronic weighing is to provide exact weight measurement. For this experimental work, the exact weight of the sample is important for calculating TS and VS and for results comparison.

4.2.1.9 Stirrer

The high-speed stirrer BHI-CSC has been used to determine the degree of beating according to the ISO 5267-1:1999(E). This stirrer is for the mechanical analysis and also other laboratory applications for stirring. The speed runs at approximately 4000 rpm under load. A dispersion cup is supported on a rest on the stand of the stirrer and has a removable baffle.

4.2.2 Degree of Beating Test Device

The degree of beating test device is also known as a Schopper Riegler apparatus (see Figure 4-9). It was the first drainability tester to be designed and is suitable for testing all kinds of pulp in aqueous suspension, the test only provides acceptable results if a sufficiently density of fibre of the correct weight is deposited on the wire screen.

The Schopper-Riegler apparatus measures the degree of work done on the fibres during stock preparation (refining / pre-treatment) and is therefore a primary tool in the evaluation of the characteristics of pulp. The apparatus consists of a drainage chamber and rate measuring funnel on a sturdy support. The drainage chamber is

fitted with a wire screen (100 cm²) at its lower end and is sealed 25 mm above the screen when the sealing cone is lowered. After filling 1 litre of suspension into the drainage chamber the sealing cone is raised. As the filtrate drains into the rate measuring funnel a fibre pad is formed on the screen, slowing down the process depending on the mechanical treatment to which the pulp has been subjected. The discharge from the side orifice is collected in a graduated cylinder. The function of Schopper Riegler apparatus is used to determine the 'Degree of Beating' carried out on the feedstock. The procedure was done according to the international standard ISO 5267-1:1999(E).

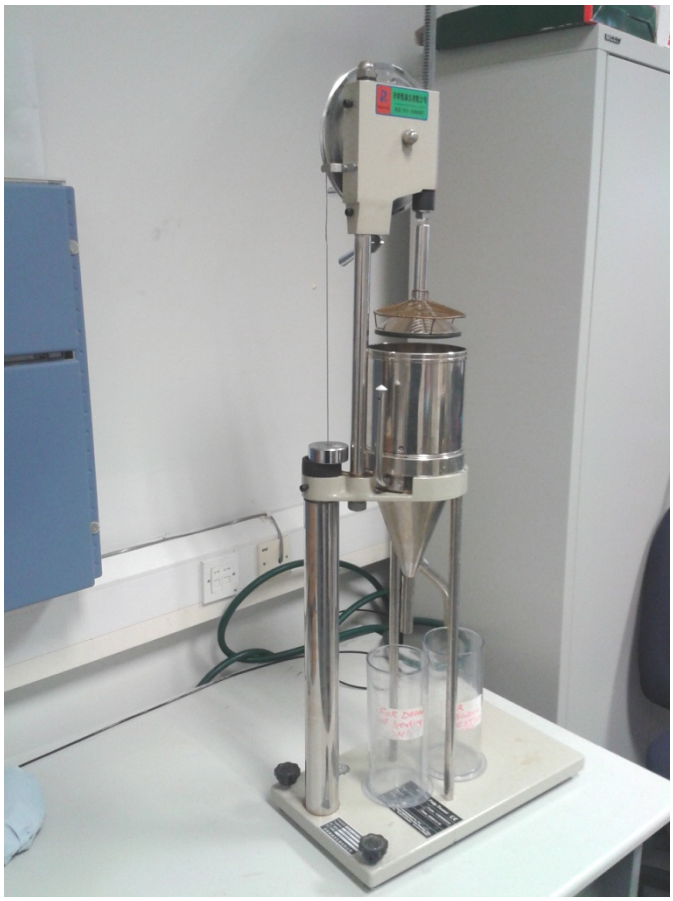


Figure 4-9: Schopper-Riegler apparatus.

4.2.3 Laboratory Glassware.

In this experimental work different laboratory glassware, such as conical flask (500 ml), dish plate, beakers, burette, pipette, connecting tube, stopper cap, round bottom flask, and volumetric flask were used.

4.2.3.1 Volumetric Flask

In Figure 4-10 a 500 mL measuring cylinder is shown. The function of this equipment is to measure the volume of the gas. Water is filled in the flask and marks a suitable water level for comparison result. The inverted 250 mL cylinder is placed in the cylinder. When gas is pumped into the cylinder the water level will rise. Mark the water level and subtract the initial selected water level to get the volume of the gas

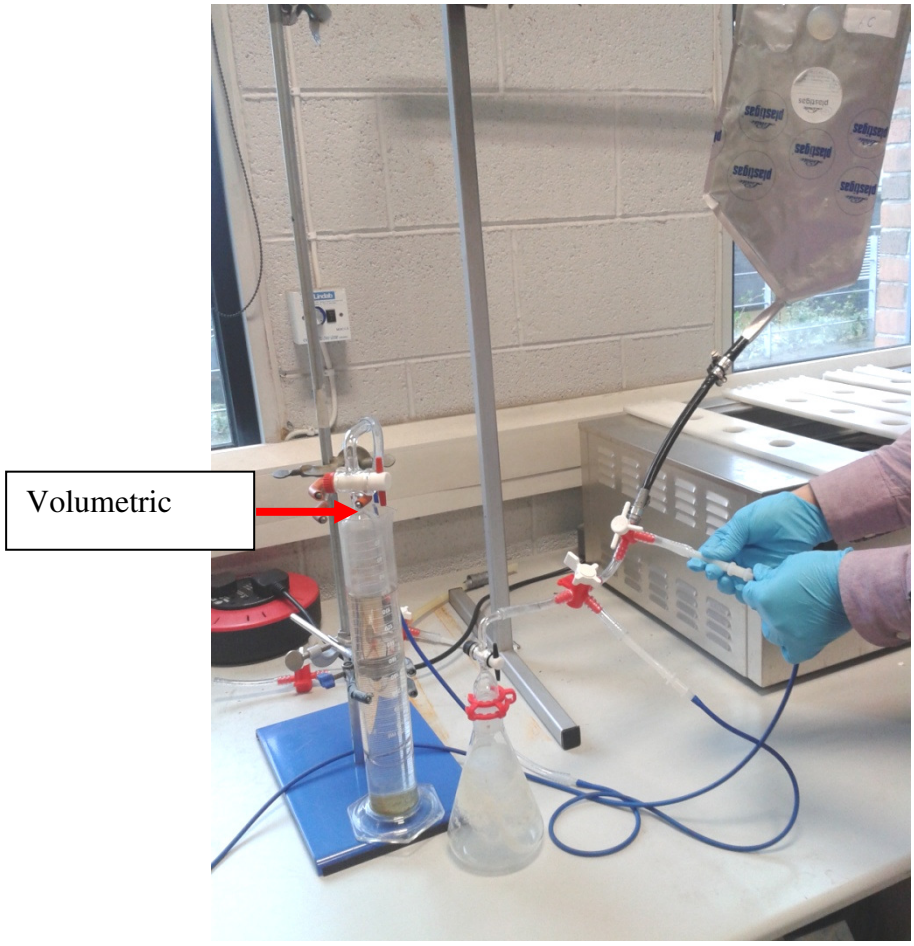


Figure 4-10: Biogas measurement system.

4.2.3.2 Round Bottom Flask

The function of this equipment is to aid preparation of the anaerobic condition by extracting the gas with the electronic pump into the round bottom flask. The bubble present shows that air is releasing and the water in the flask prevents air from flowing back into the system. This will also be in use when the process of biogas measuring carried out.

4.2.3.3 Nitrogen Tank.

Atmospheric air consists of about 78% nitrogen and it is regarded as a neutral gas. In order to achieve anaerobic condition nitrogen has been used in this work to eliminate oxygen or any gas contamination in the system (bioreactor), the process achieved by flushing nitrogen gas in to the system through the 3 ways valve A, and extracting it using an electronic pump (mentioned above) through the 3 way valve, B.

4.2.4 Bioreactor design.

Figure 4-11 shows the design of bio-reactor, which is composed of a flask 500 mL, sintered glass stopper**,** plastic clips, adjustable jubilee clips, 2 way valves, 3 way valves, quick release tubing connectors, plastic tube, and a plastic bag used to store biogas.

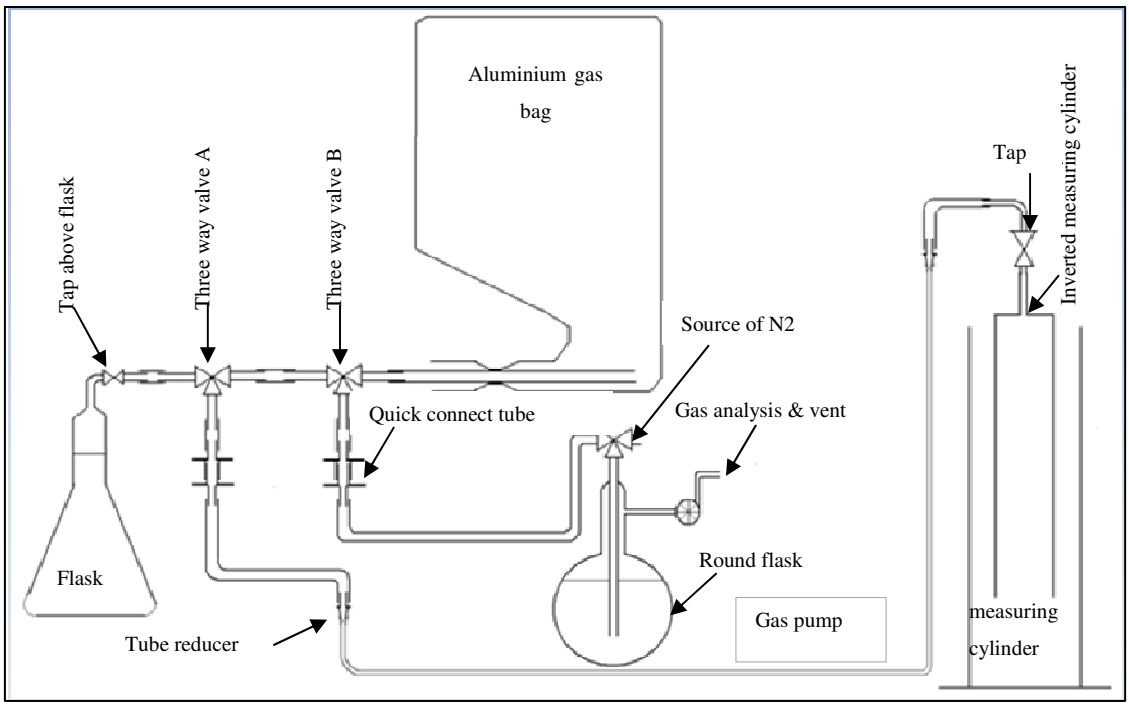


Figure 4-11: Design of Bioreactor.

Starting from the conical flask, after the substrate has been mixed, it is corked with the sintered glass stopper and the clip, the connecting tube is then linked up with the three-way valve and onto the aluminium gasbag. This practical demonstration is shown in Figure 4-12

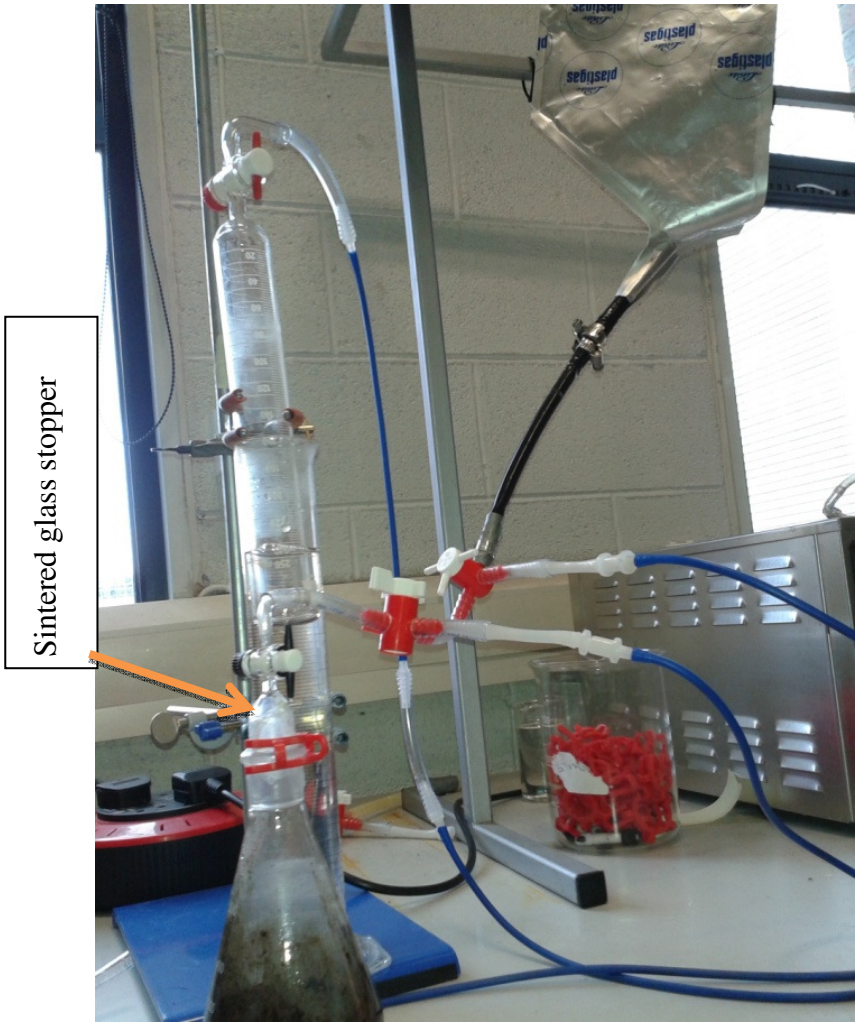


Figure 4-12: Bioreactor system.

4.2.5 Experimental procedure

Two approaches have been employed to conduct the experimental work in this study. The RSM approach was used to conduct the optimisation of all experimental work (The RSM technique has been covered in chapter 3 and experimental procedure according to RSM technique will covered in the chapter of optimisation, *vide supra*). The OVAT approach was employed for the experiments that aimed to investigate the effect of the Hollander Beater device (Beating Treatment) on biogas yield from

different lignocellulosic materials anaerobically digested with digester sludge in batch mood. The experiment settings were carried out according to VDI 4630 [215]. For each substrate in addition to untreated sample, minimum of three levels of beating were identified. For clarity, the samples of each substrate comprised of four samples in total for the experiment, with different conditions carried out in triplicate. For each condition there was a reactor for the chemical analysis of biogas so as to have the content of the biogas produced and then analysed. In order to eliminate the effect of the inoculum on biogas production, three reactors were fed with same amount of sludge (200 mL) to evaluate the sludge contribution. In order to determine both the identification and clarity, the different reactors were labelled and marked. 200 mL of substrate pulp and 200 mL of sludge were placed in a conical flask (reactor) and each was sealed with a sintered glass stopper and one-way valve to prevent the entry of air. Thereon, the conical flasks were connected to the aluminium bags and then, the nitrogen gas was pumped into the aluminium bags and all parts of the system (reactors) to remove the excess air that may be present. Here, nitrogen gas was extracted along with the atmospheric air contents by the vacuum pump to prevent air contamination present in the system. The pumping and extraction of nitrogen was repeated three times for each reactor. Water baths were filled with water up to the maximum fill level and were operated at temperature 37^{o}C. All reactors were then placed in the water baths as shown in Figure 4-13.

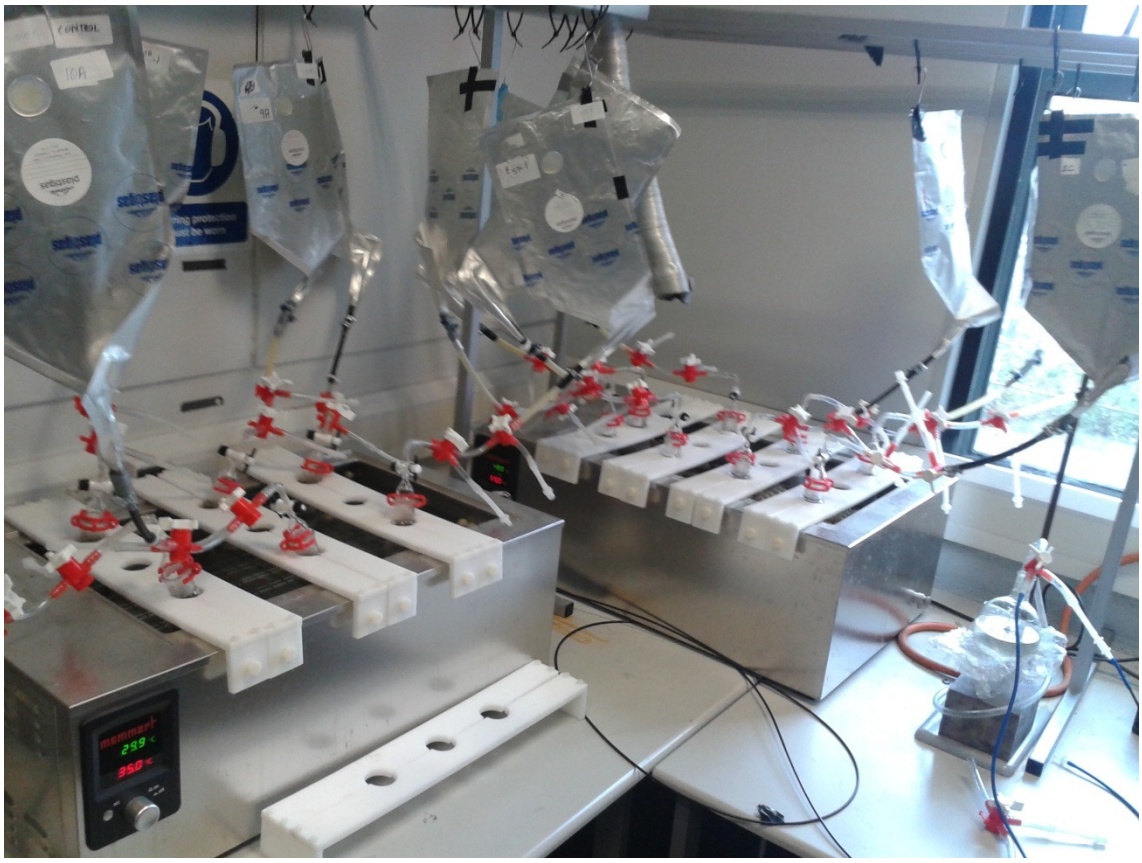


Figure 4-13: Bioreactors placed in the heating unit.

4.2.6 Analysis

Total Solid (TS) for each sample was calculated. Drying was performed at 105 ^{o}C using the laboratory oven until constant weight was achieved (calculation details will be covered later). Volatile Solid (VS) was calculated for each sample according to Laboratory Analytical Procedure #005 [216], (details of procedure will be presented later). pH was measured for substrate in all levels of the beating treatment, the pH meter was used and described above. In order to evaluate the effect of treatment on lignocellulosic materials in terms of particle size reduction and change of material structure; Scanning Electron Microscopy (SEM) was used to analyse the samples before and after the beating treatment to visually estimate the effect of treatment on the structure of the lignocellulosic material. The degree of beating for each level of treatment was used to determine the drainability after different levels of treatment which reflect the particle size of each level. Four different sizes of sieve (2 mm, 1 mm, 800 µm and 355 µm) were also used. Drager X-am 7000 gas analyser described above was used to measure the concentration of CH_4, CO_2 and other traces of gases in biogas produced for each condition. Volumetric flasks were used to

measure the volume of biogas for all samples every three days during the retention time of the process according to equations presented in appendix A. The percentage of improvement of biogas yield was calculated by following:

$$x = \frac{b - c}{c} * 100 \quad (3.1)$$

Where:

x is the percentage of increase of biogas production.

b is the volume of biogas produced from treated samples.

c is the volume of biogas produced from untreated samples.

Determine the Total Solid contents of substrate

Total Solid or dry matter was determined for each sample by calculating the percentage of moisture content in the substrate.

For untreated samples the following steps were followed:

1- Weights of the three empty dry dish plates were measured.

2- The samples of substrate were selected randomly and placed into each dish plate (the amount of sample must be the same amount of sample placed in reactor).

3- Each dish plate with wet substrate was placed on the weighing scales one by one where the total wet weight was measured.

4- The net wet weight of each sample was measured by subtracting the empty dish plate weight.

5- Three samples were placed in the oven which was set at 105 ^{0}C for a period of 24 h or till the weight remained constant in order to extract all the moisture contents in each sample.

6- By subtracting total dry sample weight from empty dish plate weight, the net dry sample weight can be found.

7- Then the average net dry sample weight can be taken.

The percentage of Moisture Content (MC) can be calculated using the simple following equation:

$$MC\% = \frac{\text{net wet sample weight} - \text{net dry sample weight}}{\text{net wet sample weight}} \times 100 \qquad (3.2)$$

Dry matter of the treated substrate was determined for each level of treatment as follows:

1- The weight of the nine dry empty beakers was measured (three beakers for each level of beating).

2- For each level of beating, about 200 mL of pulp was collected randomly from the beating bath and collected into beakers.

3- Each beaker with pulp substrate samples was placed on the weighing scale one by one and the total wet weight of each beaker with pulp substrate was measured.

4- Net wet weight of each sample was measured by subtracting the empty beaker weight. Nine samples were placed in the oven which was set at 105 ^{0}C for a period of about 42 hours till the weight constant in order to extract all the moisture contents in each sample.

5- The weight of each dry sample was measured and this will be the total dry sample weight.

6- Then the average net dry sample weight can be taken.

The percentage of Moisture Content (MC) can be calculated using equation (3.2).

Determination of Volatile Solid (VS) of substrate

Determination of VS for each sample was done in line with the Laboratory Analytical Procedure #005 [216], using a 105 ^{o}C dried test specimen, and laboratory high temperature furnace described above. The procedure can be summarized in following:

1- Crucible was placed in the muffle furnace; to bring it to constant weight by igniting and maintaining the temperature at 575 ±25^{o}C.

2- The crucible was then removed from the furnace, and cooled to room temperature in a desiccator, and weighed as the tare weight (zero).

3- Approximately 0.5 to 1.0 g, of a test specimen was placed into the crucible and weighed, the weight (container plus sample minus tare weight of container) as the initial weight of the test specimen (W_2).

4- The container and contents was placed into the furnace and ignited at 575 ±25^{o}C for more than three hours, heat was slowed at the start to avoid flaming.

5- Then the container or crucible with its contents was removed to a desiccator, after to cool to room temperature, then the weight has to been taken and recorded.

6- The heating was repeated for one hour periods until the weight after cooling is constant to within 0.3 mg. The final weight of the ash, (W_1) was recorded, as the container plus ash weight minus container tare weight.

The percentage of ash and VS can be calculated, based on the initial weight of the test specimen, as follows:

$$Ash\ \% = w_1/w_2 \times 100 \quad (3.3)$$

$$VS\ \% = 100 - Ash\ \% \quad (3.4)$$

4.2.7 Experimental setup for maize silage

The experiment was setup according to the procedure, covered in section 4.2.5 above. 30 L's of tap water and c.a. 1.5 Kg of maize silage were taken and added to the beater, then the device was operated and the digital height indicator adjusted to digit "1". The first sample was taken after 20 minutes of beating. The second sample

was taken after 1 hour beating time and third sample was taken after 3 hours beating time of treatment.

Reactors labelled *A1*, *A2*, *A3*, and *A4* for without treatment were used as a control, and *B1*, *B2*, *B3* and *B4* for the first level of beating sample, *C1*, *C2*, *C3*, and *C4* for second level of beating sample and *D1*, *D2*, *D3* and *D4* for third level of beating sample, according to VDI guideline [215]. 13 g of untreated maize silage were placed in each conical flask labelled *A*, 200 mL tap water was added. 200 mL of maize silage pulp treated for 20 minutes was placed into each of the conical flasks labelled *B*. 200 mL of maize silage pulp treated for 1 hour was placed into each conical flask labelled *C*. 200 mL of maize silage pulp treated for 3 hours was placed into the each conical flasks labelled *D*. 200 mL of sludge was also added into each flask of all categories A, B, C and D (ratio 1:1) . In order to eliminate the effect of the inoculum on biogas production, three reactors were fed with same amount of sludge (200 mL) to evaluate the sludge contribution. Each conical flask was sealed with a stopper and the tap was closed to prevent the entry of air. Thereafter, the conical flasks were connected to the aluminium bags. Nitrogen gas was pumped into the aluminium bags and all parts of the system (reactors) using a 3 way valve to clean the excessive air. Then, the extraction of nitrogen gas and atmospheric air by the vacuum pump was carried out to prevent air contamination and growth of anaerobes present in the sludge and in the presence of oxygen gas. The pumping and extracting of nitrogen gas was repeated three times for each reactor. Water baths were filled with water up to the maximum fill level and were operated at temperature 37 ±1 ^{0}C. All reactors were placed in the water baths as shown in Figure 4.21. Shaking the conical flasks once a day over the period of the AD process ensured a more complete biological reaction. The water level in the baths was checked every day and more water was added to counteract the effects of evaporation. The biogas was measured every 3 days for a total period of 21 days for the AD process.

4.2.8 Experimental setup for fresh grass

Reactors labelled A10, A11, A12, and A13 for without treatment sample which used as a control, and B10, B11, B12 and B13 for first level of beating sample, C10, C11, C12, and C13 for second level of beating sample and D10, D11, D12 and D13 for third level of beating sample, according to VDI guideline [215].

13 g of untreated grass was placed in each conical flask labelled *A*, and 200 mL of tap water added. 200 mL of grass pulp treated for 5 minutes was placed into the each conical flask labelled *B*. 200 mL of grass pulp treated for 15 minutes was placed into each conical flask labelled *C*. 200 mL of maize silage pulp treated for 40 minutes was placed into each conical flask labelled *D*. 200 mL of sludge was also added into each flask of all categories A, B, C and D (ratio 1:1) . In order to eliminate the effect of the inoculum on biogas production, three reactors were fed with the same amount of sludge (200 mL) to evaluate the sludge contribution. Each conical flask was sealed with a stopper and the tap was closed to prevent the entry of air into the system. Thereafter, the conical flasks were connected to the aluminium bags. Nitrogen gas was pumped into the aluminium bags and all parts of the system (reactors) using 3 way valves to clean the excessive air input. Nitrogen gas was extracted and the atmospheric air contents by vacuum pump to prevent air contamination and also the growth of the anaerobes present in the sludge in the presence of oxygen. The pumping and extracting of nitrogen gas were repeated three times for each reactor. Water baths were filled with water up to the maximum fill level and were operated at temperature 37^0C ±1. All reactors were placed in the water baths as shown in Figure 4.20. Shaking the conical flasks once a day over the period of the AD process ensured a more complete biological reaction. The water level in the baths was checked every day and more water was added to counteract the effects of evaporation. The biogas was measured every 3 days for total period of 21 days for the AD process.

4.2.9 Experimental setup for potato waste

The experiment was setup according to the detailed procedure as covered in previous chapter. 30 L of tap water and c.a. 1.5 Kg of potato waste were taken and added to the beater, then the device was operated and the digital height indicator adjusted to digit “1”. In this experiment 4 levels of treatment has been conducted, the first sample was taken after 5 minutes of beating. The second sample was taken after 15 minutes beating time. The third sample was taken after 35 minutes beating time, and the fourth sample was taken after 60 minutes beating time of treatment.

Reactors labelled A1, A2, A3, and A4 for without treatment sample used as a control, B1, B2, B3 and B4 for first level of beating sample, C1, C2, C3, and C4 for

second level of beating sample, D1, D2, D3 and D4 for third level of beating sample, E1, E2, E3 and E4 for fourth level of treatment, all according to VDI guideline [215].

15 g of untreated potato waste was placed in each conical flask labelled A, where 200 mL of tap water was added. 200 mL of potato waste pulp treated for 5 minutes was placed into each conical flask labelled B. 200 mL of potato waste pulp treated for 15 minutes was placed into each conical flask labelled C. 200 mL of potato waste pulp treated for 35 minutes was placed into each conical flask labelled D. And 200 mL of potato waste pulp treated for 60 minutes was placed into each conical flask labelled E. 200 mL of sludge were also added into each flask of all categories A, B, C, D and E. In order to eliminate the effect of the inoculum on biogas production, three reactors were fed with same amount of sludge (200 mL) to evaluate the sludge contribution. Each conical flask was sealed with a stopper and the tap was closed to prevent the entry of the air. Thereafter, the conical flasks were connected to the aluminium bags. Nitrogen gas was pumped into the aluminium bags and all parts of the system (reactors) using 3 way valves to clean the excessive air. Then the extraction of nitrogen gas and the atmospheric air contents by the vacuum pump was carried out to prevent air contamination in the system. The pumping and extracting of nitrogen gas were repeated three times for each reactor. Water baths were filled with water up to the maximum fill level and were operated at 37 ^{0}C ±1. All reactors were placed in the water baths as shown in Figure 4.20. Shaking the conical flasks once a day over the period of the AD process ensured a more complete biological reaction. The water level in the baths was checked every day and more water was added to counteract the effects of evaporation. The biogas was measured every 3 days for total period of 21 days for the AD process.

Chapter 5

BEATING TREATMENT RESULTS & DISCUSSION

5.1 Introduction

This chapter shows results from the beating treatment of the lignocellulosic materials; maize silage, fresh grass and potato-waste. There are considerable variations in the results from these biomass materials which indicate that their production rate, in terms of biogas, will be different. This is in essence an indication that the beating treatment as a new mechanical treatment using the Hollander beater machine does have an effect on yield.

Generally, this chapter will further highlight and discuss other analytical parts as in;

1 Showing the effect of treatment on the particle size through SEM analysis of the pulp matter and degree of beating;
2 Cumulative analysis to specify the percentage increment of biogas production after beating treatment;
3 Composition of biogas;
4 Energy analysis;
5 Regression analysis to interpret the relationship between biogas production and degree of beating.

5.2 Maize silage

5.2.1 Analysis

All the analysis and calculations mentioned in chapter 4, section 4.2.6 have been conducted. The Total Solids (TS) of untreated sample was 4.47 g, 20 minutes beating treatment sample was 2.57 g, 1-hour beating time sample was 2.9 g, while the TS of 3-hours beating time sample was 3.1 g. Tables 5.1 – 5.4 depicted the details of the TS analysis.

The Volatile Solid VS of untreated sample was 96.3% of TS, 20 minutes beating treatment sample was 95.9% of TS of sample, 1-hour beating time sample was 95.9%, and for 3-hours beating time sample was also 95.9% of TS. Tables 5.5 – 5.8 depicted the details of the VS analysis.

The pH was measured for all samples before and after digestion, which was within the optimum range [217] (see Table 5.9).

Table 5.1: Total dry solid content for each sample without treatment.

Sample No.	dish plate weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
1	173.1	186.1	13	177.7	4.6
2	137.3	150.3	13	141.6	4.3
3	112.2	125.2	13	116.7	4.5
Average					4.47

Table 5.2: Total dry solid content for each sample with 20 minutes treatment.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
1	172.5	373.3	200.8	175.2	2.7
2	231.7	430.6	198.9	234.3	2.6
3	148.5	346.6	198.1	150.9	2.4
Average			199.85		2.57

Table 5.3: Total dry solid content for each sample with 1 hour treatment.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
1	231.4	432.6	201.2	234.5	3.1
2	230.8	434.3	203.5	233.6	2.8
3	112.2	314.3	202.1	115	2.8
Average			202.27		2.90

Table 5.4: Total dry solid content for each sample with 3 hours treatment.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
1	127	341.6	214.6	130.1	3.1
2	113.1	314.1	201	116.1	3
3	112	322.9	210.9	115.3	3.3
Average			208.83		3.13

Table 5.5: Percentage of ash in untreated sample.

Sample No.	Crucible weight	Crucible + sample weight	Sample weight (W2)	Crucible + ash weight	Ash weight (W1)	Ash %
1	54.6263	55.2486	0.6223	54.6499	0.0236	3.7924
2	54.6261	55.3721	0.746	54.6533	0.0272	3.6461
Average						3.7

Table 5.6: Percentage of ash in 20 minutes beating sample.

Sample No.	Crucible weight	Crucible + sample weight	Sample weight (W2)	Crucible + ash weight	Ash weight (W1)	Ash %
1	54.626	55.2676	0.6416	54.6536	0.0276	4.3017
2	54.6264	55.2477	0.6213	54.6529	0.0265	4.2653
Average						4.3

Table 5.7: Percentage of ash in 1-hour beating sample.

Sample No.	Crucible weight	Crucible + sample weight	Sample weight (W2)	Crucible + ash weight	Ash weight (W1)	Ash %
1	54.6261	55.397	0.7709	54.6567	0.0306	3.9694
2	54.6268	55.2383	0.6115	54.6521	0.0253	4.1374
Average						4.1

Table 5.8: Percentage of ash in 3-hour beating sample.

Sample No.	Crucible weight	Crucible + sample weight	Sample weight (W2)	Crucible + ash weight	Ash weight (W1)	Ash %
1	54.6262	55.2717	0.6455	54.6531	0.0269	4.1673
2	54.6266	55.2667	0.6401	54.6523	0.0257	4.0150
Average						4.1

Table 5.9: pH value (average value) of samples of each level of treatment.

Maize silage	untreated	20 Minutes Treatment	1-hour Treatment	3-hours Treatment
Before Digestion	7.79	7.72	7.78	7.96
After Digestion	7.6	7.87	7.86	8.06

5.2.2 Result and discussion

5.2.2.1 SEM analysis of the structural deformation of maize silage

The effect of beating treatment can be visually measured from the Scanning Electronic Microscope micrograph images. Figure 5 1 shows the maize silage structure before treatment and Figures 5- 2 to 5-4 exhibit the structure of maize silage after beating treatment. This is a clear indication that there has been significant damage and changes in the structure of maize silage in terms of reduction in particle size and increase surface area, also the crystalline structure of cellulose cells has been disrupted and invariably led to it being deformed. Therefore, the lignin component would have been broken down as a result. This in fact would assist the fermentation process as reported in [192] and [218].

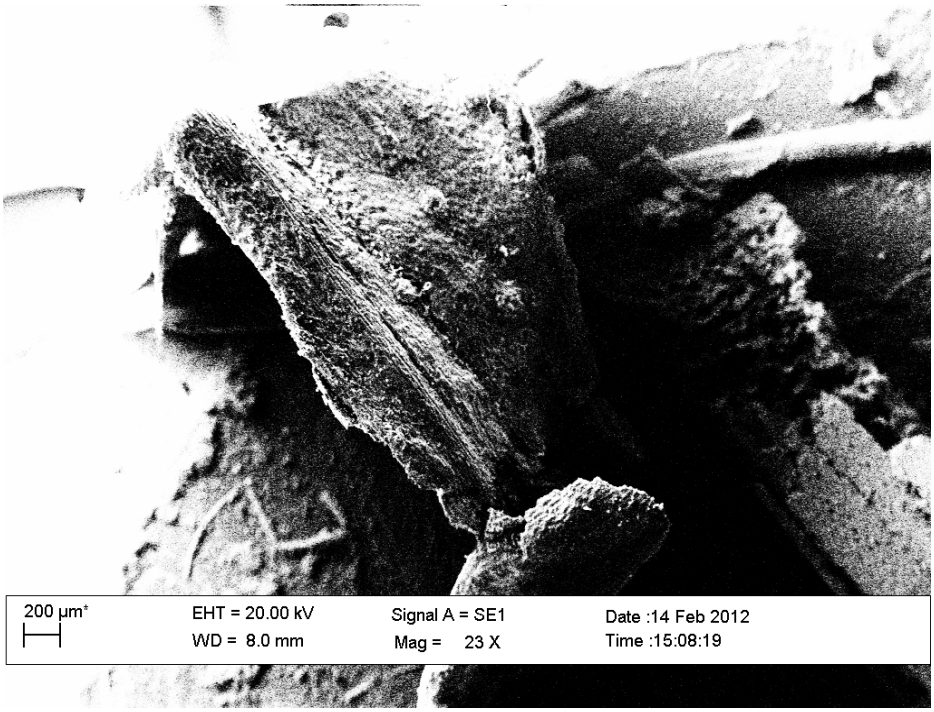


Figure 5-1: Maize silage without treatment.

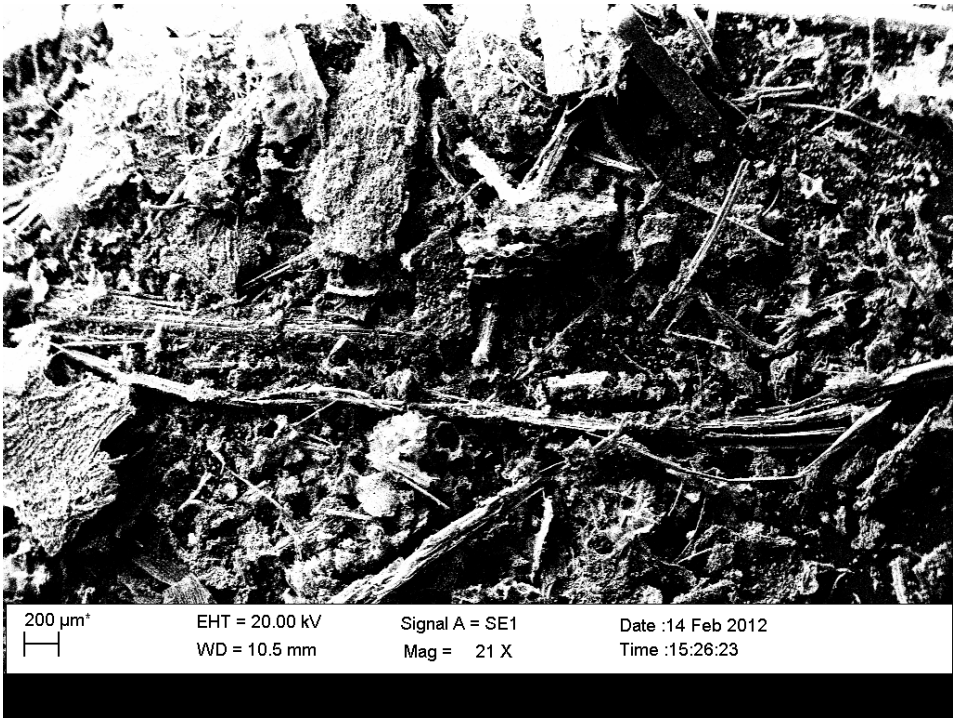


Figure 5-2: Maize silage with 20 mins beating.

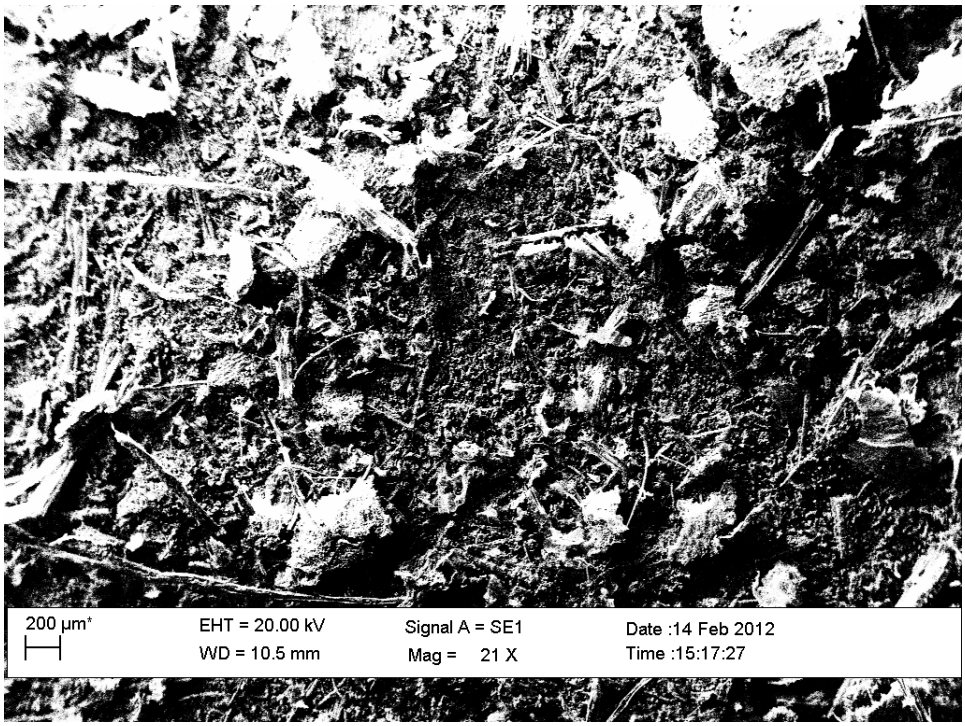


Figure 5-3: Maize silage with 60 minutes beating.

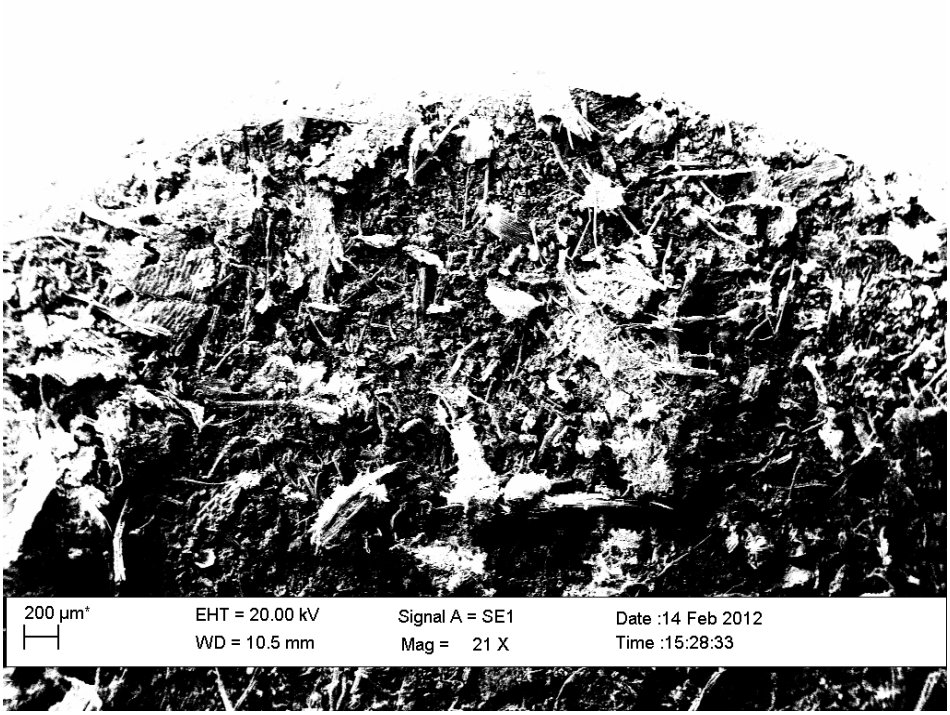


Figure 5-4: Maize silage with 180 minutes beating.

5.2.2.2 Degree of Beating Analysis

This analysis provides information on the effect of the treatment on the substrate with respect to particle size and the degree of beating. The Schopper Riegler apparatus described in section 4.2.2 was used to determine the degree of beating for the three levels of treatment. The test was done in duplicate. Table 5.10, and Figure 5-5 depicting the result of test and indicating that there is a relationship between beating time and degree of beating.

Table 5.10: Degree of beating of three levels of treatment.

	20 minutes	60 minutes	180 minutes
SR reading 1	82	86	89
SR reading 2	82	86	88
Average reading	**82**	**86**	**88.5**

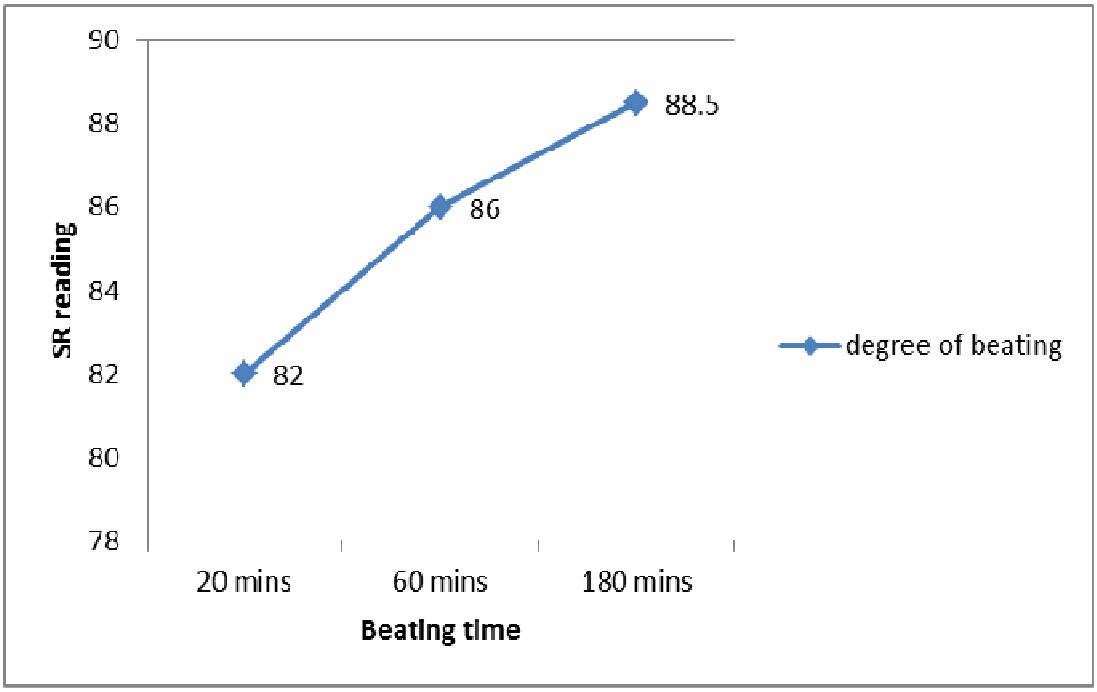


Figure 5-5: Degree of beating for maize silage after three levels of beating treatment.

5.2.2.3 Biogas measurement

An average of 897.3 mL of biogas was produced by the sludge reactors during the 21 the days of the experiment, which represents the sludge contribution to the biogas formation. This amount has been eliminated. Table 5.11, and Figure 5-6, show the amount of biogas produced every three days during the retention time of the process.

Table 5.11 and figure 5.6 clearly show that the beating mechanical treatment has a significant effect on the anaerobic digestion of maize silage. Results indicate the influence of treatment can be higher in the early days and then gradually diminished until absent in the final days of the process. The difference between the productivity of 1 g VS of untreated maize silage and the 1 g VS of treated maize silage (beating for 20 minutes) was 58% in the first collection of biogas which was in the 3rd day of the retention time of the process

Table 5.11: Collection of Biogas through the Retention Time of the AD Process.

Beating time	Biogas collection time (days)						
	3 (ml/g VS)	6 (ml/g VS)	9 (ml/g VS)	12 (ml/g VS)	15 (ml/g VS)	18 (ml/g VS)	21 (ml/g VS)
0 min	307.45	153.80	54.57	43.25	33.34	24.49	17.7
20 min	486.19	138.48	80.76	41.72	23.86	15.16	9.5
60 min	461.88	121.82	67.39	38.36	21.12	12.22	11.3
180 min	438.40	143.88	68.01	41.07	18.19	11.89	8.8

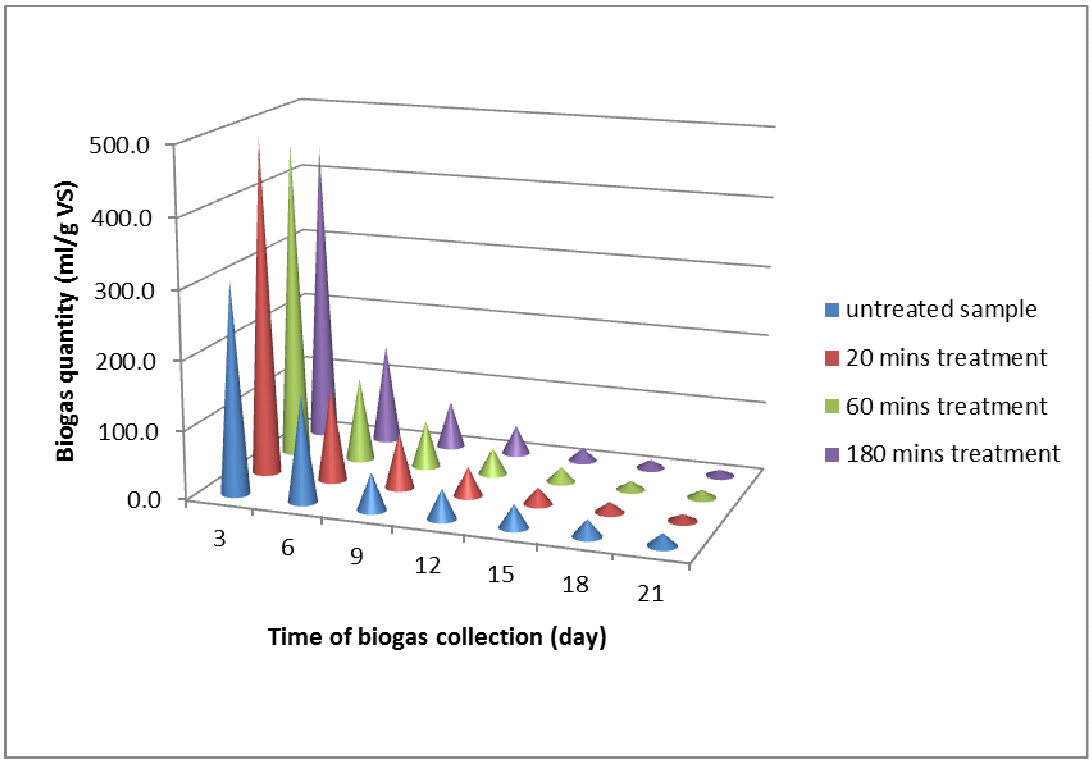


Figure 5-6: The productivity of untreated and treated maize silage samples.

5.2.2.4 Cumulative analysis

The biogas yield from all samples is in range 635 – 796 mL/g VS of maize, which is in the range quoted in section 4.1 [193, 194 and 7]. The cumulative analysis

expressed in Table 5.12, and presented in Figure 5-7, indicates that the total biogas produced after the beating treatment is higher. It can be seen that the highest amount of biogas was 796 mL/g VS produced after 20 minutes beating treatment, which achieved an improvement of 25.4% of biogas yield in comparison with the untreated sample. In contrast, it was found that the amount of biogas produced after 1-hour of the beating treatment is 734 mL/g VS and after 3-hours beating treatment is 730 mL/g VS, which achieved an improvement of about 15.7% and 15.1% of biogas yield respectively in comparison with untreated sample. This could be due to the effect of the particle size of the maize silage. The longer the beating times the smaller the particle size. Too small a particle size will dynamically accelerate the rate of hydrolysis and acidogenisis reactions, and then volatile fatty acids (VFA) are produced rapidly, resulting in an imbalance of production and consumption of VFA leading to accumulation of VFA, and inhibition of biogas production [219, 220].

Table 5.12: Collected Biogas Before and After Beating Treatment (Cumulative Data).

Beating time	Biogas collection time (days)						
	3 (ml/g VS)	6 (ml/g VS)	9 (ml/g VS)	12 (ml/g VS)	15 (ml/g VS)	18 (ml/g VS)	21 (ml/g VS)
0 min	307.4	461.2	515.8	559.1	592.4	616.9	634.6
20 min	486.2	624.7	705.4	747.2	771.0	786.2	795.7
1 hour	461.9	583.7	651.1	689.4	710.6	722.8	734.1
3 hours	438.4	582.3	650.3	691.4	709.6	721.4	730.2

Also from results there is indication that the optimum beating time will be around 20 minutes and also might be less than, which make this new method of treatment (Beating Treatment) might be cost effective.

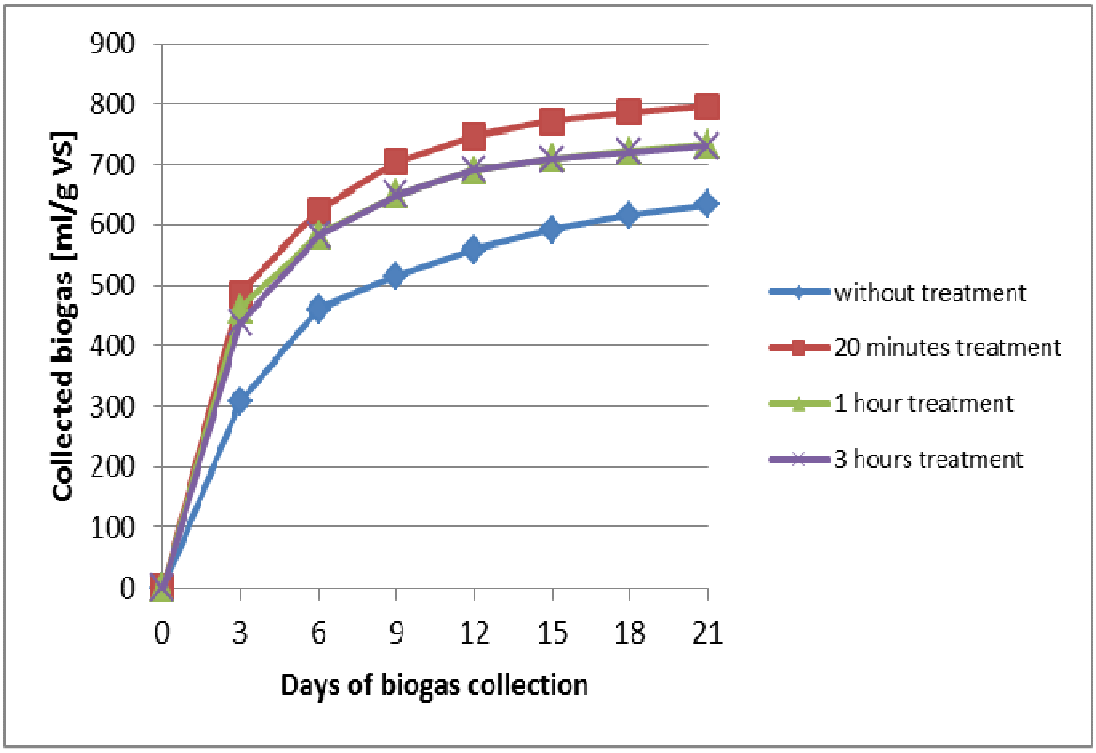


Figure 5-7: Comparison between the amounts of biogas generated from maize silage before and after beating treatment.

5.2.2.5 Biogas composition analysis

The fourth sample of each condition of experiment (A4, B4, C4 and D4) was used for concentration of biogas composition analysis. The concentration values were obtained using the gas analyser described in chapter 3. As expressed in Table 5.13, and depicted in Figure 5-8, the biogas composition was in agreement with [29]. The composition of biogas produced on average about 53% CH_4, 36% CO_2, and about 10% traces gases (Oxygen O_2 Nitrogen N_2, Hydrogen Sulphide H_2S, and Ammonia NH_3)

The methane (CH_4) content of the biogas from both the treated and untreated maize silage was close to 53%, this result is comparable with Stewart DJ et al [195]. The CH_4 concentration showed a value of 51% for untreated sample, 53% for 20 minutes beating time sample, 55% for 1-hour beating time sample and 54% for 3-hours beating time sample. The analysis indicates that CH_4 yield was 320 mL/g VS, 416.9 mL/g VS, 398.6 mL/g VS, 387.2 mL/g VS for untreated sample, 20 minutes beating treatment, 1-hour beating treatment and 3-hours beating time of treatment

respectively. This result in the line with S. Schittenhelm [193], T. Amon et al [194], and Z. Asam et al [7].

The fourth sample of each condition of experiment (A4, B4, C4 and D4) was used to determine the concentration of biogas and composition analysis. The concentration values were obtained by using the gas analyser described in chapter 3. As expressed in Table 5.13, and depicted in Figure 5-8, the biogas composition were in agreement with [29]. The composition of biogas produced on average 53% CH_4, 36% CO_2, and about 10% traces gases (Oxygen O_2 Nitrogen N_2, Hydrogen Sulphide H_2S, and Ammonia NH_3)

The methane (CH_4) content of the biogas from both the treated and untreated maize silage was close to 53%, this result is comparable with Stewart DJ et al [195]. The CH_4 concentration showed a value of 51% for untreated sample, 53% for 20 minutes beating time sample, 55% for 1-hour beating time sample and 54% for 3-hours beating time sample. The analysis indicate that CH_4 yield was 320 ml/g VS, 416.9 ml/g VS, 398.6 ml/g VS, 387.2 ml/g VS for untreated sample, 20 minutes beating treatment, 1-hour beating treatment and 3-hours beating time of treatment respectively. This result is in line with S. Schittenhelm [193], T. Amon et al [194], and Z. Asam et al [7].

Table 5.13: Concentration of biogas composition.

Elements (%)	without treatment	20 minutes treatment	1 hour treatment	3 hours treatment
CH_4	51	53	55	54
CO_2	37	35	36	36
other gases	12	12	9	10

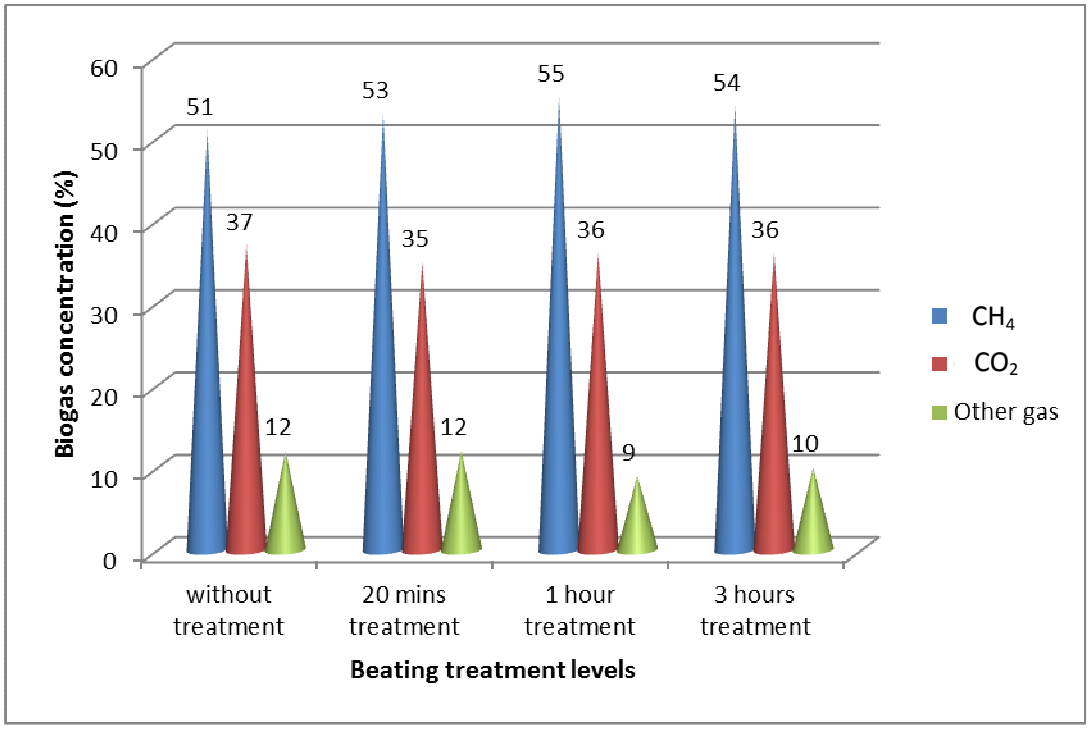


Figure 5-8: Biogas chemical composition (maize silage).

5.2.2.6 Regression Analysis

From the results presented in Figure 5.5, it is clear that there is a relationship between beating time and degree of beating. By using regression analysis and adding trendline to the chart presented in Figure 5.5, it was found that there is a polynomial relationship between beating time and degree of beating. By extending the trendline the degree of beating at zero can be predicted, (see Figure 5-9).

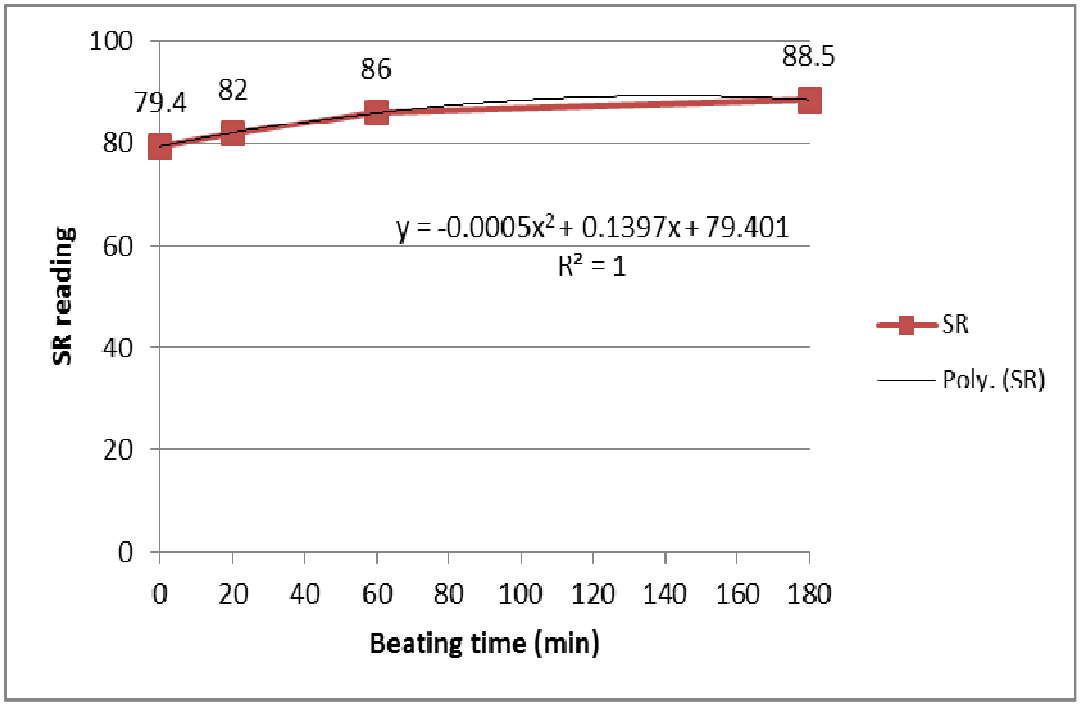


Figure 5-9: The relationship between beating time and (SR).

From the results presented in Table 5.12 it can be deduced that at any given quantity of maize silage the increase in the degree of beating or increase in the time of beating is inversely proportional to the quantity of biogas production. By using the trendline function and using the predicted value of the zero beating time, it was found that there is a 3 order polynomial relationship between two-mentioned variable (biogas production and degree of beating). Table 5.14 and Figure 5-10 depicting the relationship between these variables and describe it mathematically. Also from figure 5-10 it is clear that the production of biogas has the same trend during the retention time of digestion, but the interest observation is that the productivity after day fifteen is insignificant, which means that the decreased retention time from 21 days to 15 days can be suggested.

Table 5.14: The relationship between degree of beating and biogas production.

Beating time	SR	ml/g VS @ 3days	ml/g VS @ 6days	ml/g VS @ 9days	ml/g VS @ 12days	ml/g VS @ 15days	ml/g VS @ 18days	ml/g VS @ 21days
0 min	79.5	307.4	461.2	515.8	559.1	592.4	616.9	634.6
20 min	82	486.2	624.7	705.4	747.2	771.0	786.2	795.7
1 hour	86	461.9	583.7	651.1	689.4	710.6	722.8	734.1
3 hours	88.5	438.4	582.3	650.3	691.4	709.6	721.4	730.2

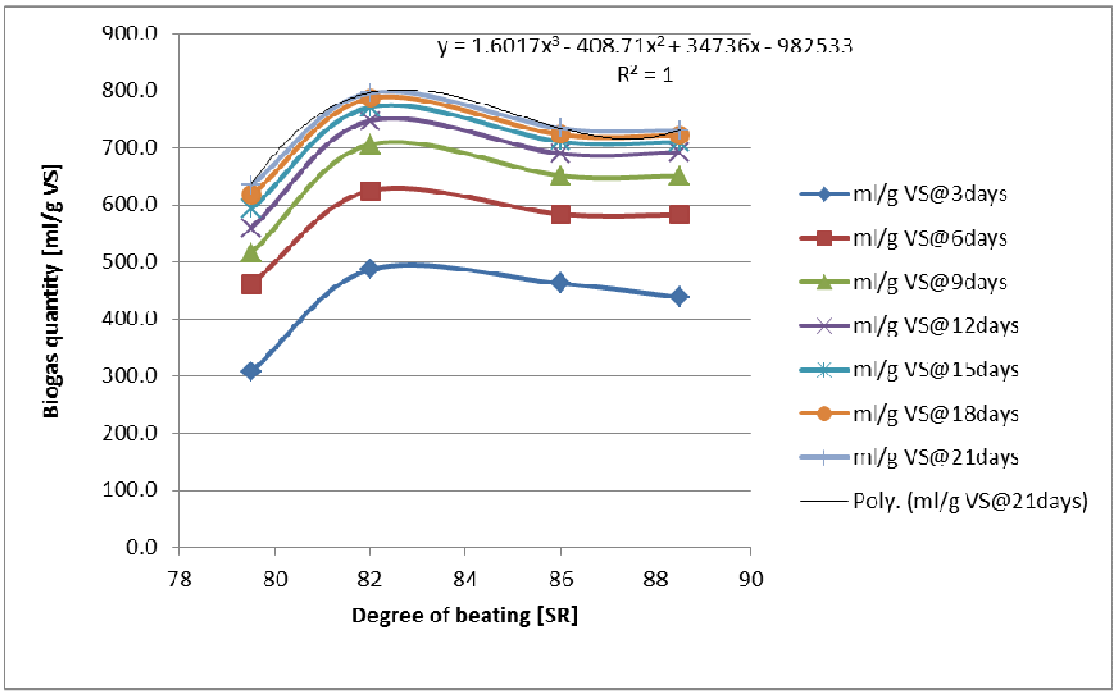


Figure 5-10: Third polynomial relationship between biogas production and degree of beating.

5.2.2.7 Energy analysis

The mechanical pre-treatment is considered to be one of the most expensive processing steps in biomass converting to fermentable sugars [152]. Nevertheless, as mentioned in chapter 2 mechanical pre-treatment is required to alter the biomass structure, to increase the specific surface area, and to decrease cellulose crystallinity, so that hydrolysis to monomeric sugars can be achieved more rapidly and with higher yields. In order to evaluate the economic feasibility at the lab scale of beating treatment, the specific energy consumption was calculated and compared with the biogas energy produced. Appendix "B" contains all details and equations that have been used for this analysis.

As previously discussed, the dry matter of 13g of untreated maize silage is 4.47g, implying that the total dry matter of total wet maize silage (1500g) is equal to 515.8g. The VS of the total maize silage has been treated (1500g) is 496.7g (see equation 5-1 presented in appendix "B"). The total biogas yield (Y) expected from total untreated substrate is 315.2 L (given by formula 5-2 presented in appendix "B").

It has been indicated that biogas yield from maize silage after 20 minutes beating time is 795.7 mL/g VS, 734.1 mL/g VS after 60 minutes beating time and 730.2 mL/g VS after 180 minutes beating time; therefore the total biogas yield (Y_1, Y_2 and Y_3) for three different levels of treatment will be 393.6 L, 363.2 L and 361.2 L of biogas respectively. The increment of biogas production from total treated substrate (after 20 minutes beating, 60 minutes beating and 180 minutes beating time) in comparison with total untreated substrate are 78.4 L, 48 L and 46 L of biogas respectively.

The energy content of the increment of biogas was calculated based on a value of 9810 Wh/Nm3 [221]. The electricity used to achieve treatment for each level was measured. 0.147kWh was consumed for 20 minutes beating, 0.381kWh for 60 minutes beating and 0.986Kwh was consumed for 180 minutes. Table 5.15 illustrates the amount of energy content in the increment of biogas after three different levels of beating. Also it shows that an incremental rate in percentage can be obtained through applying the beating treatment to maize silage. Thus it was found that the first level of treatment has a positive energy balance. The second level (60 minutes beating) and third level of treatment (180 minutes beating) have a negative energy balance, (see Table 5.15).

Table 5.15: Energy analysis.

Beating Time	Increment of Biogas (l/kg VS)	CH_4 %	Content of Energy Produced (EP) (kWh/l)	Electricity Used (EU) - (kWh)	% Energy Balance of (EU) vs. (EP)
20 min	78.4	53	0.41	0.147	35.85
60 min	48	55	0.26	0.381	146.4
180 min	46	54	0.24	0.986	410.8

5.3 Fresh grass

5.3.1 Analysis

All the analysis and calculation mention in chapter 4 section 4.2.6 and conducted in previous experiment have been conducted. The Total Solid (TS) of untreated sample was 2.13 g, 5 minutes beating treatment sample was 1.4 g, 15 minutes beating time sample was 1.93 g, while the TS of 40 minutes beating time sample was 1.9 g. Tables 5.16 – 5.19 depict the details of the TS analysis.

The VS of untreated sample was 90.3% of TS, 5 minutes beating treatment sample was 96% of TS of sample, 15 minutes beating time sample was 95.5%, and for 40 minutes beating time sample was also 94.8% of TS. Tables 5.20 – 5.23 depicted the details of the VS analysis.

The pH was measured for all samples before and after digestion, this was deemed within the optimum range [217] (see Table 5.24).

Table 5.16: Total dry solid content for each sample of grass (without treatment).

Sample No.	dish plate weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
1	173.2	186.2	13	175.3	2.1
2	231.7	244.7	13	233.8	2.1
3	148.4	161.4	13	150.6	2.2
Average					2.13

Table 5.17: Total dry solid content for each sample with 5 minutes treatment

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
4	114.6	218.5	103.9	116	1.4
5	116.2	221.3	105.1	117.5	1.3
6	110.5	214.8	104.3	112	1.5
Average			104.5		1.40

Table 5.18: Total dry solid content for each sample with 15 mins treatment.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
7	111.4	214.6	103.2	113.4	2
8	116.2	218.2	102	118	1.8
9	111.9	216.8	104.9	113.9	2
Average			103.37		1.93

Table 5.19: Total dry solid content for each sample with 40 mins treatment.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
10	112.2	222.1	109.9	114.3	2.1
11	110.3	231	120.7	112.2	1.9
12	117.1	236.3	119.2	118.8	1.7
Average			116.60		1.90

Table 5.20: Percentage of ash in untreated sample.

sample No.	container weight	container + sample weight	sample weight (W2)	container + ash weight	ash weight (W1)	Ash%
1	54.6282	55.2871	0.6589	54.6938	0.0656	9.955987
2	54.628	55.2763	0.6483	54.6893	0.0613	9.455499
Average						9.7

Table 5.21: Percentage of ash in 5 minutes beating sample.

sample. No.	container weight	container + sample weight	sample weight (W2)	container + ash weight	ash weight (W1)	Ash%
1	54.6277	55.2082	0.5805	54.6504	0.0227	3.910
2	54.6279	55.2712	0.6433	54.654	0.0261	4.057
Average						4.0

Table 5.22: Percentage of ash in 15 minutes beating sample.

sample No.	container weight	container + sample weight	sample weight (W2)	container + ash weight	ash weight (W1)	Ash%
1	54.6285	55.3034	0.6749	54.6585	0.03	4.445
2	54.6284	55.2483	0.6199	54.6572	0.0288	4.646
Average						4.5

Table 5.23: Percentage of ash in 40 minutes beating sample.

sample No.	container weight	container + sample weight	sample weight (W2)	container + ash weight	ash weight (W1)	Ash%
1	54.6283	55.2693	0.641	54.6624	0.0341	5.320
2	54.6278	55.2361	0.6083	54.6585	0.0307	5.047
Average						5.2

Table 5.24: pH value of samples of each level of treatment.

Grass	Untreated sample	5 Minutes Treatment	15 Minutes Treatment	40 Minutes Treatment
Before Digestion	7.9	8.1	8.16	8.1
After Digestion	7.79	7.8	7.74	7.78

5.3.2 Result and discussion

5.3.2.1 SEM analysis

Figure 5-11 shows the grass structure before treatment while Figure 5-12, Figure 5-13, Figure 5-14 illustrates the grass structure after the three different levels of beating treatment. It is evident from the SEM analysis that there are changes in the microstructure of the grass after the beating treatment that has been applied over the period of its analytical processes. This will result in the reduction of particle sizes thereby leading to an increment of the surface area.

In essence, due to the lignin and cellulose being able to be broken, that will in a way speed up the fermentation process, and invariably leads to much moisture production that will give rise to more biogas to be produced at the end [192] and [218].

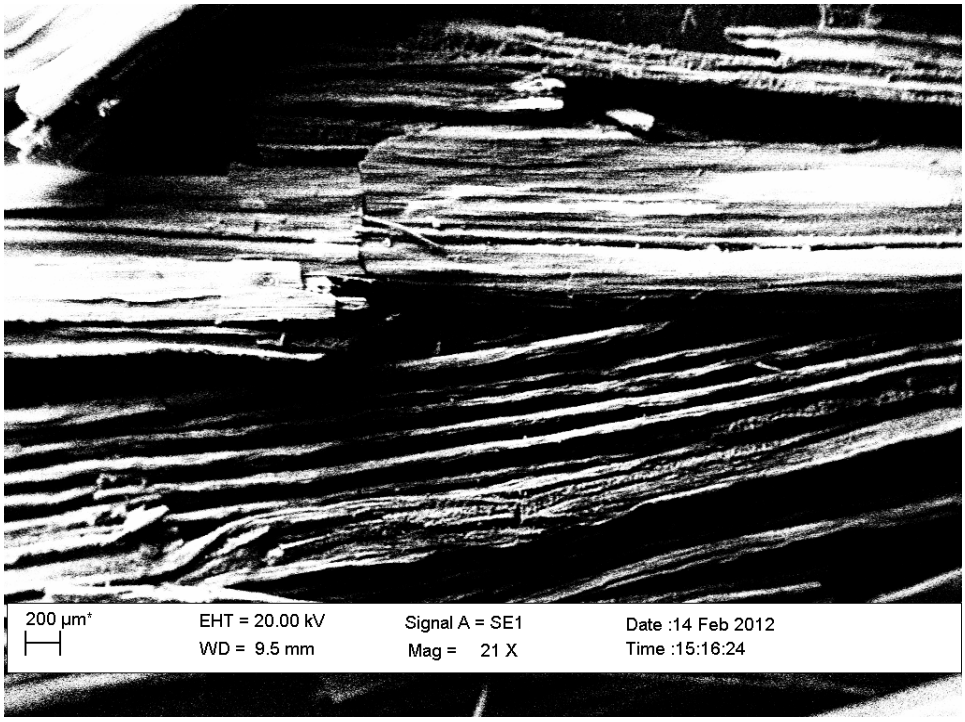


Figure 5-11: Grass without treatment.

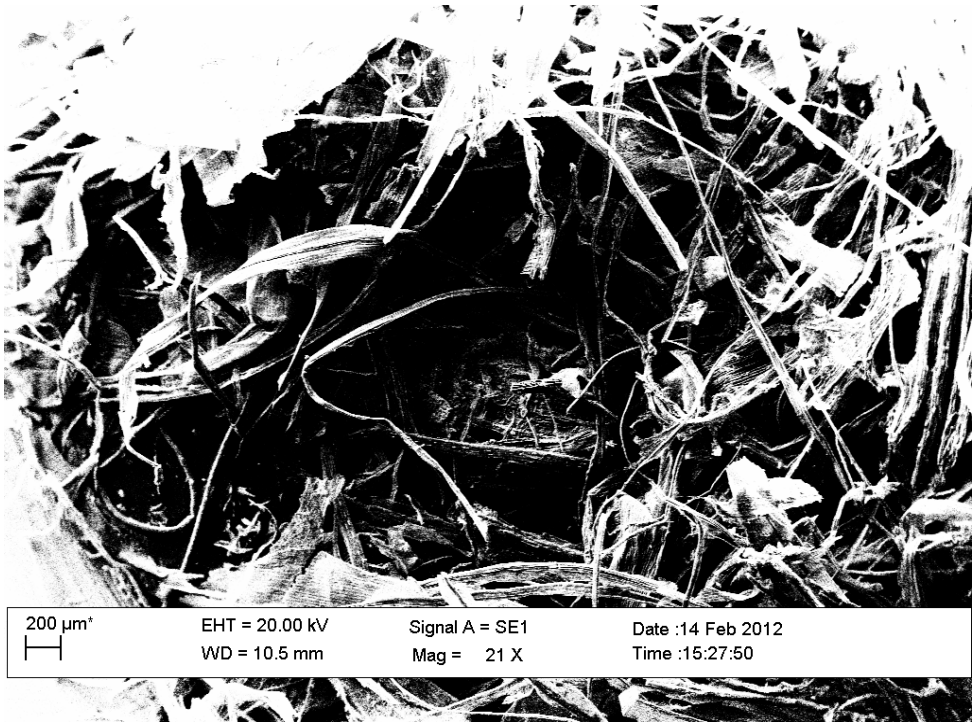


Figure 5-12 Grass with 5 minutes beating.

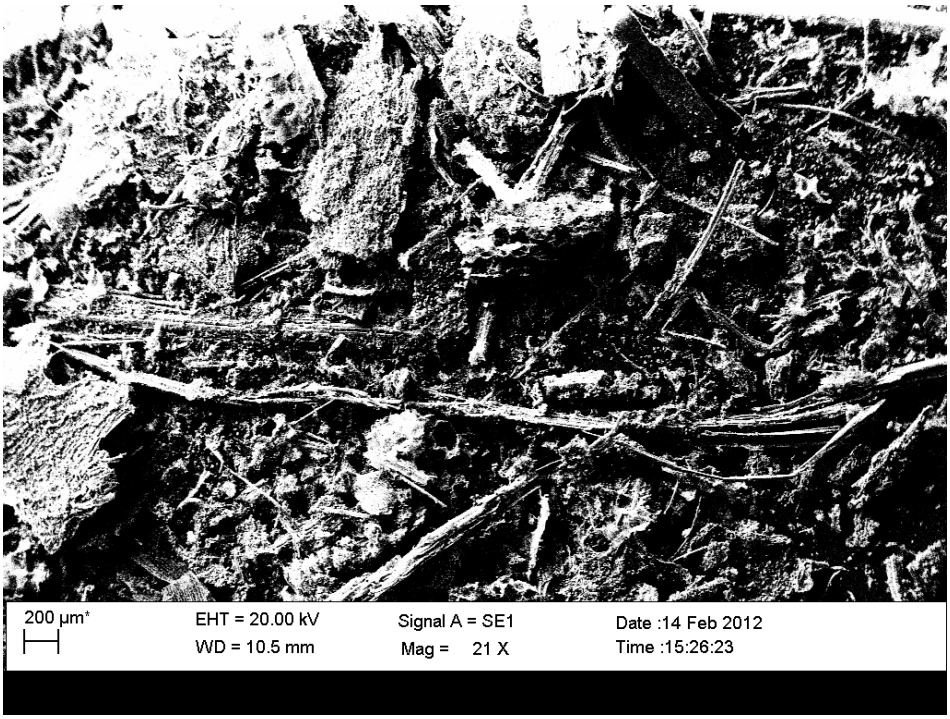


Figure 5-13Grass with 15 minutes beating.

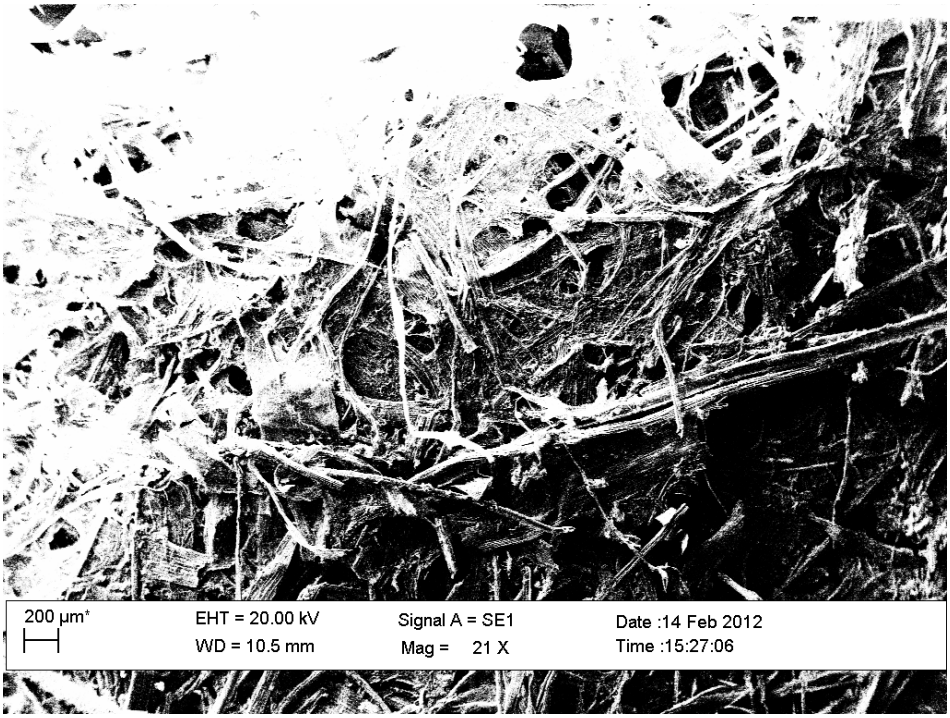


Figure 5-14Grass with 40 minutes beating.

5.3.2.2 Degree of Beating Analysis

The same device (Schopper Riegler apparatus) has been used to determine the degree of beating for the three levels of treatment of fresh grass. The test was done in duplicate. It can be seen from Table 5.25, the average SR reading of first level (5 minutes beating) was 67 SR, the average SR reading for second level (15 minutes beating) was 71.5 SR, while the average SR reading for third level (40 minutes) was 75 SR.

The degree of beating value might be useful as an indication for the particle size reduction of the substrate after each level of beating. Figure 5-15 depicting the result of test and indicating that there is a relationship between beating time and degree of beating.

Table 5.25: degree of beating of three levels of treatment.

Beating Time	5 minutes	15 minutes	40 minutes
SR Reading 1	67	71	75
SR Reading 2	67	72	75
Average SR Reading	**67**	**71.5**	**75**

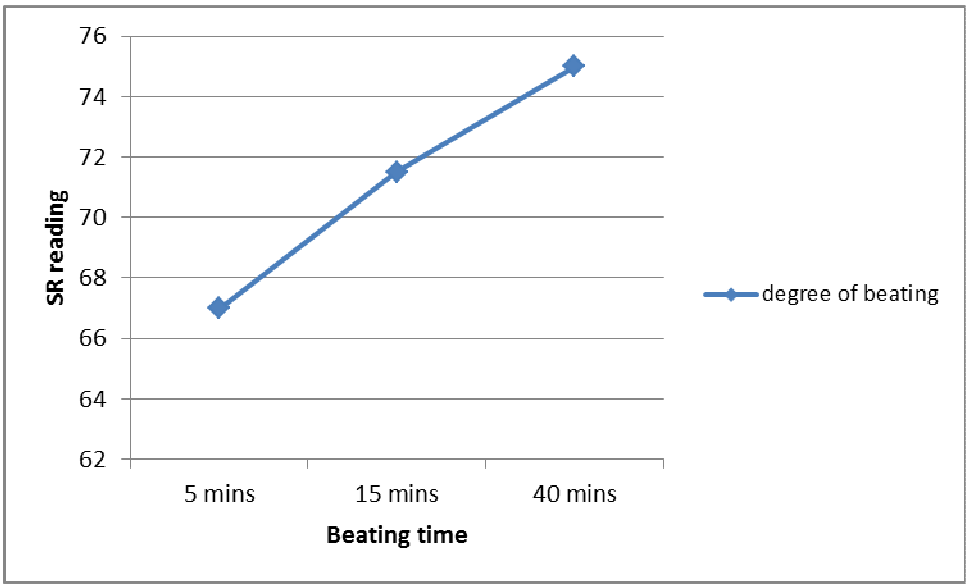


Figure 5-15: Degree of beating for grass after three levels of beating treatment.

5.3.2.3 Biogas measurement

An average of 776 mL of biogas was produced by the sludge reactors during the 21 days of the experiment, which represents the sludge contribution to the biogas

formation. This amount has been eliminated. Table 5.26, and Figure 5-16, clearly show that the beating mechanical treatment has a very significant effect on the anaerobic digestion of grass. Results indicate the influence of treatment can be higher in the early days and then gradually diminished until absent in the final days of the process. The difference between the productivity of 1 g VS of untreated grass and the same quantity of treated grass (beating for 5 minutes) was very high in the first collection of biogas. The biogas yield was high for first level (5 minutes beating), corresponding to about 3 times the biogas yield for the untreated sample. While the biogas yield for second and third level of treatment (15 minutes beating time and 40 minutes beating time respectively), corresponds to c.a. 2.8 times the biogas yield for untreated sample.

Table 5.26: Collection of Biogas through the Retention Time of the AD Process.

Beating time	Biogas collection time (days)						
	3 (ml/g VS)	6 (ml/g VS)	9 (ml/g VS)	12 (ml/g VS)	15 (ml/g VS)	18 (ml/g VS)	21 (ml/g VS)
0 min	194.7	176.5	137.2	80.7	37.9	24.9	17.2
5 min	588.7	140.0	95.4	48.2	33.4	31.8	20.0
15 min	567.0	143.7	74.4	40.4	27.1	26.3	25.9
40 min	536.7	149.6	65.5	36.3	27.4	23.7	22.2

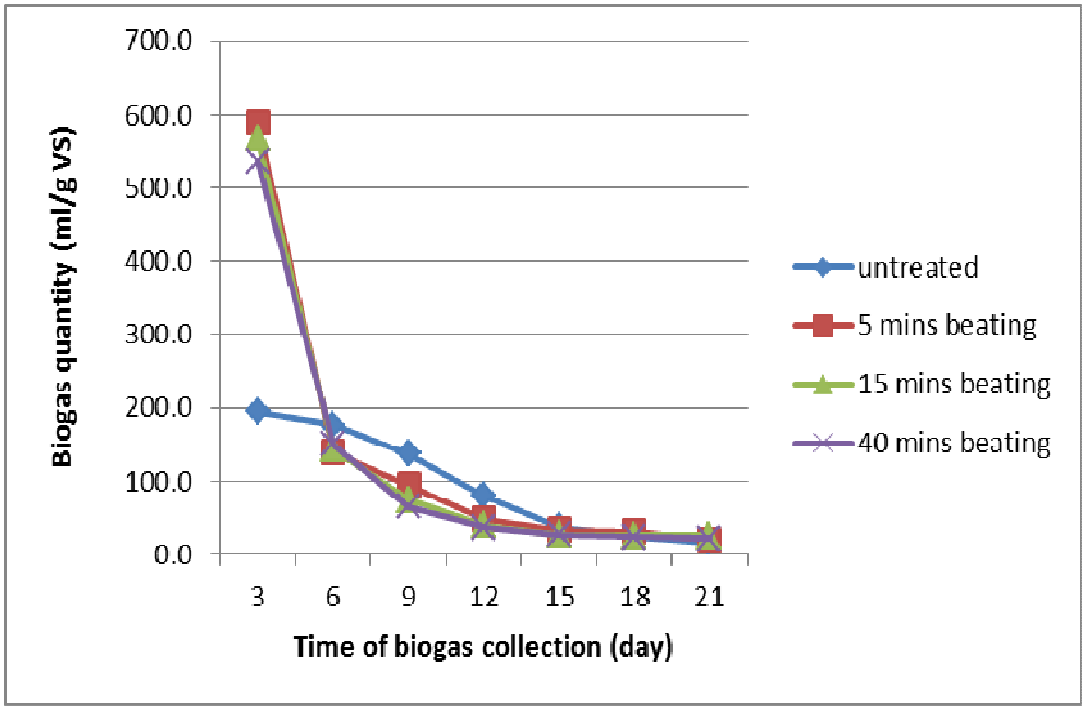


Figure 5-16: The productivity of untreated and treated samples of grass.

5.3.2.4 Cumulative analysis

The biogas yield from all samples is in range 669 – 957 mL/g VS of grass, which is in the range documented by Nizami and Murphy [203]. The cumulative analysis expressed in Table 5.27, and presented in Figure 5-7, indicates that the total biogas produced after the beating treatment is higher. It can be seen that the highest amount of biogas was 957.4 mL/g VS produced after 5 minutes beating treatment, which achieved an improvement of 43.1% of biogas yield in comparison with untreated sample. In contrast, it was found that the amount of biogas produced after 15 minutes beating treatment is 904.8 mL/g VS and after 40 minutes beating treatment is 861.5 mL/g VS, which achieved an improvement of about 35.2% and 28.8% of biogas yield respectively in comparison with the untreated sample. This could be due to the effect of the particle size of the grass. The longer the beating time the smaller the particle size. Too small a particle size will dynamically accelerate the rate of hydrolysis and acidogenisis reactions, and then volatile fatty acids (VFA) are produced rapidly, resulting in imbalance of production and consumption of VFA leading to accumulation of VFA, and inhibition of biogas production. [219 and 220].

Table 5.27: Collected biogas before and after beating treatment (cumulative data).

Beating time	Biogas collection time (days)						
	3 (ml/g VS)	6 (ml/g VS)	9 (ml/g VS)	12 (ml/g VS)	15 (ml/g VS)	18 (ml/g VS)	21 (ml/g VS)
0 min	194.7	371.2	508.4	589.1	627.0	651.9	669.1
5 min	588.7	728.7	824.1	872.3	905.6	937.4	957.4
15 min	567.0	710.7	785.1	825.5	852.6	878.9	904.8
40 min	536.7	686.3	751.8	788.1	815.5	839.3	861.5

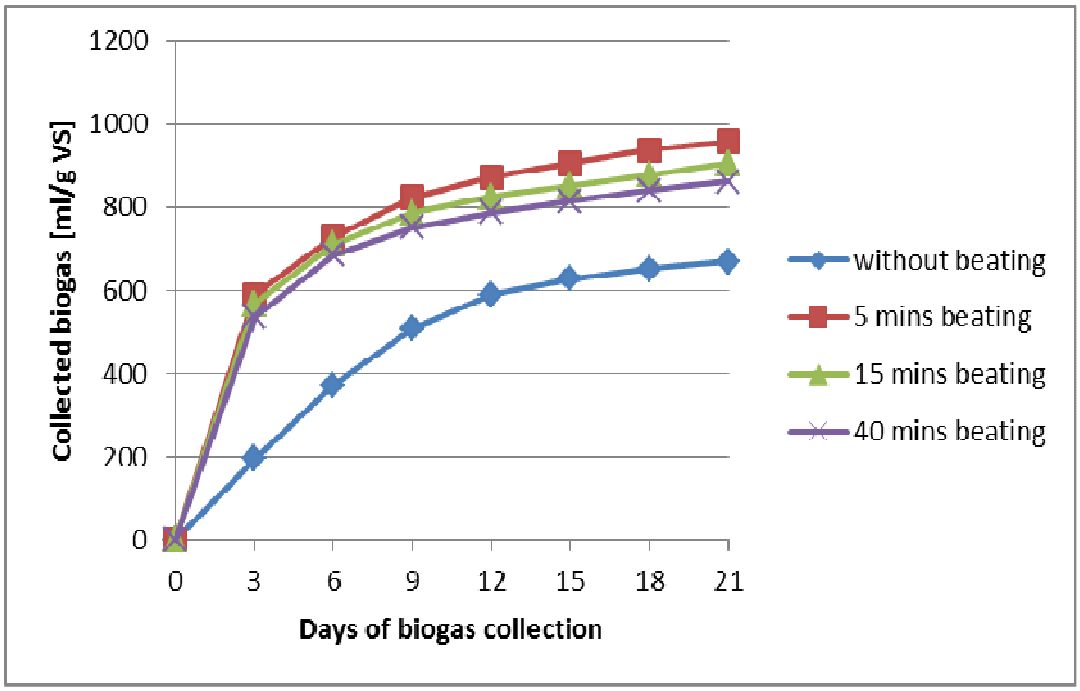


Figure 5-17: Comparison between the Amounts of Biogas Generated From Grass Before & after beating treatment.

5.3.2.5 Biogas composition analysis

The fourth reactor of each condition of the experiment (A13, B13, C13 and D13) was used for the concentration of biogas and its composition analysis. The concentration values were obtained using the gas analyser. As expressed in Table 5.28 and depicted in Figure 5-18, the biogas composition was in agreement with Jönsson et al., [29]. The average methane yield was 51.5% of biogas produced. The average of carbon dioxide was 38%, while the other gases (Oxygen O_2 Nitrogen N_2, Hydrogen Sulphide H_2S, and Ammonia NH_3) were 10%.

The methane (CH_4) content of the biogas from both the treated and untreated fresh grass was 51%, this result is comparable with [200 - 203]. The CH_4 concentration showed a value of 53% for the untreated sample, 50% for 5 minutes beating time sample, 51% for 15 minutes beating time sample and 52% for 40 minutes beating time sample. The analysis indicate that CH_4 yield was 354.6 mL/g VS, 478.7 mL/g VS, 461.5 mL/g VS, 448 mL/g VS for the untreated sample; 5 minutes beating treatment, 15 minutes beating treatment and 40 minutes beating time of treatment

respectively. This result is in line with Murphy et al [202], Nizami and Murphy [203] and comparable with Mahnert et al [209] .

Table 5.28: Concentration of Biogas Composition.

Gas (%)	without treatment	5 mins treatment	15 mins treatment	40 mins treatment
CH_4	53	50	51	52
CO_2	37	38	38	39
other gases	10	12	11	9

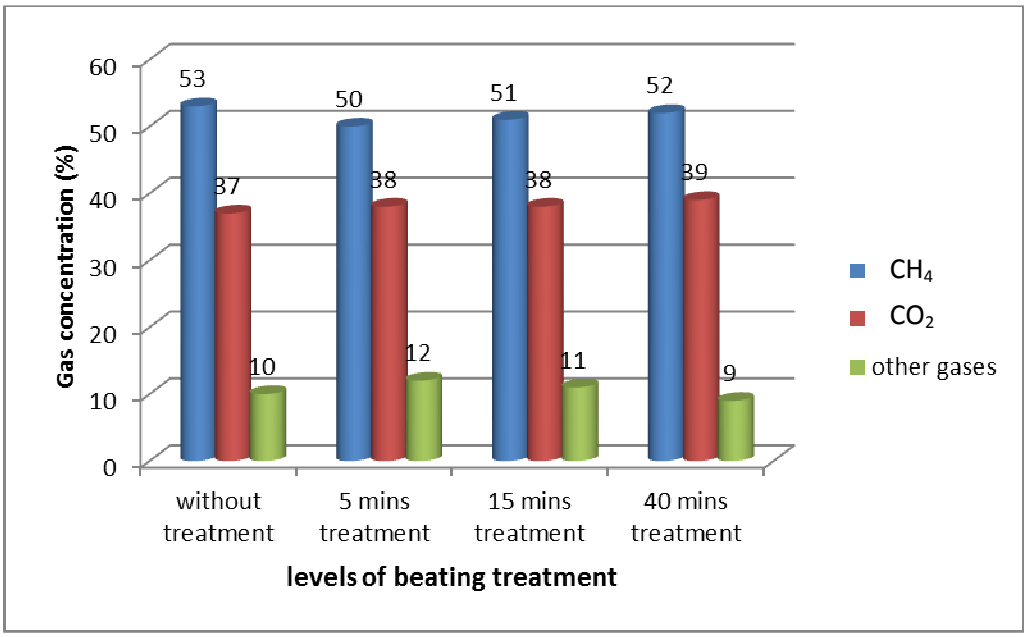


Figure 5-18: Biogas chemical composition (fresh grass).

5.3.2.6 Regression Analysis

In fitting a trendline to the chart presented in figure 5.12, it was found that there is a 2nd order polynomial relationship between beating time and degree of beating (see figure 5.13). . By extending the trendline the degree of beating at zero beating time can be predicted,

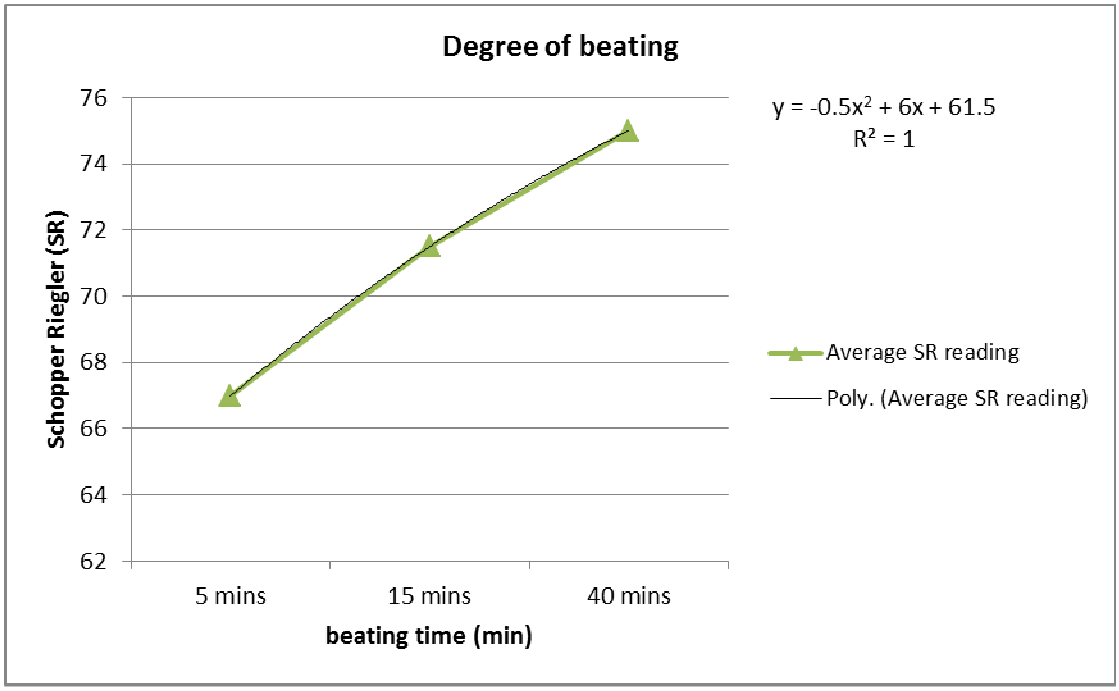


Figure 5-19: The relationship between beating time degree of beating.

From the results presented in Table 5.27, it can be deduced that at any given quantity of grass, the increase in the degree of beating (i.e., time of beating) is inversely proportional to the quantity of biogas production (see Table 5.29). With further analysis, it was found that there is a 3rd order polynomial relationship between the biogas production and degree of beating. Figure 5-20, depicts the mathematical and graphical relationship between these two variables. Furthermore, it can be seen that the production of biogas has the same trend during the retention time of digestion; the interesting observation is that the 15 days of retention time can be suggested as the increase in productivity afterwards is insignificant.

Table 5.29: the relationship between degree of beating and biogas production.

SR	ml/g VS @ 3 days	ml/g VS @ 6 days	ml/g VS @ 9 days	ml/g VS @ 12 days	ml/g VS @ 15 days	ml/g VS @ 18 days	ml/g VS @ 21 days
61.5	194.7	371.2	508.4	589.1	627.0	651.9	669.1
67	588.7	728.7	824.1	872.3	905.6	937.4	957.4
71.5	567.0	710.7	785.1	825.5	852.6	878.9	904.8
75	536.7	686.3	751.8	788.1	815.5	839.3	861.5

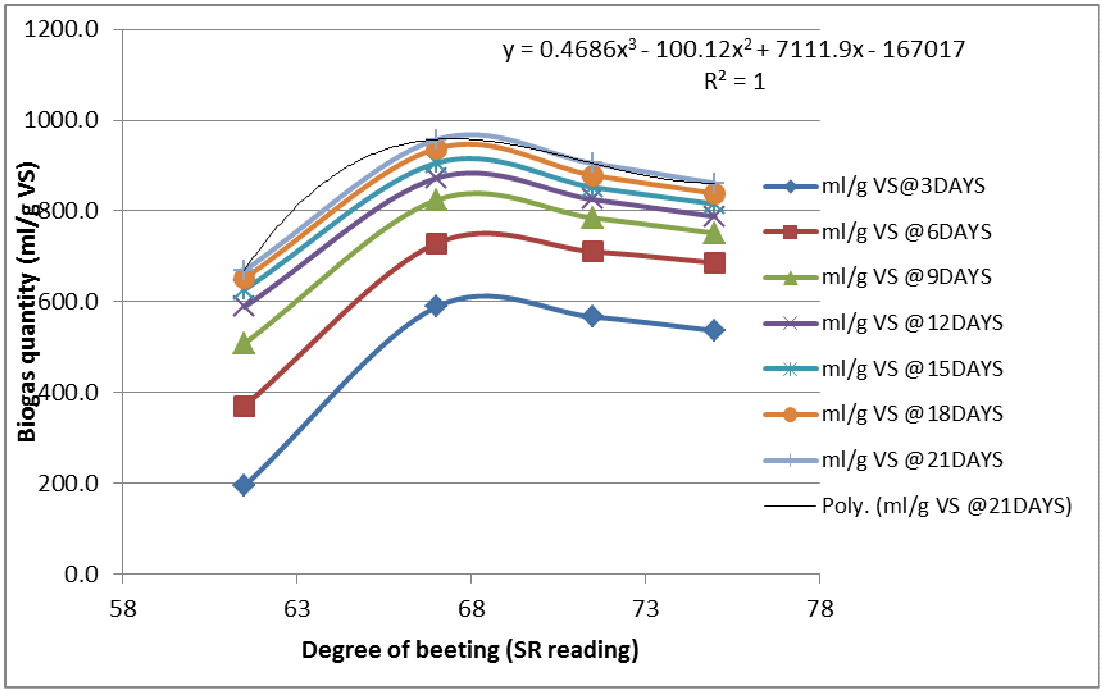


Figure 5-20: The relationship between degree of beating and biogas production.

5.3.2.7 Energy analysis

Equations 5.1 – 5.5 (presented in appendix B) have been used to evaluate the economic feasibility at lab scale of beating treatment for grass as renewable energy resource (calculation with details presented in appendix C).

Aforementioned, the dry matter of 13 g of untreated fresh grass is 2.13g, implying that the total dry matter of total wet maize silage (1000g) is equal to 163.9g. The VS of the total grass has been treated (1000g) is 148g (see formula 5-1 presented in appendix "A"). The total biogas yield (Y) expected from total untreated substrate is 99 L (given by formula 5-2 presented in appendix "B").

It has been indicated that biogas yield from grass after 5 minutes beating time is 957.4 mL/g VS, 904.8 mL/g VS after 15 minutes beating time and 861.5 mL/g VS after 40 minutes beating time; therefore the expected biogas yield from total substrate after three different levels of treatment (Y_1, Y_2 and Y_3) will be 150.7 L, 141.6 L and 133.9 L of biogas respectively. The increment of biogas production from total treated substrate (after 5 minutes beating, 15 minutes beating and 40 minutes beating time) in comparison with total untreated substrate are 51.7 L, 42.6 L and 34.9 LL of biogas respectively. For more details see Appendix "C".

The energy content of the increment of biogas was calculated based on a value of 9810 Wh/Nm^3 [221]. The electricity used to achieve treatment for each level was measured. 0.054 KWH was consumed for 5 minutes beating, 0.11 KWH for 15 minutes beating and 0.233 KWH was consumed for 40 minutes. Table 5.27 illustrates the amount of energy content in the increment of biogas after three different level of beating. Also it shows the incremental rate in percentage can be obtained through applying the beating treatment to grass. It was found that first and second level of treatment have a positive energy balance., while third level of treatment (40 minutes beating) have negative energy balance (see Table 5.30).

Table 5.30: Energy analysis.

beating time	increment of biogas (l/x_{total} VS)	CH4 (%)	content of Energy Produced [EP] (kWh/l)	Electricity Used [EU] (kWh)	% energy balance [EU] vs. [EP]
5 minutes	51.7	50	0.25	0.054	21.6
15 minutes	42.6	51	0.21	0.11	52.4
40 minutes	34.9	52	0.18	0.233	129.4

5.4 Potato waste

5.4.1 Analysis

In addition to SEM analysis, wet sieve analysis was conducted to estimate the effect of treatment on particle size of substrate by using five different size of sieves [162]. The analysis based on the percentage of the pulp (substrate with water after treatment) doesn't fell in whatever size fraction.

The Total Solid TS of untreated sample was 3.57g, 5 minutes beating treatment sample was 2.43 g, 15 minutes beating time sample was 3.07g, 35 minutes beating time sample was 2.73 g, while the TS of 60 minutes beating time sample was 2.67 g. Tables 5.31 – 5.35 depicted the details of the TS analysis.

The VS of untreated sample was 91.4% of TS, 5 minutes beating treatment sample was 93.6% of TS of sample, 35 minutes beating time sample was 95%, and for 60 minutes beating time sample was 94.8% of TS. Tables 5.36 – 5.40 depicted the details of the VS analysis.

The pH was measured for all samples after digestion, it was within the optimum range [217] (see Table 5.41).

Table 5.31: Total dry solid content for untreated sample.

Sample No.	dish plate weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
1	123.4	138.4	15	127.1	3.7
2	173.2	188.2	15	176.9	3.7
3	137.4	152.4	15	140.7	3.3
Average					3.57

Table 5.32: Total dry solid content for 5 minutes treatment sample.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
4	114.9	306.8	191.9	117.3	2.4
5	110.4	304.6	194.2	112.9	2.5
6	113.4	308.4	195	115.8	2.4
Average			193.05		2.43

Table 5.33: Total dry solid content for 15 minutes treatment sample.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
7	111.5	308	196.5	114.6	3.1
8	116.2	310.9	194.7	119.3	3.1
9	111.9	294.4	182.5	114.9	3
Average			191.23		3.07

Table 5.34: Total dry solid content for 35 minutes treatment sample.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
10	111.5	310	198.5	114.4	2.9
11	114.2	312.1	197.9	116.8	2.6
12	117	313.4	196.4	119.7	2.7
Average			197.60		2.73

Table 5.35: Total dry solid content for 60 minutes treatment sample.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
13	112.1	308.8	196.7	114.7	2.6
14	116.3	307.5	191.2	118.8	2.5
15	112.8	308.6	195.8	115.7	2.9
Average			194.57		2.67

Table 5.36: Percentage of ash in untreated sample.

sample No.	container r weight	container + sample weight	sample weight (W2)	container + ash weight	ash weight (W1)	Ash %
1	54.6271	55.2948	0.6677	54.685	0.0579	8.6716
2	54.6272	55.3472	0.72	54.6879	0.0607	8.4306
Average						8.6

Table 5.37: Percentage of ash in 5 minutes beating sample.

sample No.	container r weight	container + sample weight	sample weight (W2)	container + ash weight	ash weight (W1)	Ash %
1	54.6282	55.3196	0.6914	54.6721	0.0439	6.3494
2	54.628	55.3472	0.7192	54.6749	0.0469	6.5211
Average						6.4

Table 5.38: Percentage of ash in 15 minutes beating sample.

sample No.	container weight	container + sample weight	sample weight (W2)	container+ ash weight	ash weight (W1)	Ash %
1	54.6291	55.3173	0.6882	54.6759	0.0468	6.8003
2	54.6285	55.348	0.7195	54.6749	0.0464	6.4489
Average						6.6

Table 5.39: Percentage of ash in 35 minutes beating sample.

sample No.	container weight	container + sample weight	sample weight (W2)	container + ash weight	ash weight (W1)	Ash %
1	54.6278	55.2385	0.6107	54.6579	0.0301	4.9288
2	54.628	55.2732	0.6452	54.6611	0.0331	5.1302
Average						5.0

Table 5.40: Percentage of ash in 60 minutes beating sample.

sample No.	container weight	container + sample weight	sample weight (W2)	container + ash weight	ash weight (W1)	Ash %
1	54.6287	55.2842	0.6555	54.6637	0.035	5.3394
2	54.6283	55.269	0.6286	54.66	0.0317	5.0430
Average						5.2

Table 5.41: pH value of samples of each level of treatment.

potato waste	untreated sample	5 min beating sample	35 beating sample	60 min beating sample
after digestion	7.05	7.11	7.03	7.24

5.4.2 Result and Discussion

5.4.2.1 SEM analysis

The effect of beating treatment on potato waste can be visually measured using Scan electron microscopy. Figure 5-21 shows the potato structure before treatment and Figures 5-21 to 5-25 exhibiting the structure of potato waste after the different levels of beating treatments. From these figures it is a clear indication that there has been significant damage and changes in the structure of potato waste in terms of reduction of particle size and increase surface area, also the crystalline structure of cellulose cells has been disrupted and invariably led to its deformation. This is in fact would assist the fermentation process as reported in [192] and [218].

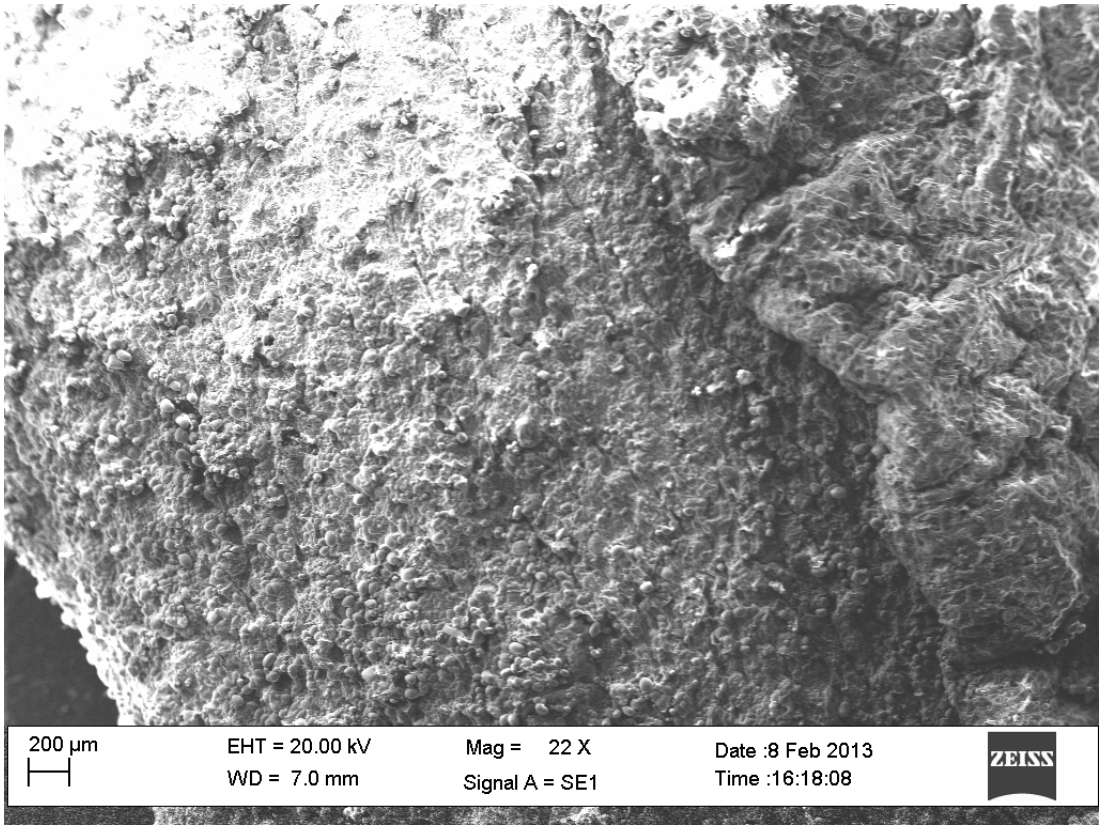


Figure 5-21: Untreated potato waste sample.

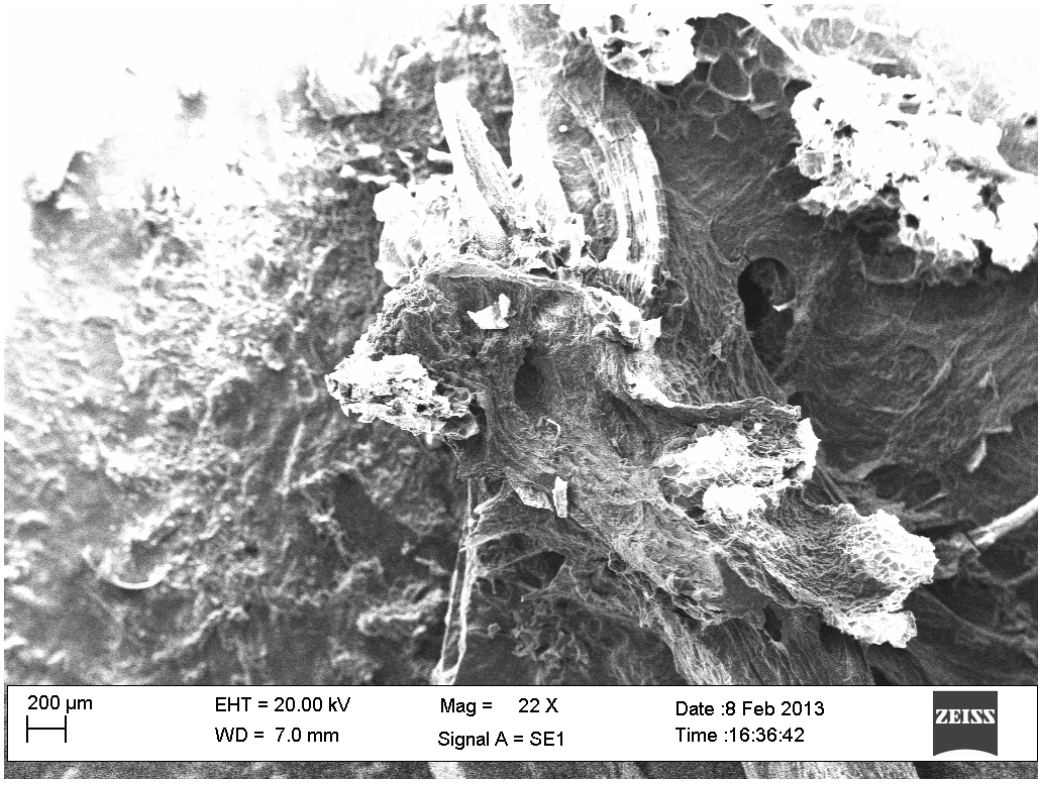


Figure 5-22: potato waste after 5 minutes treatment.

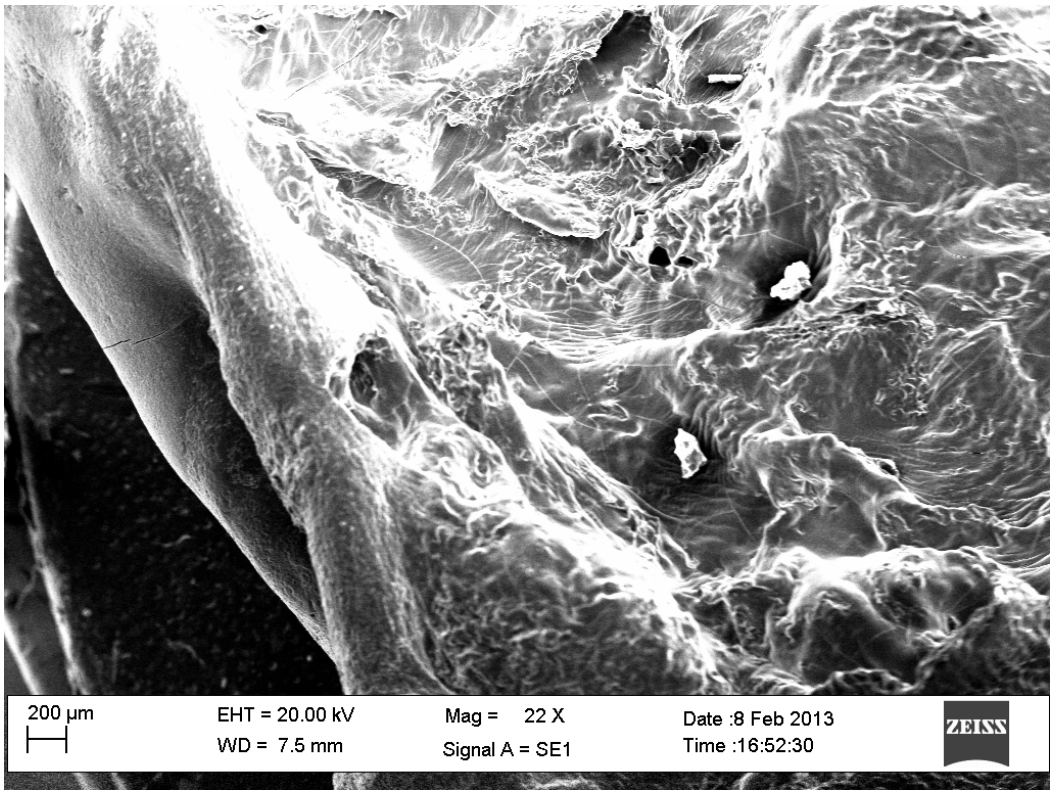


Figure 5-23: Potato waste after 15 minutes treatment.

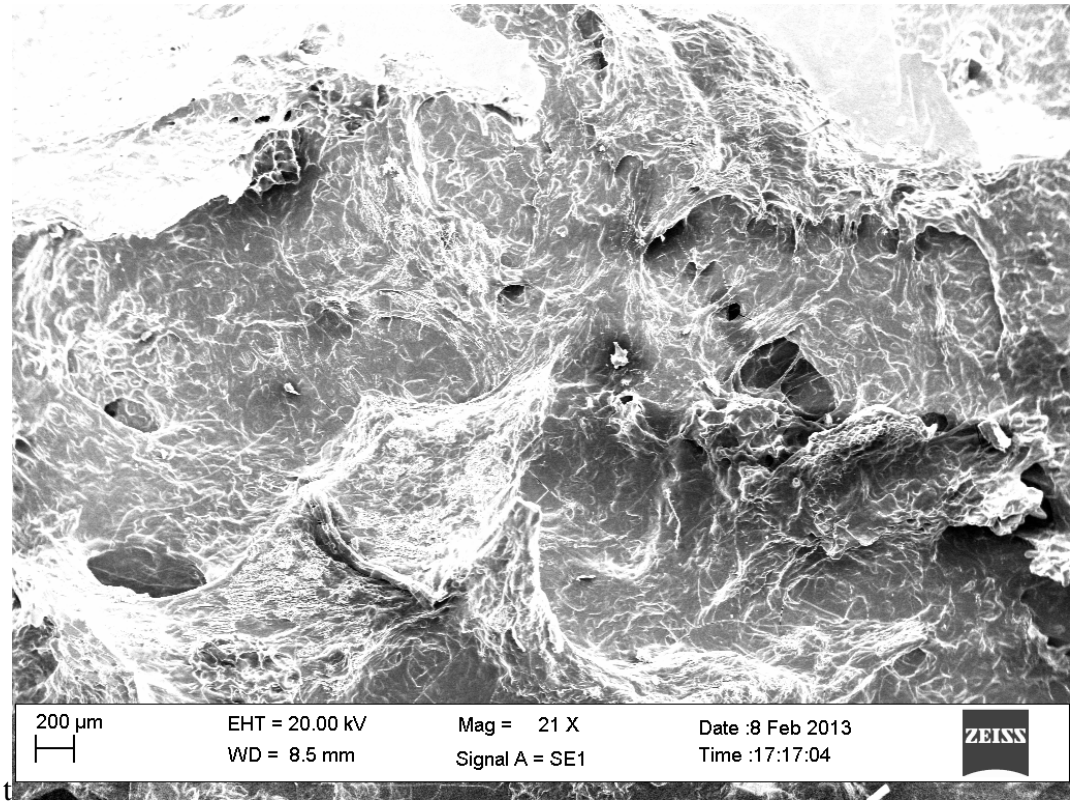


Figure 5-24: Potato waste after 35 minutes treatment.

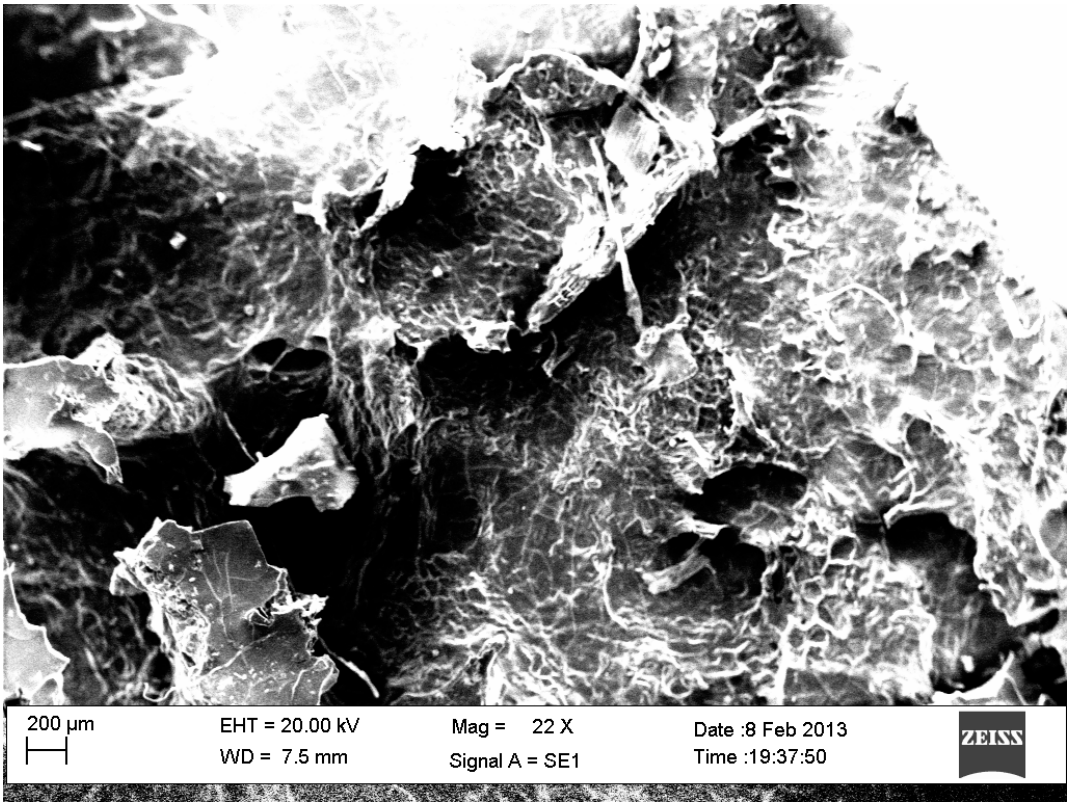


Figure 5-25: Potato waste after 60 minutes treatment.

5.4.2.2 Wet sieve analysis

This is expressed in Table 5.42, and presented in Figure 5-26 showing that all levels of treatment produce particles of sizes approximately less than 4 mm. For the first level of beating 4.4% of pulp did not fall in to the sieve (dropdown) with 4 mm, and 6.9%, 8.7%, 9.8%, 9.8% did not fell in sieves with 2 mm, 1 mm, 0.800 mm and 0.355 mm respectively. For the second level of beating 1.1% of pulp did not fall in sieve with 4 mm while 3.8%, 6.4%, 7.5% and 8.6% did not fall in to the sieve with 2 mm, 1 mm, 0.8 mm and 0.355 mm respectively. For third level of beating 0.7% of pulp did not fall in to the sieve with 4 mm, while 2.9%, 4.9%, 6.5% and 7.6% did not fall in to the sieve with 2 mm, 1 mm, 0.8 mm and 0.355 mm respectively. Finally for fourth level (60 minutes of beating treatment) only 0.4% % of pulp did not fall in to the sieve with 4 mm while 1.6%, 4.3%, 6% and 6.3% did not fall in to the sieve with 2 mm, 1 mm, 0.8 mm and 0.355 mm respectively. For more details see appendix D.

Table 5.42: Wet sieve analysis.

Beating time	Sieves size				
	4 mm	2 mm	1 mm	0.8 mm	0.355 mm
5 min	4.4	6.9	8.7	9.8	9.8
15 min	1.1	3.8	6.4	7.5	8.6
35 min	0.7	2.9	4.9	6.5	7.6
60 min	0.4	1.6	4.3	6	6.3

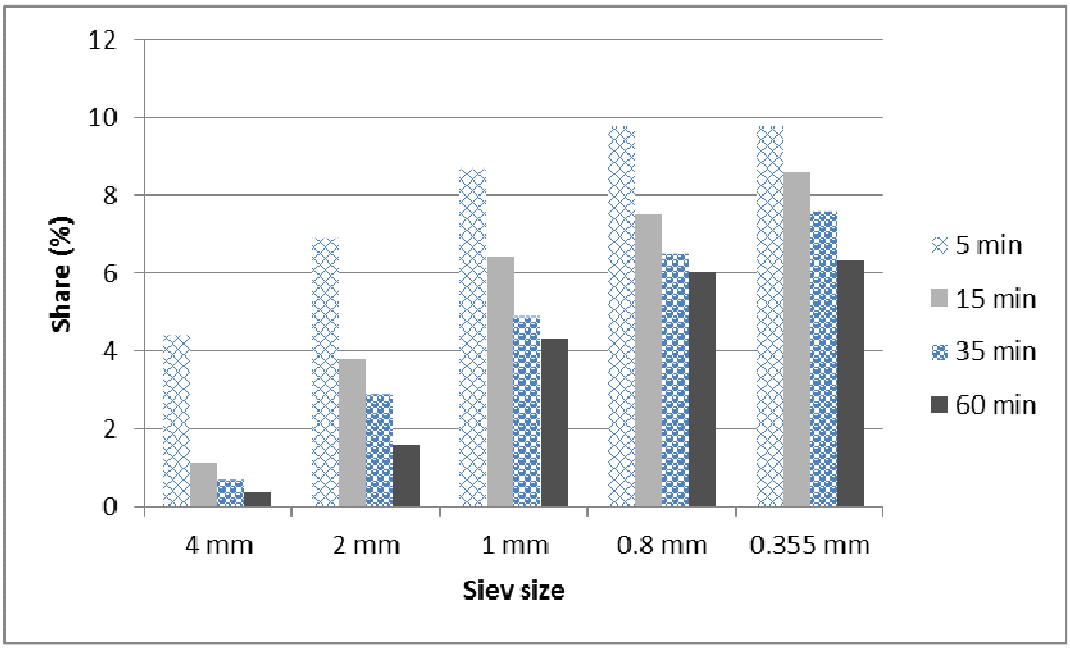


Figure 5-26: Wet sieve analysis.

5.4.2.3 Biogas Measurement

The amount of biogas produced by the sludge reactors during the 21 the days of the experiment was 839.3 mL on average, this amount has been eliminated. The same trend of influence of beating mechanical treatment on maize silage and grass was observed with potato waste substrate. Table 5.43, and Figure 5-27, clearly show that the mechanical beating treatment has a significant effect on the anaerobic digestion of potato waste. Results indicate the influence of treatment can be higher in the early days and then gradually diminished until absent in the final days of the process. The difference between the productivity of 1_g VS of untreated sample and the same quantity of treated sample (beating for 5 minutes) was 67% in the first collection of biogas which was in the 3rd day of the retention time of the process.

Table 5.43: Collection of biogas through the retention time of the AD process.

Beating time	Biogas collection time (days)						
	3 (ml/g VS)	6 (ml/g VS)	9 (ml/g VS)	12 (ml/g VS)	15 (ml/g VS)	18 (ml/g VS)	21 (ml/g VS)
0 min	347.67	207.69	53.14	25.46	17.16	10.72	5.44
5 min	580.86	160.30	60.01	35.96	27.23	22.04	7.23
15 min	528.38	188.52	36.56	32.89	23.44	16.79	9.87
35 min	395.50	267.58	47.58	36.81	23.58	14.88	7.04
60 min	346.39	268.55	40.81	38.15	22.12	18.41	10.76

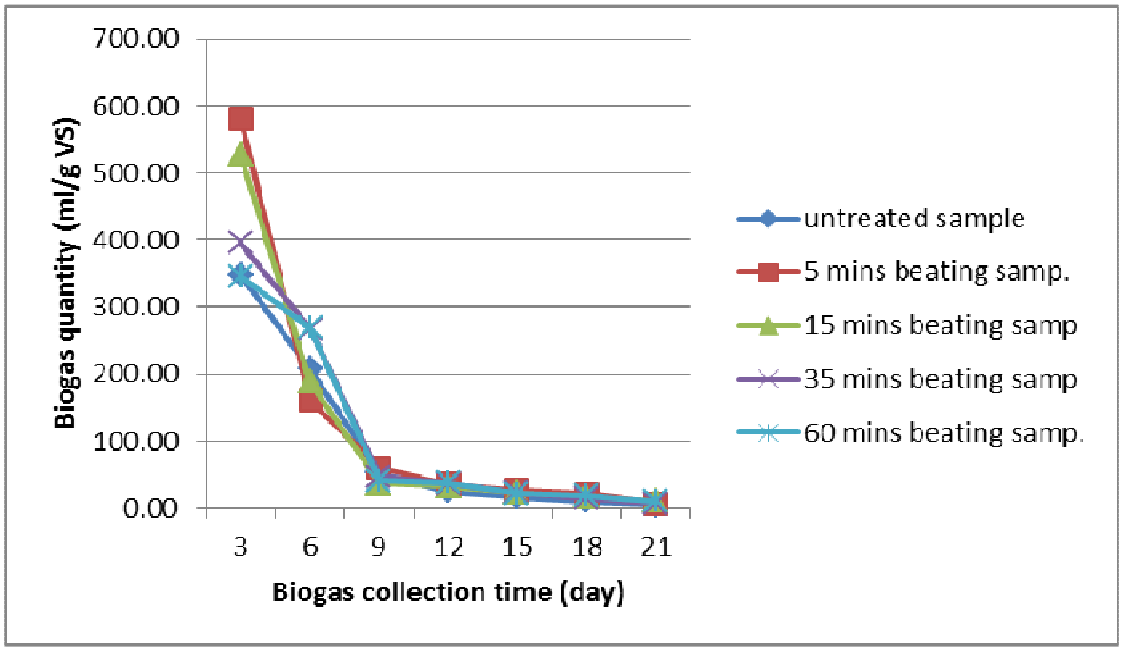


Figure 5-27: The productivity of untreated and treated samples of potato waste.

5.4.2.4 Cumulative analysis

The biogas yield from all samples of potato waste was in range 667 – 894 mL/g VS of potato waste, which is in agreement with Stewart DJ et al [195] and B. Linke [212]. The cumulative analysis expressed in Table 5.44, and presented in Figure 5-28, indicates that the total biogas produced from potato waste after the beating treatment is higher. It can be seen that the highest amount of biogas was 893.6 mL/g VS produced after 5 minutes beating treatment, which achieved an improvement of 33.9% of biogas yield in comparison with untreated sample. In contrast, it was found that the amount of biogas produced after 15 minutes beating treatment is 836.5 mL/g VS and after 35minutes beating treatment is 793 mL/g VS, while after 60 minutes

was 745.2 mL/g VS, which achieved an improvement of about 25.4%, 18.8% and 11.7% of biogas yield respectively in comparison with the untreated sample. The same trend of biogas yield from maize silage and grass after different levels of beating treatment were observed. This could be due to the effect of the particle size of the maize silage. The longer beating times the smaller the particle size. Too small a particle size will dynamically accelerate the rate of hydrolysis and acidogenisis reactions, and then VFA are produced rapidly, resulting in an imbalance of production and consumption of VFA leading to accumulation of VFA, and inhibition of biogas production. This is because the early stages of the anaerobic solubilisation process, especially the hydrolysis and acidogenesis steps, are significantly affected by physicochemical conditions such as temperature and pH rather than by the effects of biological factors [219 and 220].

Table 5.44: Biogas Production from Potato Waste Before and After Beating Treatment (Cumulative Data).

Beating time	Biogas collection time (days)						
	3 (ml/g VS)	3 (ml/g VS)	3 (ml/g VS)	3 (ml/g VS)	3 (ml/g VS)	3 (ml/g VS)	3 (ml/g VS)
0 min	347.67	555.35	608.49	633.96	651.12	661.84	667.28
5 min	580.86	741.16	801.17	837.13	864.36	886.41	893.64
15 min	528.38	716.90	753.46	786.34	809.78	826.57	836.45
35 min	395.50	663.08	710.65	747.46	771.04	785.92	792.96
60 min	346.39	614.93	655.75	693.89	716.01	734.43	745.18

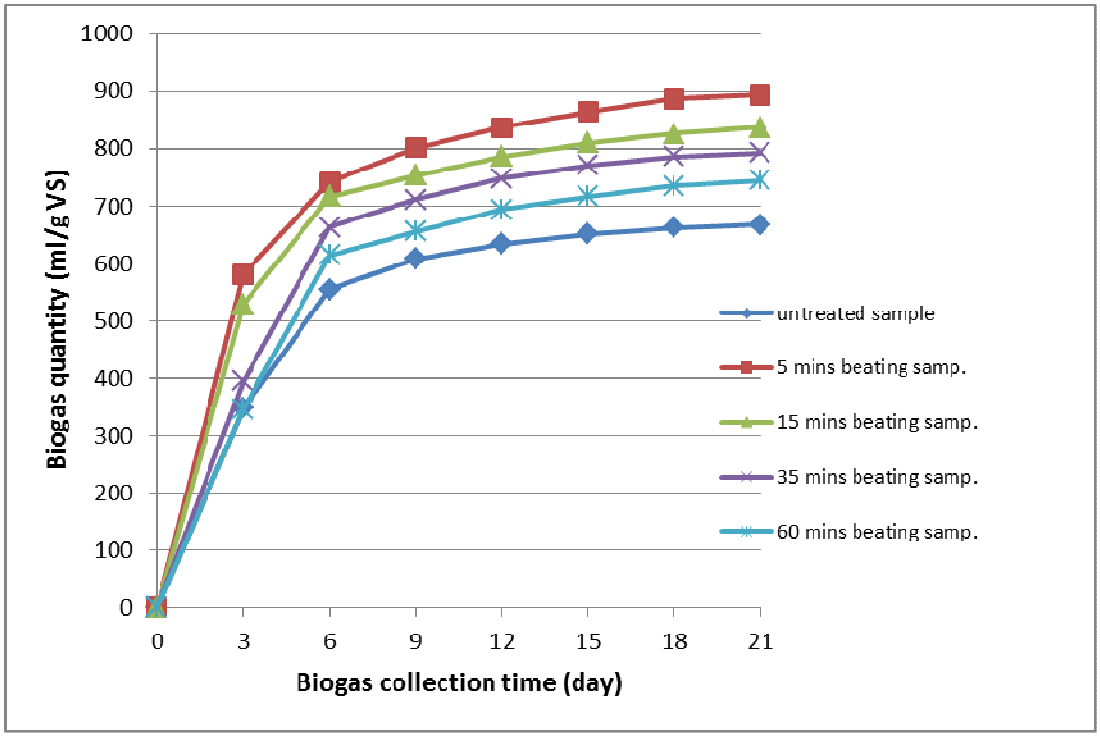


Figure 5-28: Comparison between the amounts of biogas generated from potato Waste Before & After Beating Treatment.

5.4.2.5 Biogas composition

The fourth reactor of each condition of experiment (A4, B4, C4 and D4) was used for the concentration of biogas and further composition analysis. The concentration values were obtained using the gas analyser. As expressed in Table 5.45, and depicted in Figure 5-29, the biogas composition were in agreement with [29]. The average methane yield was 51% of biogas produced. The average carbon dioxide was 38%, while the other gases (Oxygen O_2 Nitrogen N_2, Hydrogen Sulphide H_2S, and Ammonia NH_3) were about 11%.

The methane (CH_4) content of the biogas from both the treated and untreated maize silage was close to 51%, this result is in line with [195 and 212]. The CH_4 concentration showed a value of 51% for untreated sample, 51% for 5 minutes beating time sample, 50% for 15 minutes beating time sample, 52% for 35 minutes beating time sample and 50% for 60 minutes beating time sample. The analysis indicates that CH_4 yield was 338.7 mL/g VS, 551 mL/g VS, 417 mL/g VS, 411 mL/g VS and 351 mL/g VS for untreated sample, 5 minutes beating treatment sample, 15

minutes beating treatment sample, 35 minutes beating time sample and 60 minutes beating time of treatment sample respectively. This result is comparable with [195] and [210 - 212].

Table 5.45: Concentration of biogas composition.

Elements (%)	Untreated sample	5 minutes beating	15 minutes beating	35 minutes beating	60 minutes beating
CH_4	51	51	50	52	50
CO_2	40	39	38	37	39
other gases	9	10	12	11	11

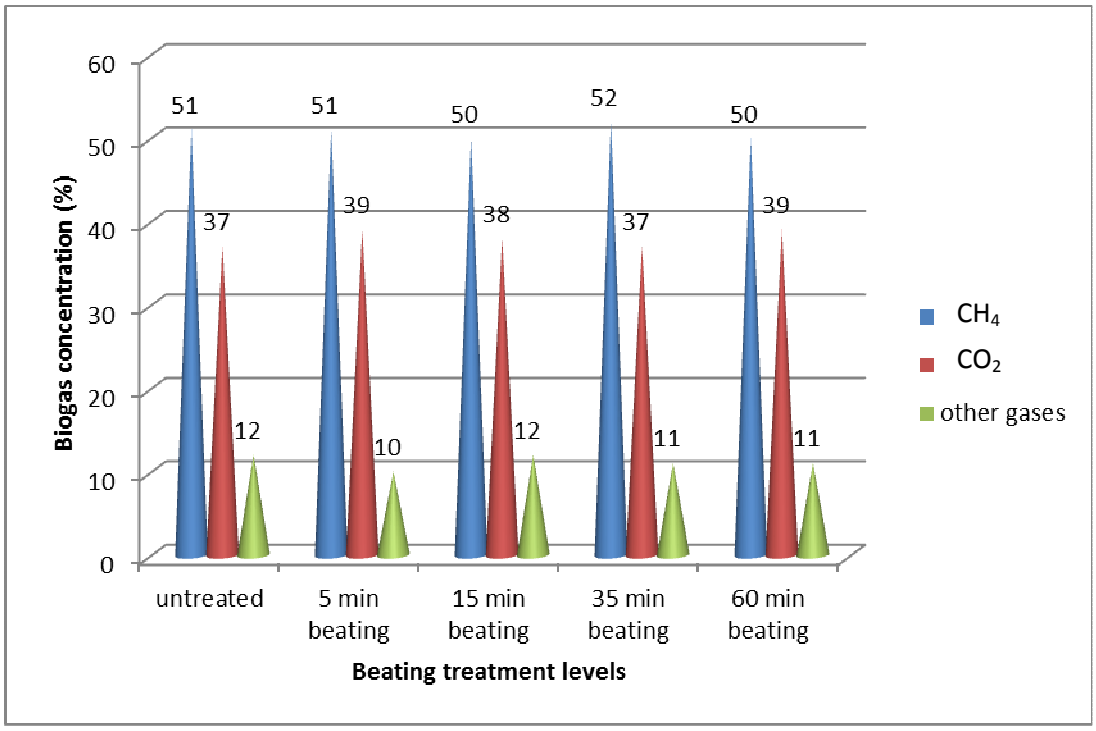


Figure 5-29: Biogas chemical composition (potato waste samples).

5.4.2.6 Energy analysis

In order to evaluate the economic feasibility at lab scale of beating treatment for potato waste, the same method and equations (formulas) used for energy analysis with previous substrates were used to analyse energy produced from potato waste as

renewable energy resource. Equations 5.1 – 5.5 (presented in appendix B) have been used.

The TS analysis of potato waste indicated that the dry matter of 15 g of untreated potato waste is 2.13 g, implying that the total dry matter of total wet potato waste (1500 g) is equal to 357 g. The VS of the total potato waste has been treated (1500 g) is 326.3 g (see formula 5-1 presented in appendix "B"). Cumulative analysis indicates that 1g VS of untreated potato waste produced 667.3 mL of biogas so the total biogas yield (Y) expected from total untreated substrate is 217.7 L (given by formula 5-2 presented in appendix "B").

Cumulative analysis indicated that biogas yield from potato after a 5 minute beating time produced 893.6 mL/g VS, 836.5 mL/g VS after 15 minutes beating time 793 mL/g VS after 35 minutes beating time and 745.2 mL/g VS after 60 minutes beating time of treatment; therefore the expected biogas yield from total substrate after three different levels of treatment (Y_1, Y_2, Y_3 and Y_4) will be 298.6 L, 278.9 L, 269 L and 252.8 L of biogas respectively. The increment of biogas production from total treated substrate (after 5 minutes beating, 15 minutes beating, 35 minutes beating and 60 minutes beating time) in comparison with total untreated substrate are 80.9 L, 61.2 L, 51.3 L and L of biogas respectively. For more details see Appendix "E".

The energy content of the increment of biogas was calculated based on a value of 9810 Wh/Nm^3 [221]. The electricity used to achieve treatment for each level was measured. 0.043 KWH was consumed for 5 minutes beating, 0.095 KWH for 15 minutes beating, 0.193 KWH for 35 minutes beating and 0.318 KWH was consumed for 60 minutes. Table 5.42 illustrates the amount of energy content in the increment of biogas after three different level of beating. Also it shows that the incremental rate in percentage can be obtained through applying the beating treatment to grass. It was found that first and second level of treatments have a positive energy balance, while the third level of treatment (40 minutes beating) has a negative energy balance (see Table 5.46).

Table 5.46: Energy analysis (potato waste)

beating time	increment of biogas (l/x_{total} VS)	CH4 (%)	content of Energy Produced [EP] (Kwh/l)	Electricity Used [EU] (Kwh)	% energy balance of [EU] vs. [EP]
5 minutes	80.9	51	0.40	0.043	10.8
15 minutes	61.2	50	0.30	0.095	31.7
35 minutes	51.3	52	0.26	0.193	74.2
60 minutes	35.1	50	0.17	0.318	187.1

Chapter 6

OPTIMISATION OF BEATING TREATMENT

6.1 Optimisation of beating treatment

Chapter 5 covered the experiments conducted to explore the new mechanical treatment (beating treatment) to enhance biogas yield from lignocellulosic materials. Results obtained from these experiments indicate that there is a high influence on biogas yield, at the same time the results show that the degree of beating which is correlated to beating time has a 3rd order polynomial relationship with biogas production.

This chapter aims to apply Response Surface Methodology RSM (described in chapter 3, section 3.2) with the aid of Design-Expert version-7 statistical software to develop mathematical models, in the form of function showing the relationship between the parameters of AD process selected (beating time and temperature) and the responses specified (biogas production and energy consumption). These mathematical models can be used to predict the biogas production and the energy required for the amount of biogas predicted. Also to identify the optimal combinations of the process input parameters selected, using numerical and graphical optimisation, to achieve a specific target criterion.

6.2 Anaerobic digestion of lignocellulosic materials

Two materials were selected for this experiment: maize silage and potato-waste. The experiments were designed based on Central Composite Design (CCD). The results of each substrate (maize silage and potato waste) obtained from previous experiments were used to determine the range of each factor. For both materials the main experiment was performed as per the design matrices in a random order to avoid any systematic error. All conditions for each experiment were setup at the same time (individually).

6.3 Anaerobic digestion of maize silage

Maize silage with its chemical composition was obtained from UCD Lyons Research Farm, Table 4.1 in chapter 4 showing the characteristics of maize silage. The inoculum (digester sludge) was obtained from the Dublin water sewage treatment plant located in Ringsend, Dublin 2, (for characteristic composition of inoculum see section 4.1.3). For the maize silage substrate, beating time and temperature were selected as two main factors affecting the process. As mentioned in chapter 3 section 3.2.5, the range of beating time was determined based on the results obtained from previous experiments conducted according to OVAT approach. The results indicate that there was little variation in the concentration of methane, and based on that the range of beating time was determined. The range of temperature was determined to be in the range of a mesophilic condition. Table 6.1 shows the maize silage AD parameters and experimental design levels used. The experiment for each condition was set up according to design matrix illustrated in Table 6.2.

Table 6.1: Process parameters and experimental design levels.

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded
A	Beating time	hour	Numeric	0.00	1.00	-1.00	1.00
B	Temperature	^{0}C	Numeric	34.00	40.00	-1.00	1.00

Table 6.2: Design matrix for AD of maize silage

		Factor 1	Factor 2
Std.	Run	A: beating time	B: temperature
		hour	^{0}C
1	4	0	34
2	10	1	34
3	7	0	40
4	13	1	40
5	3	0	37
6	9	1	37
7	12	0.5	34
8	8	0.5	40
9	11	0.5	37
10	5	0.5	37
11	1	0.5	37
12	6	0.5	37
13	2	0.5	37

6.3.1 Experimental procedure

The bioreactor system described in chapter 3 was used for this experiment. Reactors were labelled and marked according to the design matrix. The pre-treatment was carried out on 1.5 Kg of wet maize silage with 30 L of water. Reactors for untreated biomass contain 13 g (wet) of maize silage and 200 mL tap water. Digesters of treated samples are filled with 200 ml of maize pulp (for all 0.5 or 1 hour beating time reactors). 200 mL of sludge was adding to each reactor. The experiment was carried out in duplicate for each condition. For each condition there was a reactor for the chemical analysis of biogas to have the content of the biogas analysed**.** To preserve anaerobic conditions nitrogen gas was used as described in section 4.2.5. Water baths to control temperature were set up according to the design matrix. All reactors were placed in the water baths as shown in Figure 4.20. Agitation of the flasks once a day over the period of the AD process ensured a more complete biological reaction.

6.3.2 Determine the Total Solid and Volatile Solid contents of substrate

TS and VS were determined for each sample as described in section 4.2.6 chapter 4. The total solid for untreated sample is 3.9 g, for 30 minutes beating sample is 1.73 g,

and for 1-hour beating time is 1.9 g. Tables 6.3 – 6.5 showing the calculation of total dry matter of each sample.

For VS of untreated sample is 96.3% of TS and 95.9% of TS for both 30 minutes beating time and 1 hour beating time. Tables 6.5 – 6.8 showing the calculation of VS of three samples.

Table 6.3: Total solid content for sample without treatment.

Sample No.	dish plate weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
1	173.3	186.3	13	177.2	3.9
2	137.4	150.4	13	141.3	3.9
3	148.4	161.4	13	152.3	3.9
average					3.9

Table 6.4: Total solid content for sample with 30 minutes beating.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
4	114.5	313.3	198.8	116.2	1.7
5	116.4	314.4	198	118	1.6
6	110.5	310.4	199.9	112.4	1.9
Average			198.4		1.73

Table 6.5: Total solid content for sample with 1-hour beating.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
7	111.4	312	200.6	113.2	1.8
8	112	312.1	200.1	114	2
9	111.8	313.6	201.8	113.7	1.9
Average			200.83		1.90

Table 6.6: Percentage of ash for untreated sample.

Sample No.	Crucible weight	Crucible + sample weight	Sample weight (W2)	Crucible + ash weight	Ash weight (W1)	Ash %
1	54.627	55.2486	0.6216	54.6495	0.0225	3.62
2	54.6265	55.3741	0.7476	54.6547	0.0282	3.77
Average						3.70

Table 6.7: Percentage of ash for 0.5-hour beating sample.

Sample No.	Crucible weight	Crucible + sample weight	Sample weight (W2)	Crucible + ash weight	Ash weight (W1)	Ash %
1	54.6268	55.2776	0.6508	54.6557	0.0289	4.44
2	54.6267	55.2575	0.6308	54.65349	0.02679	4.25
Average						4.34

Table 6.8: Percentage of ash for 1-hour beating sample.

Sample No.	Crucible weight	Crucible + sample weight	Sample weight (W2)	Crucible + ash weight	Ash weight (W1)	Ash %
1	54.6261	55.397	0.7709	54.6567	0.0306	3.97
2	54.6268	55.2383	0.6115	54.6521	0.0253	4.14
Average						4.05

6.4 Anaerobic digestion of potato waste

Potato waste, as the main substrate was obtained from Coles Catering Company which is a wholesaler of fresh fruit and fresh prepared vegetable located in the main vegetable market in Dublin. Chemical analysis of potato waste which is achieved by A. Mahmood et al, [213] reported in (Table 4.3 in chapter 3).

For the potato waste substrate, beating time and temperature were selected as two main factors affecting the process. As mentioned in chapter 3 section 3.2.5 and in section 6.2 in this chapter the range of beating time was determined based on the results obtained from previous experiments conducted according to One-Variable-At-a-Time (OVAT) approach. The range of temperature was determined to be in the range of a mesophilic condition [186]. Table 6.9 shows the potato waste AD parameters and experimental design levels used. The experiment for each condition was set up according to design matrix illustrated in Table 6.10 (Design matrix for AD of potato waste) below.

Table 6.9: Process parameters and experimental design levels.

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded
A	Beating time	min	Numeric	0.00	15.00	-1.00	1.00
B	Temperature	^{0}C	Numeric	30.00	40.00	-1.00	1.00

Table 6.10: Design matrix for AD of potato waste.

		Factor 1	Factor 2
Std	Run	A:beating time	B:temperature
		mins	^{0}C
1	13	0	30
2	8	15	30
3	4	0	40
4	9	15	40
5	10	0	35
6	11	15	35
7	3	7.5	30
8	6	7.5	40
9	1	7.5	35
10	2	7.5	35
11	12	7.5	35
12	5	7.5	35
13	7	7.5	35

6.4.1 Experimental procedure

The same bioreactor system described in chapter 3 has also been used for this experiment. Reactors were labelled and marked according to the design matrix. The pre-treatment was carried out on 1.5 Kg of wet potato waste with 30 L of water. Reactors for untreated biomass contain 15 g (wet) of potato waste and 200 mL tap water. Digesters of treated samples are filled with 200 mL of potato pulp (for all half or one hour beating time reactors). 200 mL of sludge was added to each reactor. The experiment was carried out in duplicate for each condition. To preserve anaerobic conditions, nitrogen gas was used as described in section 4.2.5. Water baths to control temperature were set up according to the design matrix. Then all reactors were placed in the water baths as shown in Figure 4.20. Agitation of the flasks once a day over the period of the AD process ensured a more complete biological reaction.

6.4.2 Determine the Total Solid and Volatile Solid contents of substrate

TS and VS were determined for each sample as described in section 4.2.6 chapter 4. The TS for untreated sample is 3.13 g, for 7.5 minutes beating sample is 1.7 g, and for 15 minutes beating time is 1.73 g. Tables 6.11 – 6.13 shows the calculation of total dry matter of each sample.

For the VS of untreated sample is 93% of TS, and 93.5% of TS for 7.5 minutes beating time sample and VS of 15 minutes beating time was 93.6% of TS. Tables 6.14 – 6.16 showing the calculation of volatile sold of three samples.

Table 6.11: Total solid content for sample without treatment.

Sample No.	dish plate weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
1	173.3	188.3	15	176.3	3
2	137.4	152.5	15.1	140.7	3.3
3	110.1	125.1	15	113.2	3.1
Average					3.13

Table 6.12: Total solid content for sample with 7.5 minutes treatment.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
4	116.9	306.2	189.3	118.6	1.7
5	114.6	307.4	192.8	116.4	1.8
6	113.2	306.9	193.7	114.8	1.6
Average			191.05		1.70

Table 6.13: Total solid content for sample with 15 minutes beating.

Sample No.	beaker weight	total wet weight	net wet sample weight	total dry weight	net dry sample weight
7	113.2	306.6	193.4	114.9	1.7
8	110.5	305.6	195.1	112.3	1.8
9	116.3	312.7	196.4	118	1.7
Average			194.97		1.73

Table 6.14: Percentage of ash for untreated sample.

sample No.	Crucible weight	crucible + sample weight	sample weight (W2)	crucible + ash weight	Ash weight (W1)	Ash %
1	49.8705	50.6715	0.801	49.9274	0.0569	7.10362
2	49.8716	50.7315	0.8599	49.9305	0.0589	6.84963
Average						7.0

Table 6.15: Percentage of ash for 7.5 minutes beating time sample.

sample No.	Crucible weight	crucible + sample weight	sample weight (W2)	crucible + ash weight	Ash weight (W1)	Ash %
1	49.8716	50.7033	0.8317	49.9261	0.0545	6.55284
2	49.8723	50.6901	0.8178	49.9254	0.0531	6.49303
Average						6.5

Table 6.16: Percentage of ash for 15 minutes beating time sample.

sample No.	Crucible weight	crucible + sample weight	sample weight (W2)	crucible + ash weight	Ash weight (W1)	Ash %
1	49.8718	50.7205	0.8487	49.9258	0.054	6.36267
2	49.8721	50.6127	0.7406	49.9192	0.0471	6.35971
Average						6.4

6.5 Measurements of the Responses

In this optimisation work, three different quality features (production of biogas, CH_4 concentration and energy demand or energy consumption) were considered to characterise the quality of maize silage anaerobically co-digested with sludge after the beating treatments. Two quality features (production of biogas and energy consumption) were considered to characterise the quality of potato waste anaerobically co-digested with sludge after the beating treatment. Production of biogas is considered as the main target for any anaerobic process. Beating time as shown in the previous chapter is an important factor affecting the process; this refers to the degree of beating which is related to particle size that is produced after the beating treatment. CH_4 concentration in the biogas produced is also a very important target and if there is a variation between levels of treatment it can be considered as a

response. The energy demand to conduct the pre-treatment (beating treatment) and energy required for the mesophilic condition is also considered as a response in terms of cost indication.

6.6 Method of showing error in measurements

Absolute error, relative error and percentage error are several ways through which errors in measurement can be expressed. This has been showcased in this work that percentage error utilization shows errors between experimentally measured values as actual and that obtained from mathematical as the predicted value. This, in calculating errors in percentage, results in finding the difference between the actual value with that of the predicted value divided by the actual value and then multiplied by 100. This is as shown in equation 6.1. For the avoidance of error, or error reduced to the barest minimum, some steps were considered in this work. All the measuring instruments were calibrated. Also, all readings were repeated at least two times and an average value was calculated for each condition.

$$\text{Percentage error} = \left(\frac{\text{Actual value - Predicted value}}{\text{Actual value}} \right) \times 100 \qquad (6.1)$$

6.7 Results and discussion

The results for both materials studied in this part of work are presented, in terms of the analysis of variance (ANOVA) of each response, and the validation experiments. Also, the effects of the anaerobic digestion parameters selected (beating time and temperature) on each of the responses specified are explained and discussed.

6.7.1 Maize silage

For the maize silage substrate, three responses were specified, namely; productivity (biogas production), CH_4 concentration and energy consumption. The equipment and procedures described in chapter 4 were used to determine and record these responses. Averages of two consistent measurements of biogas production were recorded for 13 runs illustrated previously in table 6.2. An average of 856 mL of biogas was produced by the sludge reactor during the 21 days, which represents the

sludge contribution to the biogas formation. This amount has been eliminated. CH_4 concentration was measured at the end of the retention time for the process. The energy consumption was determined based on the energy used for the beating treatment and energy required for the mesophilic conditions for each run using the energy meter described in chapter 4. The values of the measured responses are listed in Table 6.17.

Table 6.17: Shows the biogas production, CH_4 concentration and energy consumption calculation.

	Response 1	Response 2	Response 3
Std	productivity	CH_4 concentration	energy consumption
	ml/g VS	%	kWh
1	578	49	65.1
2	608	52	65.48
3	663	52	126.2
4	663	54	126.58
5	611	51	94.92
6	632	53	95.3
7	621	53	65.3
8	719	55	126.4
9	733	53	95.12
10	745	54	95.12
11	721	52	95.12
12	711	53	95.12
13	732	53	95.12

6.7.1.1 Development of the mathematical models for maize silage

Design expert software V7 was used to analyse the measured responses. The fit summary output indicates that for all responses, the quadratic models are statistically recommended for further analysis as they have the maximum predicted and adjusted R^2 [184]. The test for significance of the regression models, the test for significance on individual model coefficients and the lack of fit test were performed using the same statistical package for all responses. The step-wise regression method; which eliminates the insignificant model terms automatically, was applied and the reduced suggested quadratic models are exhibited in the ANOVA Tables 6.18 to 6.20. The tables outline the analysis of variance for each response and illustrate the significant

model terms. The same tables show also the other adequacy measures R^2, adjusted R^2 and Predicted R^2. The entire adequacy measures are close to 1, which is in reasonable agreement and indicates adequate models [222, 223 and224]. The adequate precision compares the range of the predicted value at the design points to the Average Prediction error. In all cases the value of Adequate Precision are dramatically greater than 4. An Adequate Precision Ratio above 4 indicates adequate model discrimination [182]. The developed quadratic mathematical models in terms of coded factors and actual values are exhibited in Equations. 6.2 to 6.7.

For the biogas production model, the analysis of variance indicates that beating time (A), temperature (B) and the second order effect of beating time (A^2) are the most significant model terms associated with this response. However, the interaction effect between beating time and temperature (AB) is also having some effect on this response. While for the CH_4 concentration model the analysis indicates that beating time (A), temperature (B) and the second order effect of beating time (A^2) are significant model terms. Finally, for the energy consumption model, it is clear from the analysis that the main effect of the beating time (A), the temperature (B), the quadratic effects of the beating time (A^2), the temperature (B^2) are the significant terms.

Table 6.18: ANOVA table for biogas production reduced quadratic model.

	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	35665.48	4	8916.37	17.62	0.0005	significant
A-beating time	430.04	1	430.04	0.85	0.3835	
B-temp.	9454.43	1	9454.43	18.69	0.0025	
A^2	15728.68	1	15728.68	31.09	0.0005	
B^2	2018.19	1	2018.19	3.99	0.0809	
Residual	4047.3	8	505.91			
Lack of Fit	3380.17	4	845.04	5.07	0.0726	not significant
Pure Error	667.13	4	166.78			
Cor Total	39712.78	12				
R^2 = 0. 8981			Adj. R^2 = 0. 8471			
Pred. R^2 = 0. 6503			Adeq. Precision = 11.7			

Final Equation in Terms of Coded Factors:

$$\text{productivity} = +719.32 + 8.47 * A + 39.70 * B - 75.46 * A^2 - 27.03 * B^2 \quad (6.2)$$

Final Equation in Terms of Actual Factors:

$$\text{productivity} = -3966.04477 + 318.78938 * \text{beating time} + 235.49433 * \text{temp.} - 301.85739 * \text{beating time}^2 - 3.00355 * \text{temp.}^2 \quad (6.3)$$

Table 6.19: ANOVA table for CH_4 concentration reduced quadratic model.

	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	23.15	3	7.72	17.68	0.0004	significant
A-beating time	8.17	1	8.17	18.71	0.0019	
B-temp.	8.17	1	8.17	18.71	0.0019	
A^2	6.82	1	6.82	15.61	0.0033	
Residual	3.93	9	0.44			
Lack of Fit	1.93	5	0.39	0.77	0.6162	not significant
Pure Error	2	4	0.5			
Cor Total	27.08	12				
$R^2 = 0.855$			Adj. $R^2 = 0.807$			
Pred. $R^2 = 0.737$			Adeq. Precision = 13.513			

Final Equation in Terms of Coded Factors:

$$\%\ \text{of CH4} = +53.29 + 1.17 * A + 1.17 * B - 1.45 * A^2 \quad (6.4)$$

Final Equation in Terms of Actual Factors:

$$\%\ \text{of CH4} = +36.27778 + 8.14286 * \text{beating time} + 0.38889 * \text{temp.} - 5.80952 * \text{beating time}^2 \quad (6.5)$$

Table 6.20: ANOVA table for energy consumption reduced quadratic model.

	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	5601.738	4	1400.434	6E+07	< 0.0001	significant
A-beating time	0.217741	1	0.217741	6E+07	< 0.0001	
B-temp.	5599.815	1	5599.815	6E+07	< 0.0001	
A^2	0.000249	1	0.000249	6E+07	< 0.0001	
B^2	1.471819	1	1.471819	6E+07	< 0.0001	
Residual	0	8	0			
Cor Total	5601.738	12				
$R^2 = 1$			Adj. $R^2 = 1$			
Pred. $R^2 = 1$						

Final Equation in Terms of Coded Factors:

$$\text{Energy consumption} = +95.12 + 0.19 * A + 30.55 * B - 9.500E\text{-}003 * A^2 + 0.73 * B^2 \quad (6.6)$$

Final Equation in Terms of Actual Factors:

$$\text{Energy consumption} = -170.82222 + 0.41900 * \text{beating time} + 4.18111 * \text{temp.} - 0.038000 * \text{beating time}^2 + 0.081111 * \text{temp.}^2 \quad (6.7)$$

6.7.1.2 Validation of the models.

Figures 6.1 – 6.3 show the relationship between the actual and predicted values for all responses. These figures indicate that the developed models are adequate owing to the residuals in the prediction of each response being small, as the residuals tend to be close to the diagonal line. Furthermore, to confirm the adequacy of the developed models, three confirmation experiments were carried out using new randomly selected test conditions, each within the experiment range defined earlier. Using the point prediction option in the software, the values of all responses of the validation experiments were predicted using the previous developed models and compared with the experimentally measured response values for these confirmatory experiments. Table 6.21 summarises the experimental conditions, actual experimental values, predicted values and percentages of error in the prediction. It is evident that the models can adequately describe the responses within the ranges considered as the maximum error present in prediction is 8.8% which is in good

agreement. All the percentages of error are in agreement with the values reported in [223, 224 and 225].

Table 6.21: Confirmation experiments for maize silage.

Exp. No.	A	B		productivity	CH_4%	Energy consumption
1	0.00	39	Actual	712.6	50.0	111.3
			Predicted	650.0	51.4	115.6
			Error %	8.8	-2.9	-3.9
2	0.25	35	Actual	677.6	52.0	72.1
			Predicted	658.0	51.6	75.0
			Error %	2.9	0.8	-4.0
3	0.67	39	Actual	741.4	53.0	111.5
			Predicted	728.0	54.3	115.9
			Error %	1.8	-2.4	-3.9

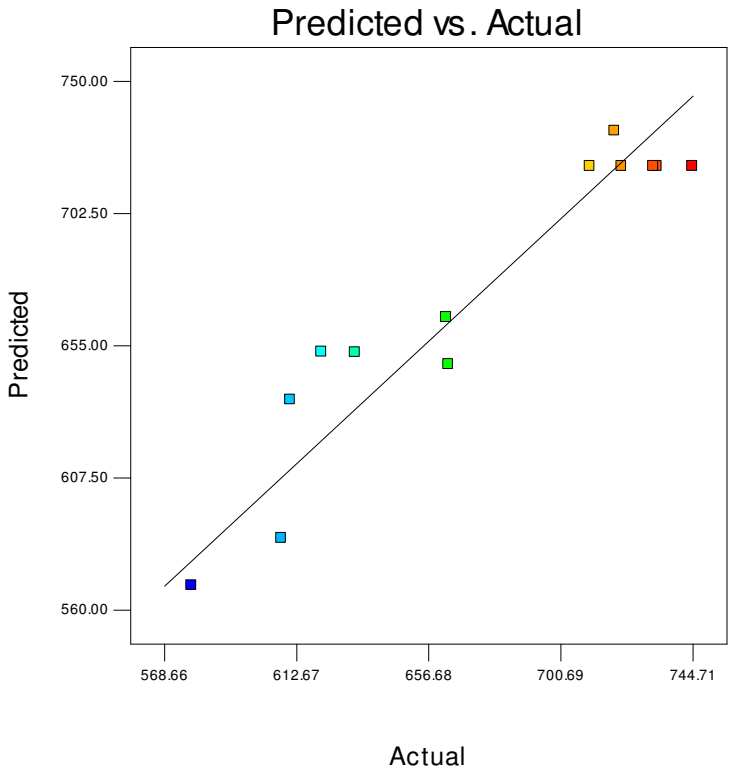


Figure 6-1: Scatter diagram for the biogas production model.

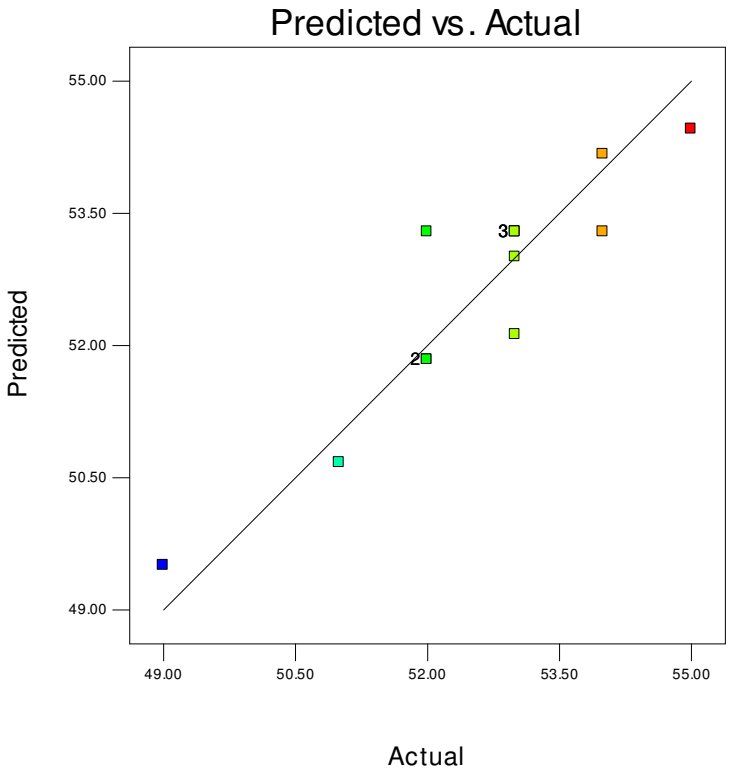


Figure 6-2: Scatter diagram for the CH4 concentration model.

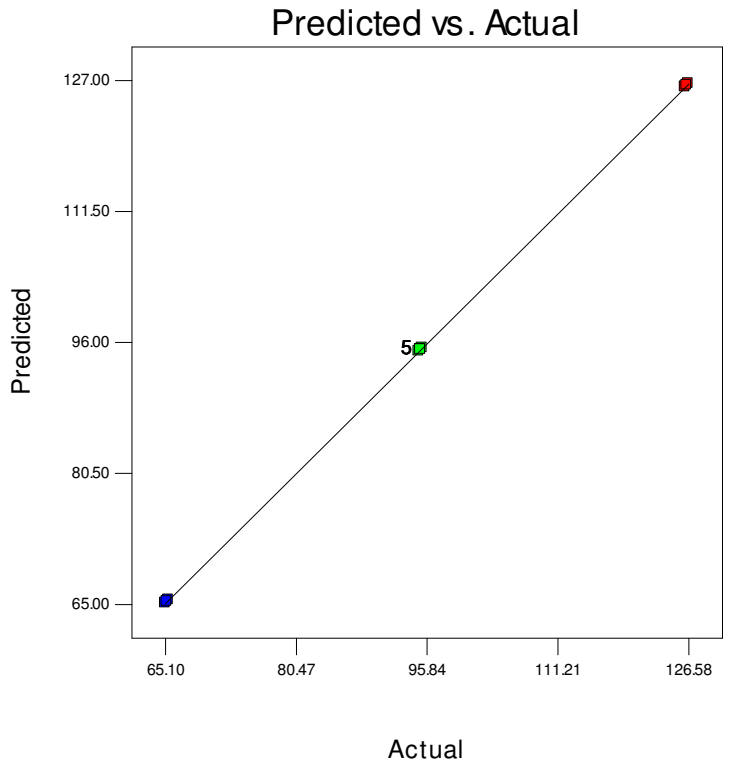


Figure 6-3: Scatter diagram for the energy consumption model.

6.7.1.3 Effect of process parameters on the responses

- **Biogas Production**

The perturbation plot for the biogas production (productivity) is illustrated in Figure 6-4. The perturbation plot helps to compare the effect of all the factors at a particular point in the design space. In a perturbation plot the lines represent the behaviours of each factor while holding the others constant (i.e. centre point by default). In the case of more than one factor this type of display could be used to find those factors that most affect the response. It is clear from figure 6.4; that the beating time factor has a strong effect on the biogas production. However, any increase in the beating time produces a general decrease in particle size. Smaller particle sizes produce a larger surface area of the substrate that is available to the microorganisms in the digestion period. This will accelerate the hydrolysis step and could enhance biogas production. This result is in line with [219].

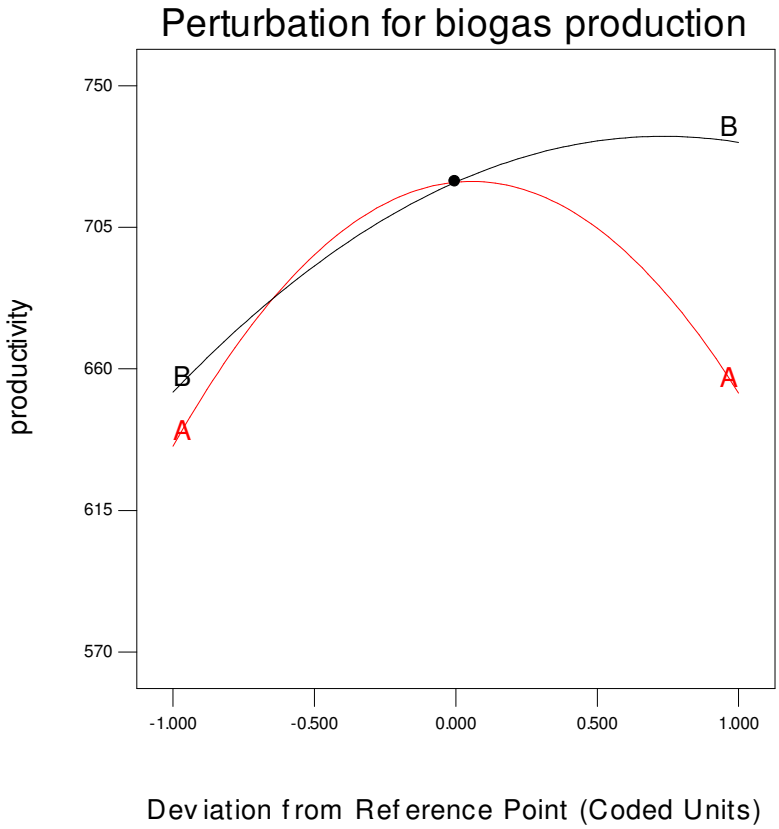


Figure 6-4: Perturbation plot exhibiting the effect of parameters on biogas production.

The results obtained in this study indicate that any increase in the beating time results in an increased biogas production up to the centre point (a beating time of about 31 min). Moreover, the results indicate that if beating were continued beyond 31 minutes this would result in a sharp decrease in biogas production, this behaviour is clear in one factor plot. This could be due to the effect of the particle size of the maize silage. The longer the beating time the smaller the particle size. Too small a particle size will dynamically accelerate the rate of hydrolysis and acidogenisis reactions, and then VFA are produced rapidly, resulting in an imbalance of production and consumption of VFA leading to accumulation of VFA, decreased pH and inhibition of biogas production [219 and 220]. For the temperature factor the results indicate that there is a positive relationship with biogas production, as temperature increases the biogas yield also increases, this is in line with the findings reported by Vindis et al [110] and Yadvika et al [226].

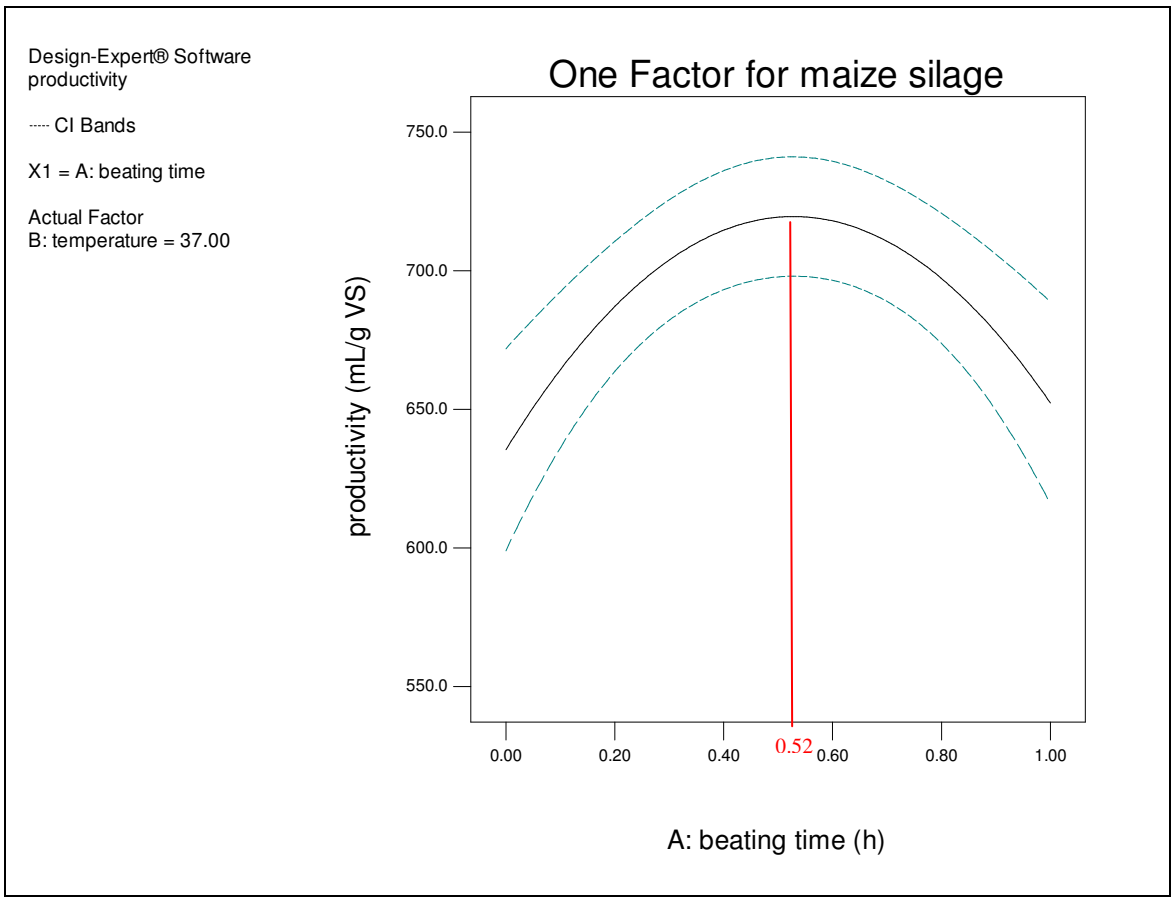


Figure 6-5: One factor plot showing the behaviour of beating time factor and its effect on biogas production.

Furthermore, the results obtained from one factor analysis indicate that as temperature increases the biogas yield also increases up to 38.2 °C above this value of temperature (38.2 °C) the yield of biogas will slightly decrease.

Figure 6-6 shows contour graph for the effect of beating time and temperature on biogas production response. The contour plots provide a two-dimensional view where all points that have the same response are connected to produce contour lines of constant responses and illustrate the optimum level of each variable on biogas production.

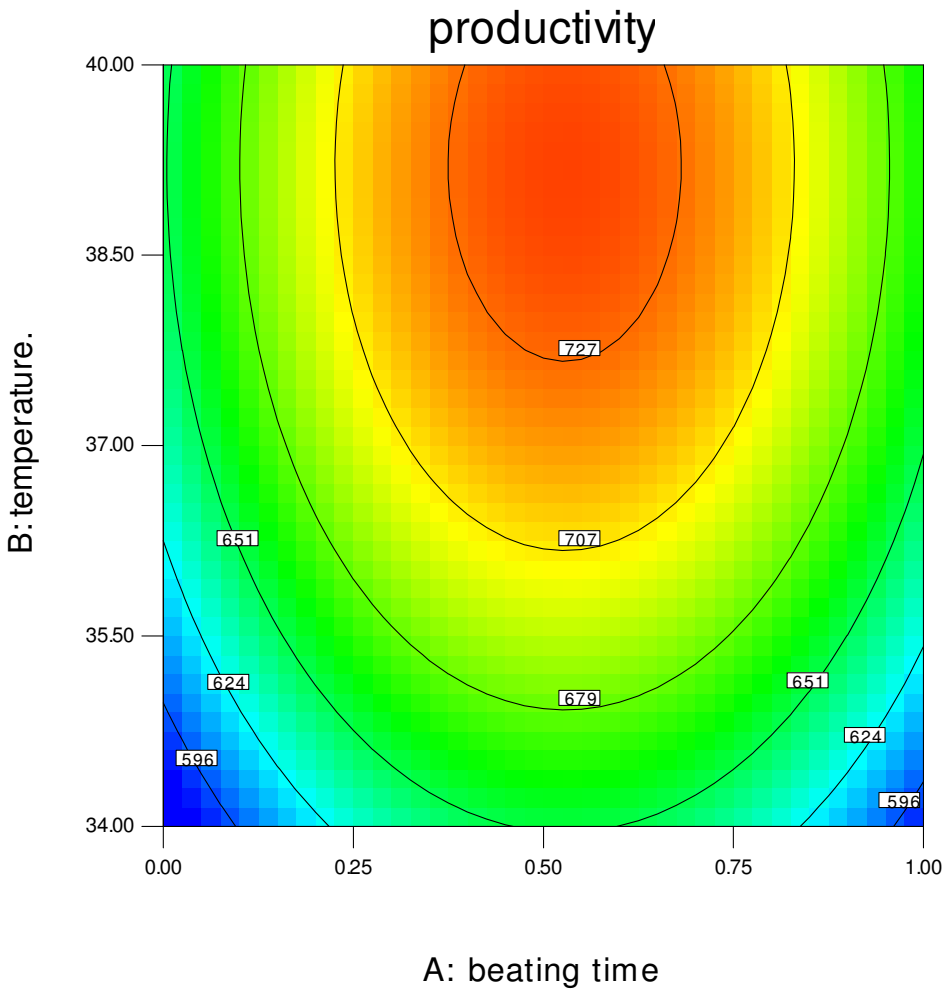


Figure 6-6: contour graph showing the effect of A and B on the biogas production.

- **CONCENTRATION OF CH_4**

It is evident from figure 6.7 that the temperature (factor A) has the most important effect on CH_4 concentration, and then the beating time (factor B). The figure shows that there is a positive relationship between the temperature and CH_4 concentration, as the temperature increased the concentration of CH_4 increased. While the same trend of behaviour of beating time factor with biogas production was observed with CH_4 concentration response. As the beating time increases the CH_4 increased up to 45 minutes beating time. Whereas the results from one factor analysis indicate that if beating were continued beyond 45 minutes this would result in a sharp decrease in

the CH_4 concentration. This could be due to the particle size effect as reported by Izumi et al. [219].

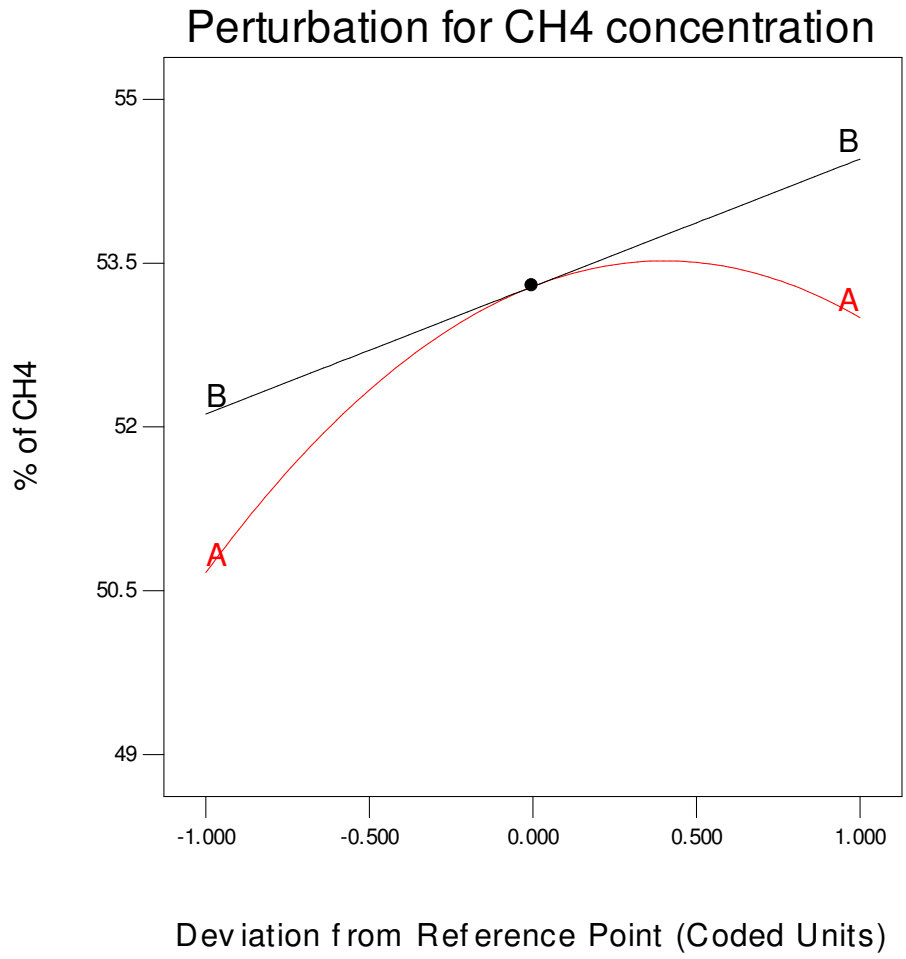


Figure 6-7: Perturbation plot exhibiting the effect of parameters on CH_4 concentration.

Figure 6-8 shows a contour graph for the effect of beating time and temperature on CH_4 concentration. The contour plots provide a two-dimensional view where all points that have the same response are connected to produce contour lines of constant responses and illustrate the optimum level of each variable on CH_4 concentration.

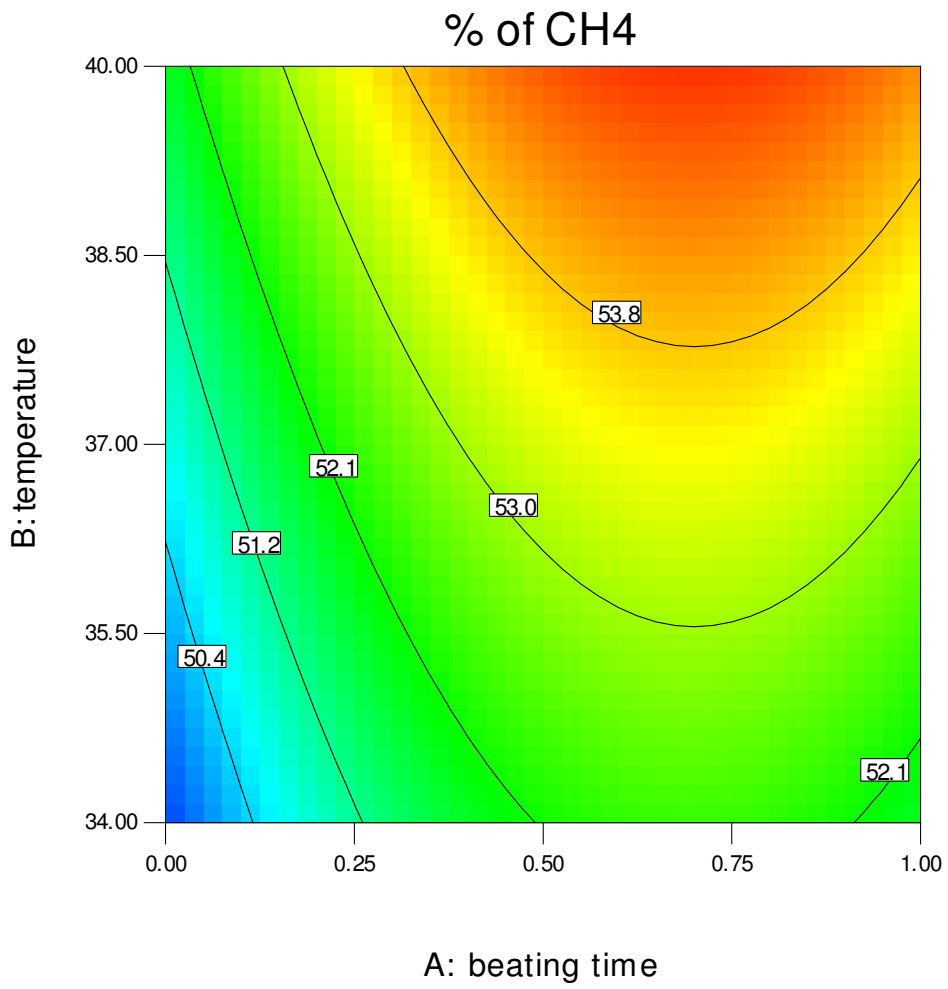


Figure 6-8: Contour graph showing the effect of A and B on the CH_4 concentration.

- **ENERGY CONSUMPTION**

Figure 6-9 is a perturbation plot demonstrating the effect of both parameters (beating time and temperature) on the energy consumption. It is evident from the results that the beating time has no significant effect on energy consumption. This finding is a strong indication that the beating treatment technique will be cost effective, as this process is simple to implement on a large scale and will produce high levels of energy at a reduced operational cost in comparison with the current state of the art. Also, it is clear that temperature has significant effects on the energy consumption and has a linear relationship with energy consumption, as any increase with temperature will increase energy consumption which was expected. This finding supports the suggestion mentioned earlier in section 5.2.4.6

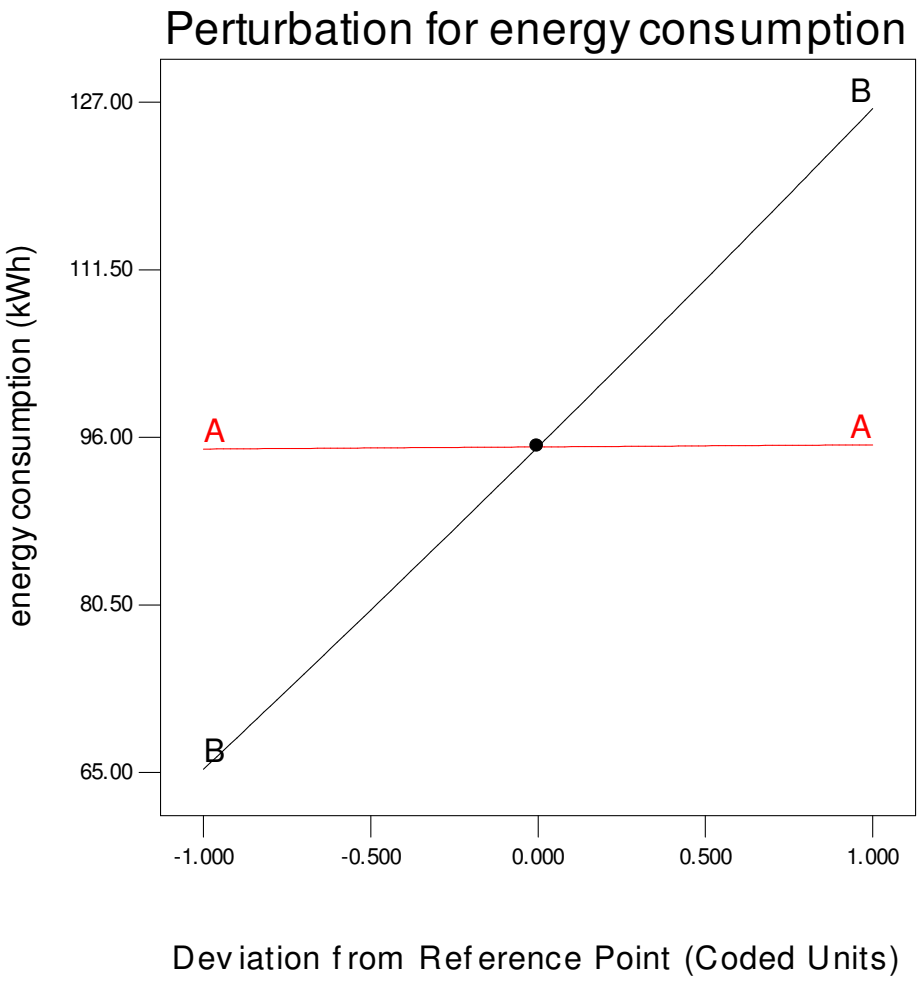


Figure 6-9: Perturbation plot exhibiting the effect of parameters on energy consumption.

Figure 6-10 is a response surface plot showing the effect of two parameters (beating time and temperature) over the response (energy consumption). Response surface plots can display the model in three dimensions; this view provides clearer views of the surface.

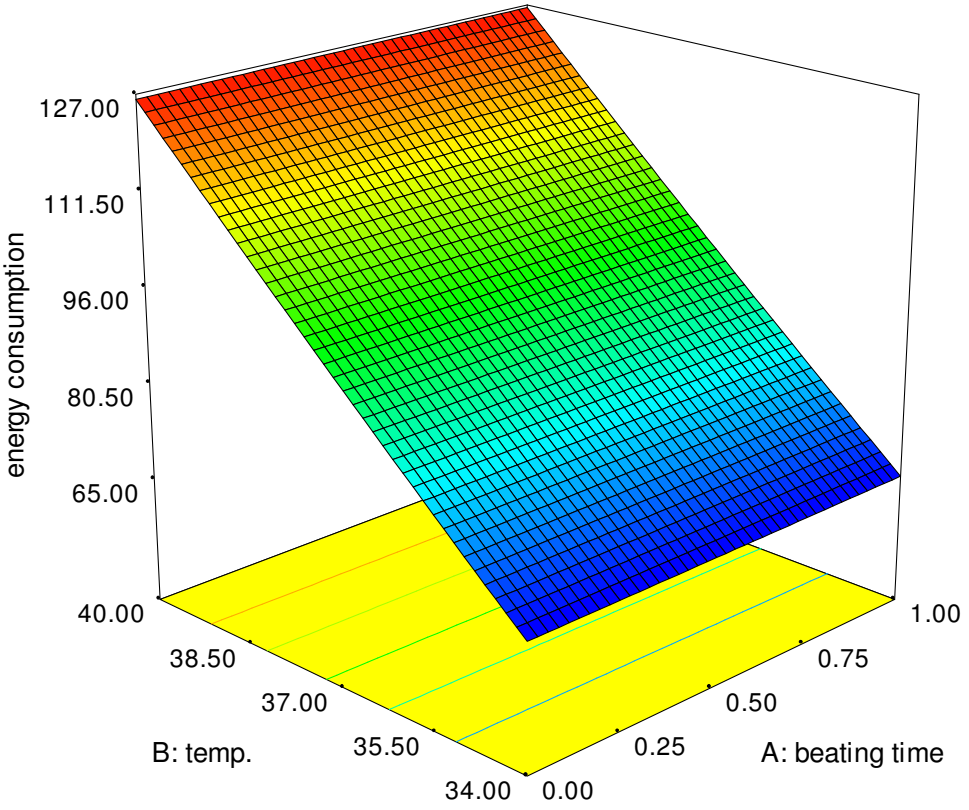


Figure 6-10: Response surface plot showing the effect of parameters on energy consumption.

6.7.2 Potato waste

For potato waste substrate, two responses were specified namely; productivity (biogas production), and energy consumption. The equipment and procedures described in chapter 4 were used to determine and record these responses. An average of two consistent measurements of biogas production was recorded for 13 runs illustrated previously in table 6.2. The sludge contribution to the biogas production has been measured and eliminated for all runs. The energy consumption was determined based on the energy used for beating treatment and energy required for mesophilic conditions for each run using the energy meter described in chapter 4. The values of the measured responses are listed in Table 6.22.

Table 6.22: Shows the biogas production, CH_4 concentration and energy consumption calculation.

	Response 1	Response 2
Std.	biogas production	energy consumption
	ml/g VS	kWh
1	643.4	56.91
2	738.8	56.997
3	727.2	126.2
4	788.8	126.287
5	691.7	72.03
6	728.1	72.117
7	687.5	56.959
8	809.4	126.249
9	751.9	72.079
10	778.1	72.079
11	796.3	72.079
12	775.6	72.079
13	783.8	72.079

6.7.2.1 Development of the mathematical models for potato waste

The same software was used to analyse the measured response. The test for significance of the regression models, tests for significance on each model coefficient and the lack of fit test were carried out. The step-wise regression method; which eliminates the insignificant model terms automatically, was applied. Two ANOVA tables for the reduced quadratics models have been obtained (see Table 6.21 and Table 6.22). These tables summarise the analysis of variance of each response and show the significant model terms, also showing the other adequacy measures R^2, adjusted R^2 and predicted R^2. The entire adequacy measures are close to 1, which are in reasonable agreement and indicate adequate models [222, 223 and 224]. The developed quadratic mathematical models in terms of coded factors and actual values are exhibited Equations 6.8 - 6.11.

For the biogas production model, the analysis of variance indicates that beating time (A), temperature (B) and the second order effect of beating time (A^2) are the most significant model terms associated with this response. While for the energy consumption model, it is clear from the analysis that the main effect of the beating

time (A), the temperature (B), the quadratic effects of the beating time (A^2), the temperature (B^2) are the significant terms.

Table 6.23: ANOVA table for biogas production reduced quadratic model.

	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	24954.29	3	8318.1	17.04	0.0005	significant
A-beating time	6221.76	1	6221.76	12.75	0.006	
B-temperature	10894.36	1	10894.36	22.32	0.0011	
A^2	7838.16	1	7838.16	16.06	0.0031	
Residual	4392.4	9	488.04			
Lack of Fit	3341.94	5	668.39	2.55	0.1932	not significant
Pure Error	1050.47	4	262.62			
Cor Total	29346.69	12				
R^2 = 0. 8503			Adj. R^2 = 0. 8004			
Pred. R^2 = 0. 6587			Adeq. Precision = 13. 602			

Final Equation in Terms of Coded Factors:

biogas production = +768.93 +32.20 *A +42.61* B -49.26 * A^2 **(6.8)**

Final Equation in Terms of Actual Factors:

biogas production = +389.19181 +17.42837 * beating time +8.52227 * temperature -0.87565 * beating time^2 **(6.9)**

Table 6.24: ANOVA table for energy consumption reduced quadratic model.

	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	8433.06	4	2108.26	6.37E+07	< 0.0001	significant
A-beating time	0.011	1	0.011	6.37E+07	< 0.0001	
B-temperature	7201.66	1	7201.66	6.37E+07	< 0.0001	
A^2	8.36E-05	1	8.36E-05	6.37E+07	< 0.0001	
B^2	1052.91	1	1052.91	6.37E+07	< 0.0001	
Residual	0	8	0			
Cor Total	8433.06	12				
R^2 = 1			Adj. R^2 = 1			
Pred. R^2 = 1						

Final Equation in Terms of Coded Factors:

$$\text{biogas production} = +72.08 + 0.044 * A + 34.64 * B - 5.500E\text{-}003 * A^2 + 19.52 * B^2 \quad \textbf{(6.10)}$$

Final Equation in Terms of Actual Factors:

$$\text{biogas production} = +786.24000 + 7.26667E\text{-}003 * \text{beating time} - 47.74100 * \text{temperature} - 9.77778E\text{-}005 * \text{beating time}^2 + 0.78100 * \text{temperature}^2 \quad \textbf{(6.11)}$$

6.7.2.2 Validation of the models.

The strength of the models developed for potato waste can be validated by Figures 6.10 and 6.11, which present the relationship between the measured and predicted response values. These scatter diagrams indicate that the developed models are adequate because the residuals in prediction of each response are negligible, since the residuals tend to be close to the diagonal line.

Furthermore, to verify the satisfactoriness of the developed models, three confirmation experiments were carried out using new randomly selected test conditions, each within the experiment range defined earlier. By using the point prediction option in the software, all the response values can be predicted by substituting these conditions into the previously developed models. Table 6.25 summarises the experimental conditions, actual experimental values, predicted values and percentages of errors. It is evident that the models can adequately describe the responses within the ranges considered as the maximum error percent in prediction is -6.6% which is in good agreement and comparable with [224 and 225].

Table 6.25: Confirmation experiments for maize silage.

Exp. No.	A	B		productivity	Energy consumption
1	0.00	33	Actual	665.2	58.17
			Predicted	670.4	61.296
			Error %	0.9	5.1
2	0.00	37	Actual	664.1	94.92
			Predicted	704.5	89.1
			Error %	5.7	-6.6
3	10.00	33	Actual	753.6	58.23
			Predicted	757.2	61.36
			Error %	0.5	5.1

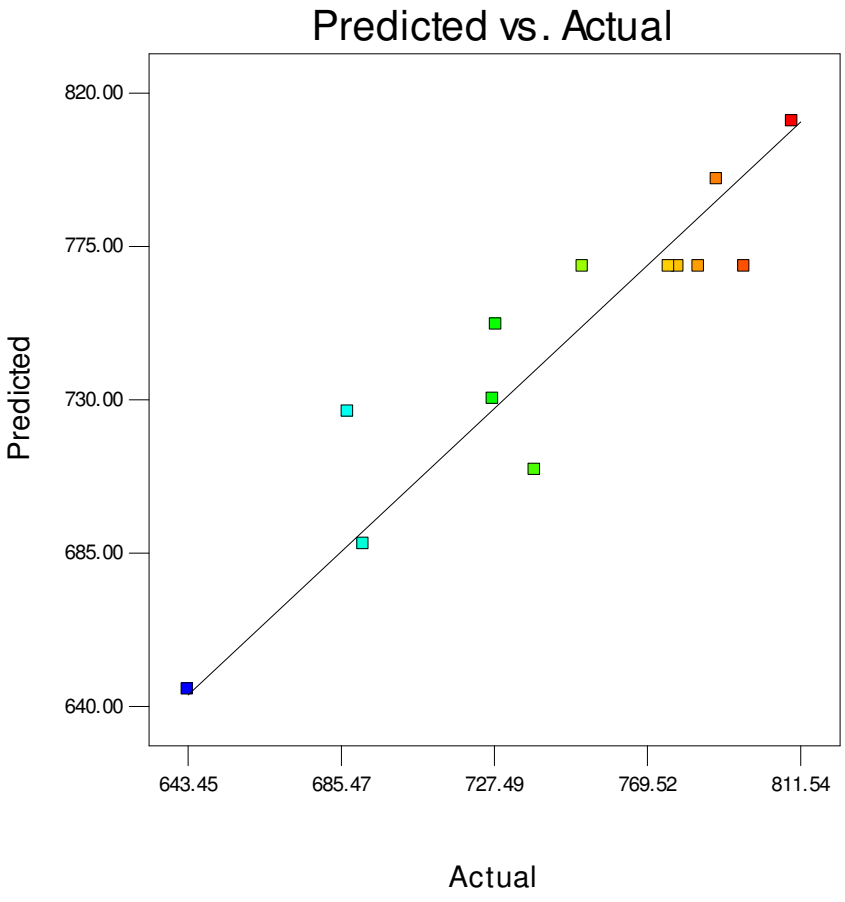


Figure 6-11: Scatter diagram for the biogas production model.

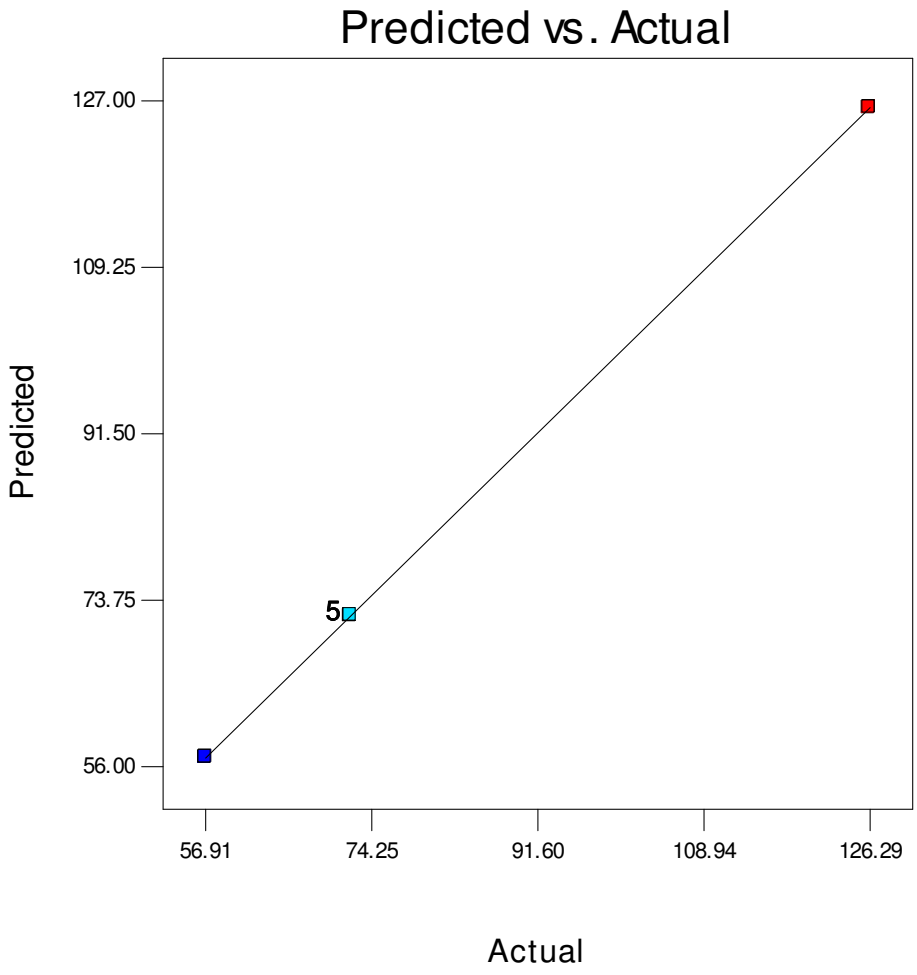


Figure 6-12: Scatter diagram for the energy consumption model.

6.7.2.3 Effect of process parameters on the responses

- **Biogas Production**

The perturbation plot for biogas production is presented in Figure 6-13. In this plot it is obvious that both factors (beating time and temperature) have significant effects on biogas production. The results show that the production of biogas increases as the beating time increased up to 10 minutes. This result is in agreement with Izumi et al. [219] as beating treatment reduces particle size and increase surface area; this will accelerate the hydrolysis step in anaerobic digestion and could enhance biogas production. This behaviour is clear in one factor plot Figure 6-14. This could be due to the effect of the particle size of the potato waste after longer beating times. The

longer the beating times the smaller the particle size. The smaller the particle size the more acceleration in rate of hydrolysis and acidogenisis reaction rates, this results in rapid production of VFA. This would lead to imbalance of production and consumption of VFA leading to accumulation of VFA, decreased pH and inhibition of biogas production. [219 and 220]. For temperature effects, the results indicate that there is a positive relationship with biogas production. As temperature increases the biogas yield also increases. This is in line with the findings reported by Vindis et al [110] and Yadvika et al [226].

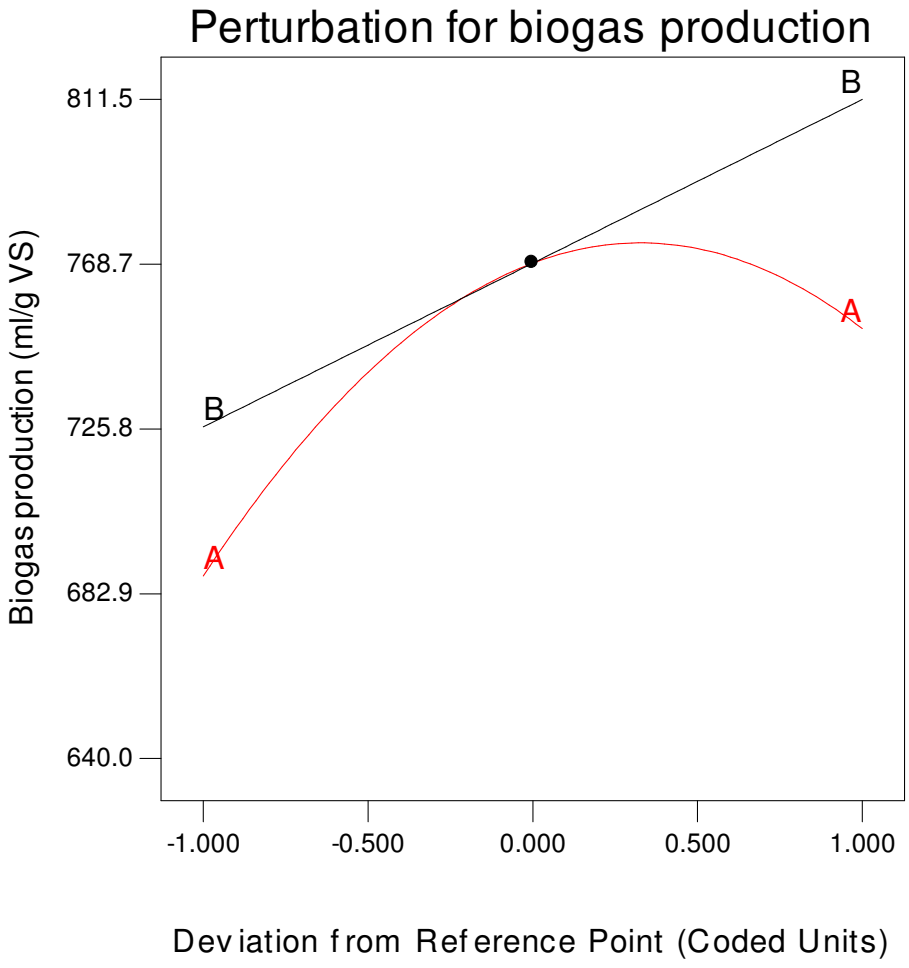


Figure 6-13: Perturbation plot exhibiting the effect of parameters on biogas Production.

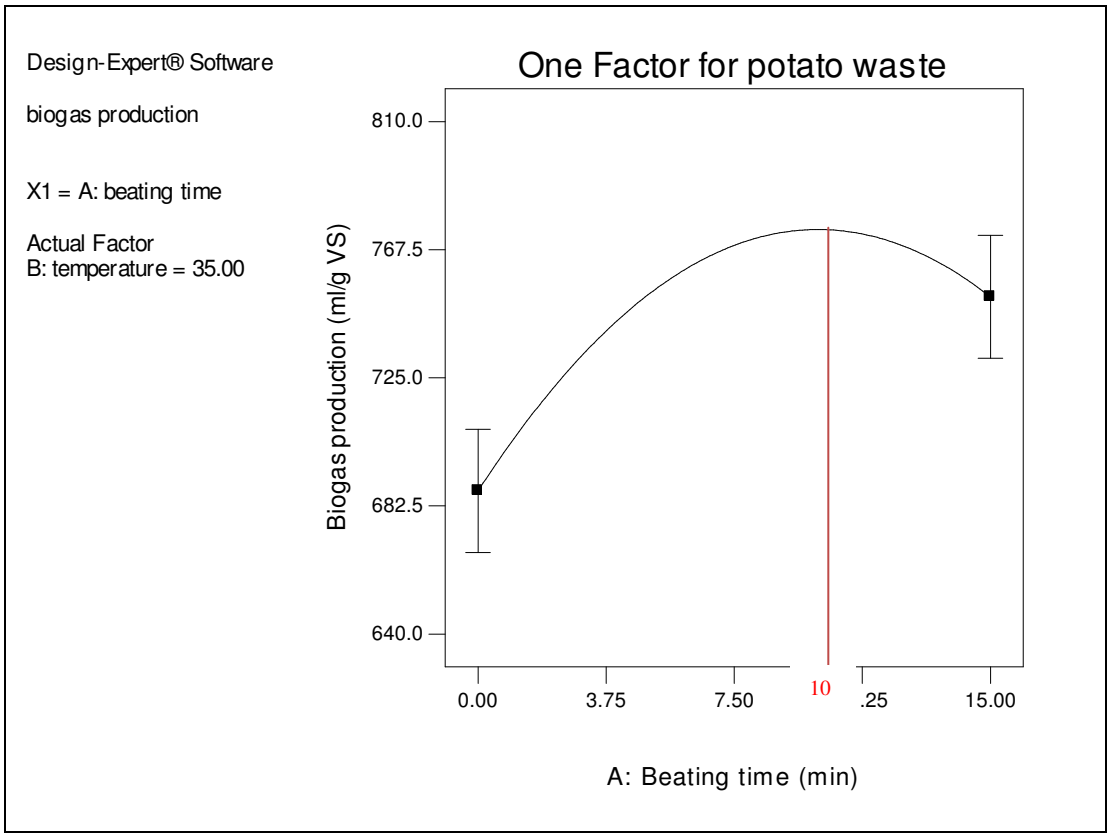


Figure 6-14: One factor plot showing the behaviour of beating time factor and its effect on biogas production from potato waste.

Figure 6-15Figure 6-15 shows a contour graph for the effect of beating time and temperature on biogas production. The contour plots provide a two-dimensional view where all points that have the same response are connected to produce contour lines of constant responses and illustrate the optimum level of each variable on biogas production.

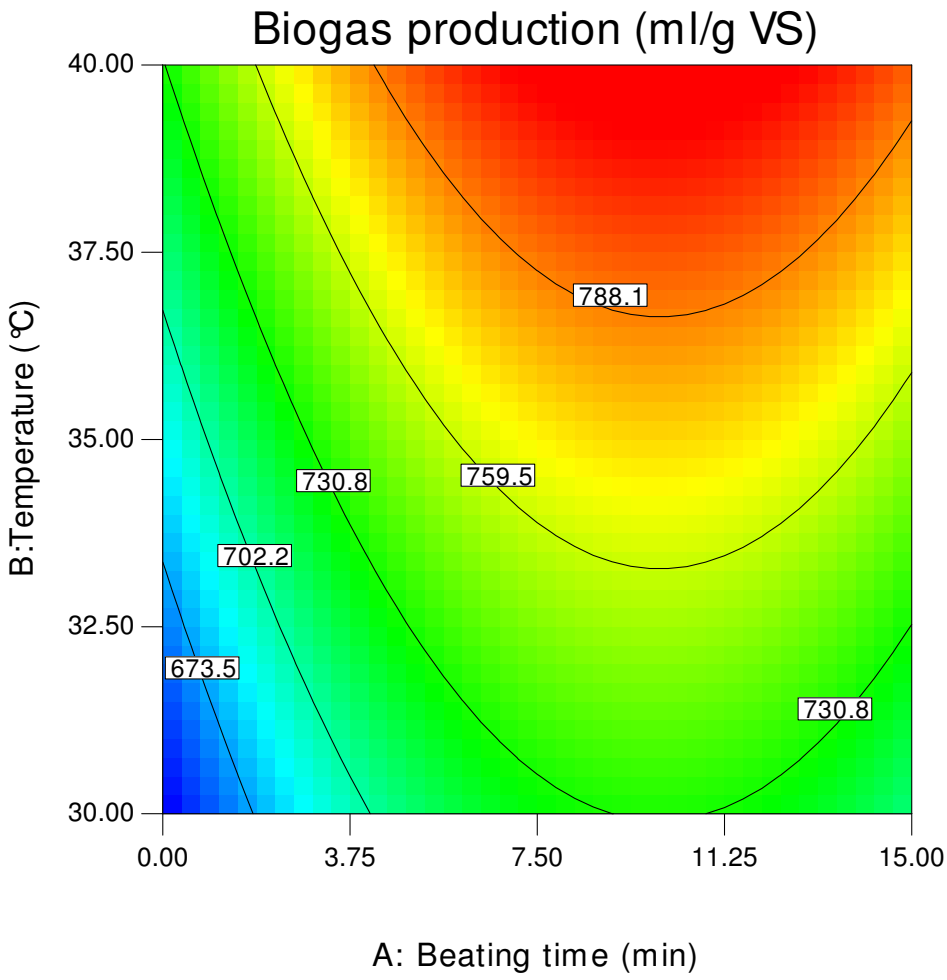


Figure 6-15: contour graph showing the effect of parameters on biogas production.

Energy consumption

It is apparent from Figure 6-16 that the beating time has no effect on the energy consumption, this finding confirms previous results obtained with the maize silage material, and gives another indication that the beating treatment will be cost effective. Also, it is clear that temperature has significant effects on energy consumption and has a linear relationship with energy consumption, as any increase with temperature will increase energy consumption which was expected. This finding gives added support to the suggestion mentioned earlier in section 5.2.4.6.

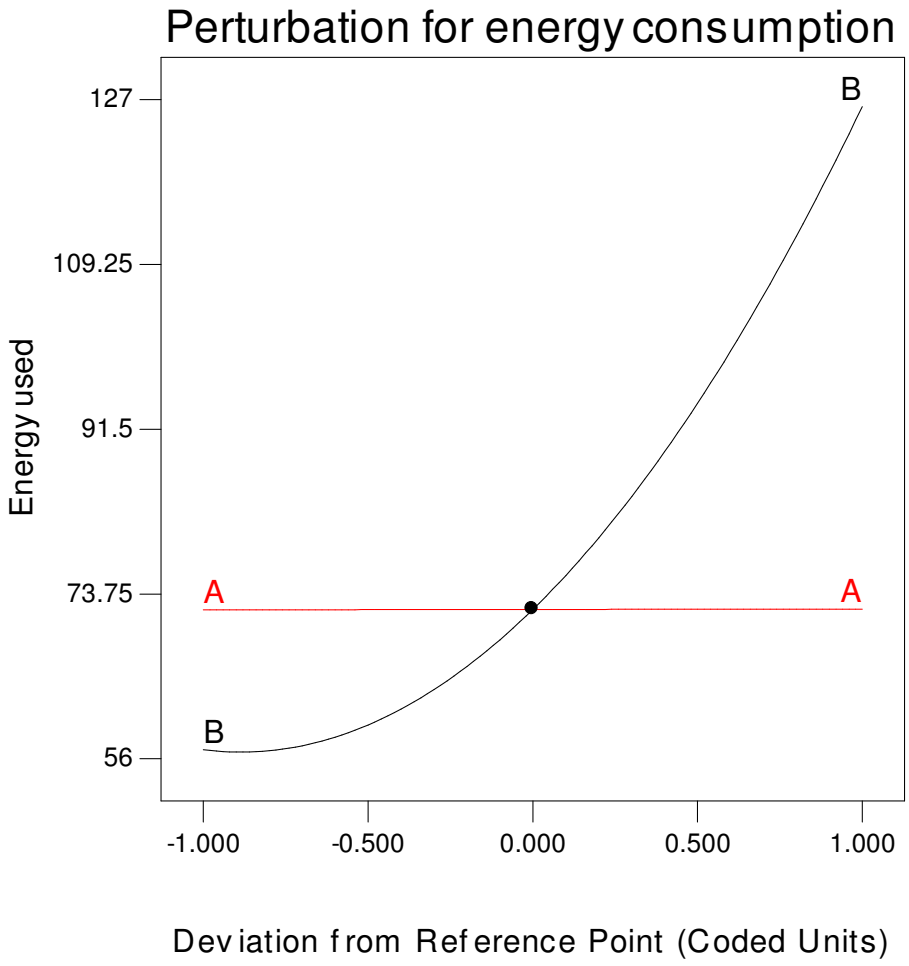


Figure 6-16: Perturbation plot exhibiting the effect of parameters on energy consumption.

The response surface plot exhibited in Figure 6-17 showing the effect of two parameters (beating time and temperature) over the response (energy consumption). Response surface plots can display the model in three dimensions; this view provides clearer view of the surface.

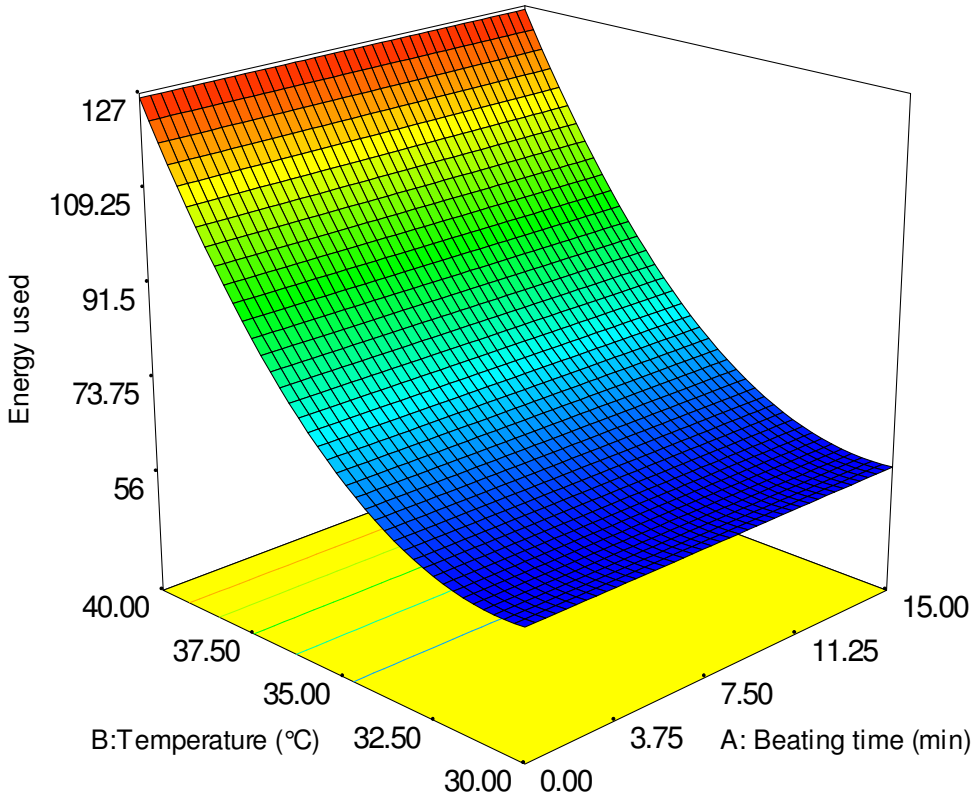


Figure 6-17: Response surface plot showing the effect of parameters on energy consumption.

6.8 Optimisation

An anaerobic digestion process is a complex biological process and has multi input and output parameters. In order to optimize this kind of process, desirability approaches (explained earlier in chapter 3) which is built in the Design expert software can be used. Two types of optimisation layout are available in Design expert. The first one, the numerical optimisation feature, which finds a point or more in the factors domain that would maximise the overall desirability. The second one, the graphical optimisation, where the optimal range of each response has to be brought from the numerical optimisation results in order to present them graphically.

In the numerical optimisation for this research four criteria were used. The difference between these three criteria is that in the first criterion there were no restrictions on the process input parameters and the output quality features were set to achieve the highest biogas production (referring to this criterion as productivity). In the second criterion, the energy consumption as indication for cost was considered; consequently, this parameter (energy consumption) was set to a minimum (referring to this criterion as Cost). Regarding the third criterion some restrictions were set in order to maximize the biogas production and minimize energy consumption. While the fourth criterion some restrictions were set in order to minimise both the beating time and energy consumption and maximise productivity while other parameters were in range.

In the graphical optimisation, the optimal range of each response has to be brought from the numerical optimisation results in order to present them graphically. The graphical optimisation allows visual selection of the optimal process conditions according to certain criterion. Graphical optimisation results in plots called overlay plots. The green/shaded areas on the overlay plots are the regions that meet the proposed criteria.

6.8.1 Maize silage

The four optimisation criteria for this material are presented in Table 6.26. This table shows that each factor and response have been allocated specific goals and orders of importance. The first criterion was aimed to maximise the production of biogas, the second criterion was aimed to minimise the cost in terms of energy used, while the third criterion was aimed to maximise both biogas production and CH_4 concentration and in contrast minimise the cost. The fourth criterion was aimed to maximise the production of biogas and minimise both the beating time and energy consumption.

6.8.1.1 Numerical optimisation

Table 6.27 shows the optimal setting of the process parameters and the corresponding response values for all criteria for maize silage. The results indicate that the optimal solutions for the first criterion were found to be: beating time of 31.8 min and AD temperature of 39.2 °C with a maximum biogas of 734.1 mL/g VS. While the results indicate that there are seven different optimum conditions for the

second criterions (see Table 6.27). The optimal conditions for the third criterion were found to be: beating time of 34.2 min and AD temperature of 35.8 °C to get 698.5 mL/g VS biogas with 53% CH_4 and 82.93 KWH of energy needed. Finally the optimal conditions for the fourth criterion were found to be: beating time of 13.2 min and AD temperature of 37.6 °C to get 697.9 mL/g VS biogas with 101.1 kWh

Table 6.26: Criteria for numerical optimisation of maize silage.

Factor or response	First criterion (productivity)		Second criterion (Cost)		Third criterion (Cost vs productivity)		Fourth criterion (minimise beating time)	
	Goal	Importance	Goal	Importance	Goal	Importance	Goal	Importance
Beating time	In range	(+++)	In range	(+++)	In range	(+++)	Minimise	(++)
Temperature	In range	(+++)	In range	(+++)	In range	(+++)	In range	(+++)
Biogas production	Maximise	(+++++)	In range	(+++)	maximise	(+++++)	maximise	(+++++)
CH_4 concentration	In range	(+++)	In range	(+++)	maximise	(+++)	In range	(+++)
Energy consumption	In range	(+++)	Minimise	(+++++)	Minimise	(+++++)	Minimise	(+)

Table 6.27: Optimal AD conditions as obtained by Design-Expert for maize silage.

	No.	Beating time	Temperature	Biogas production	% of CH4	Energy consumption	Desirability
1st criterion	1	0.53	39.2	734.1	54.2	117.94	0.937
2nd criterion	1	0.03	34	577.9	49.7	65.11	1
	2	0.06	34	586.5	50.0	65.12	1
	3	0.08	34	592.1	50.1	65.13	0.999
	4	0.15	34	610.6	50.6	65.16	0.999
	5	0.35	34	643.1	51.6	65.24	0.998
	6	0.4	34	647.9	51.8	65.26	0.997
	7	0.57	34	652.2	52.3	65.33	0.996
3rd criterion	1	0.57	35.79	698.5	53.0	82.93	0.703
4th criterion	1	0.22	37.59	697.88	52.41	101.06	0.60

6.8.1.2 Graphical optimisation

Aforementioned, the range of each response has been obtained from the numerical optimisation results in Table 6.27 to get the overlay plots. The green /shaded areas on the overlay plot in figures 6.18 – 6.21 are the regions that meet the proposed criteria. These types of graphs are useful for quick visual searching tools for the optimal conditions, especially in laboratory studies

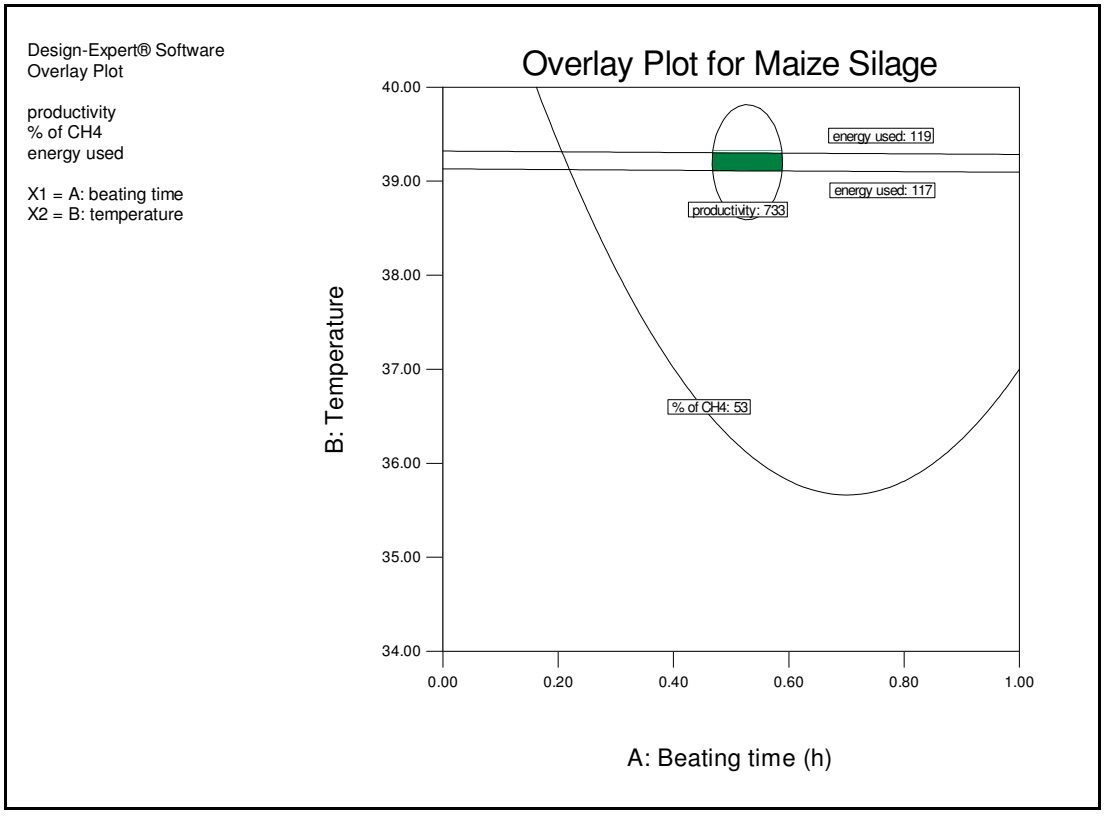


Figure 6-18: The feasible solution in green shaded area for first optimization criteria.

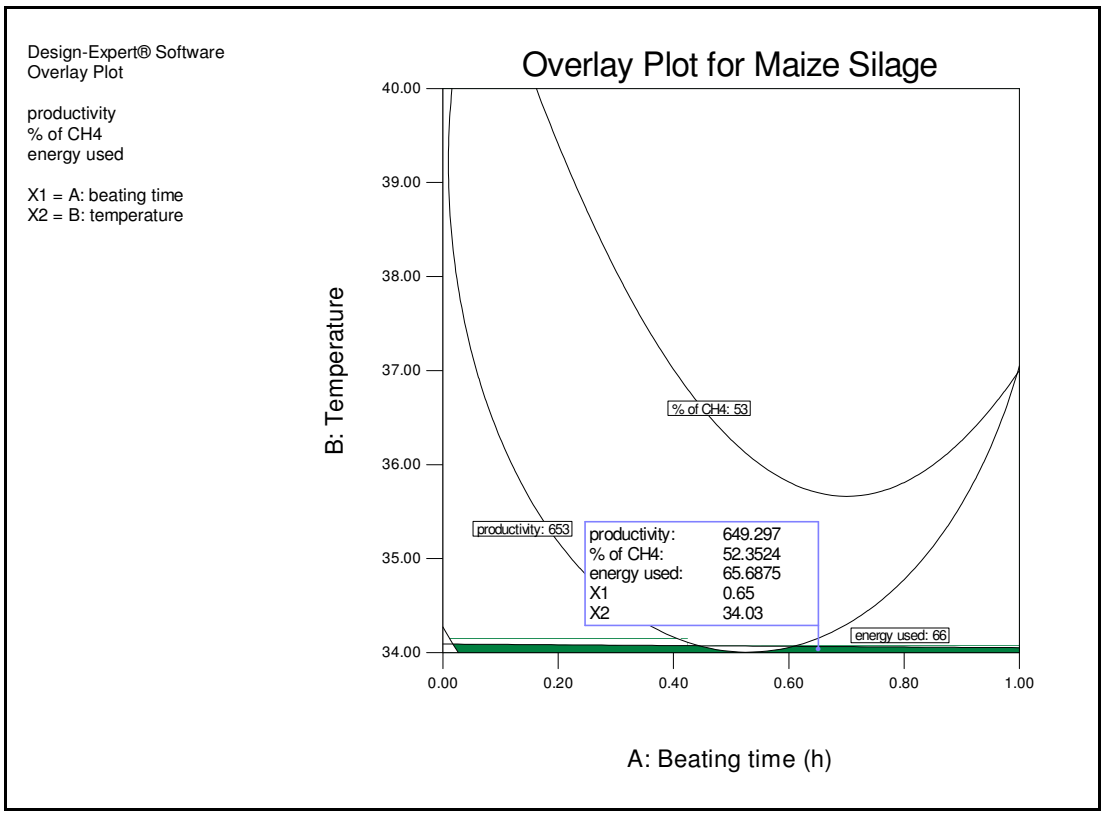


Figure 6-19: feasible solution in green shaded area for second optimization criteria.

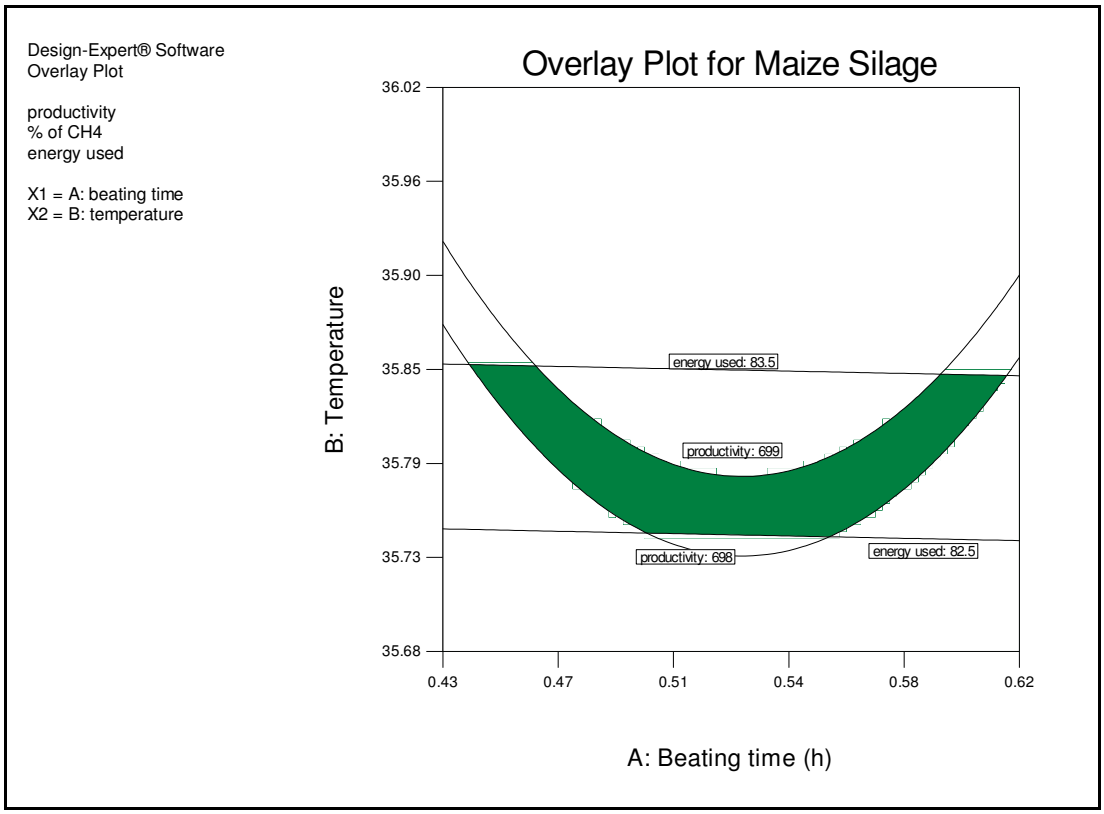


Figure 6-20: feasible solution in green shaded area for third optimization criteria.

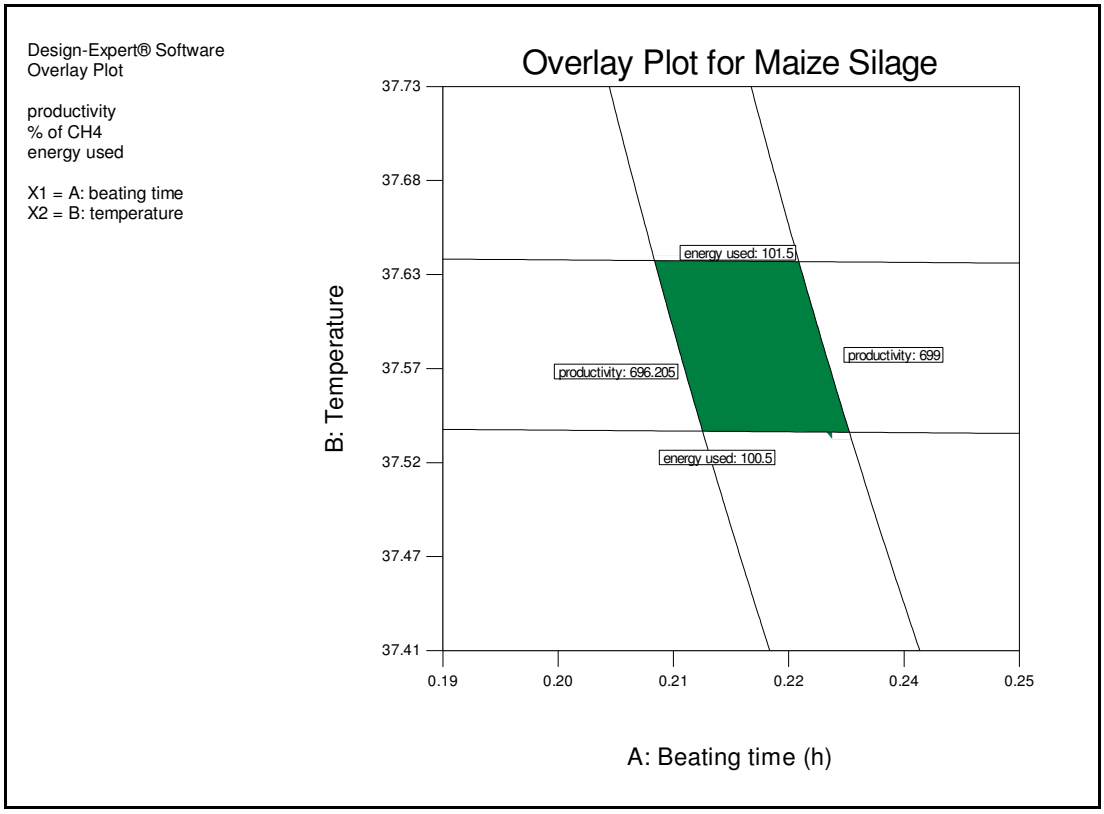


Figure 6-21: The feasible solution in green shaded area for fourth optimization criterion.

6.8.2 Potato waste

The four optimisation criteria for this material (potato waste) are presented in Table 6.28; the table shows that each factor and response has been allocated a specific goal and importance. The first criterion was aimed to maximise the production of biogas and the other parameters will be in range with default importance (+++), the second criterion was aimed to minimise the cost in terms of energy used and other parameters will be in range with default importance (+++), while the third criterion was aimed to maximise both biogas production and CH_4 concentration and in contrast minimise the cost and the input parameters will be in range with default importance (+++). Finally the fourth criterion was aimed to maximise the production of biogas and minimise both the beating time and energy consumption and the other parameters will be in range with default importance (+++).

6.8.2.1 Numerical optimisation

Table 6.29 shows the optimal setting of the process parameters and the corresponding response values for all criteria for potato waste. The results indicate that there are more than optimal solutions to achieve the highest desirability value for the first and second criteria (see table 6.29). While the optimal conditions for the third criterion was found to be: beating time of 9.94 minutes and AD temperature of 34.6 °C. to get 770.9 ml/g VS biogas with 69.53 kWh of energy needed.

Table 6.28: Criteria for numerical optimisation of potato waste.

Factor or response	First criterion (productivity)		Second criterion (Cost)		Third criterion (Cost vs productivity)		Fourth criterion (minimise beating time)	
	Goal	Importance	Goal	Importance	Goal	Importance	Goal	Importance
Beating time	Is in range	(+++)	Is in range	(+++)	Is in range	(+++)	Minimise	(++)
Temperature	Is in range	(+++)	Is in range	(+++)	Is in range	(+++)	Is in range	(+++)
Biogas production	Maximise	(+++)	Is in range	(+++)	maximise	(+++++)	maximise	(+++++)
Energy consumption	Is in range	(+++)	Minimise	(+++++)	Minimise	(+++)	Is in range	(+++)

Table 6.29: Optimal AD conditions as obtained by Design-Expert for potato waste.

	No.	Beating time	Temperature	Biogas production	Energy consumption	Desirability
1st criterion	1	10.06	39.48	812.4	118.796	1
	2	8.63	39.68	812.6	121.676	1
	3	10.27	39.32	810.9	116.576	1
	4	10.45	39.28	810.4	116.017	1
	5	10.79	39.4	811	117.66	1
2nd criterion	1	11.34	30.91	737.7	56.8254	1
	2	3.61	30.87	703.8	56.7587	1
	3	8.01	30.26	730.5	56.7857	1
	4	7.25	30.24	727.3	56.7898	1
	5	7.78	30.35	730.4	56.7483	1
3rd criterion	1	9.94	34.61	770.9	69.5296	0.786
4th criterion	1.00	5.94	40.00	802.70	126.24	0.84
	2.00	5.88	40.00	802.30	126.24	0.84
	3.00	6.28	40.00	805.00	126.24	0.84

6.8.2.2 Graphical optimisation

Aforementioned, the range of each response has been obtained from the numerical optimisation results in Table 6.29 to get the overlay plots. The green /shaded areas on the overlay plot in figures 6.22 – 6.25 are the regions that meet the proposed criteria. These types of graphs are useful for quick visual searching tools for the optimal conditions, especially in laboratory studies

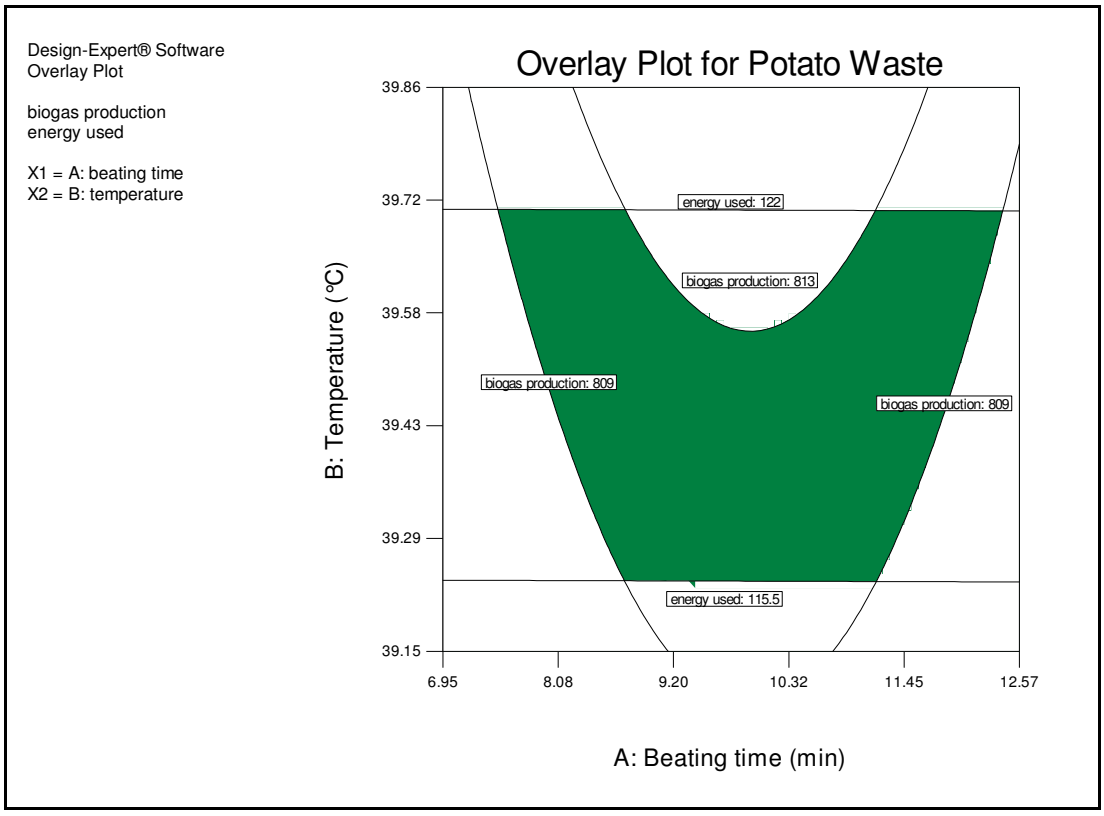


Figure 6-22: The feasible solution in green shaded area for first optimization criterion.

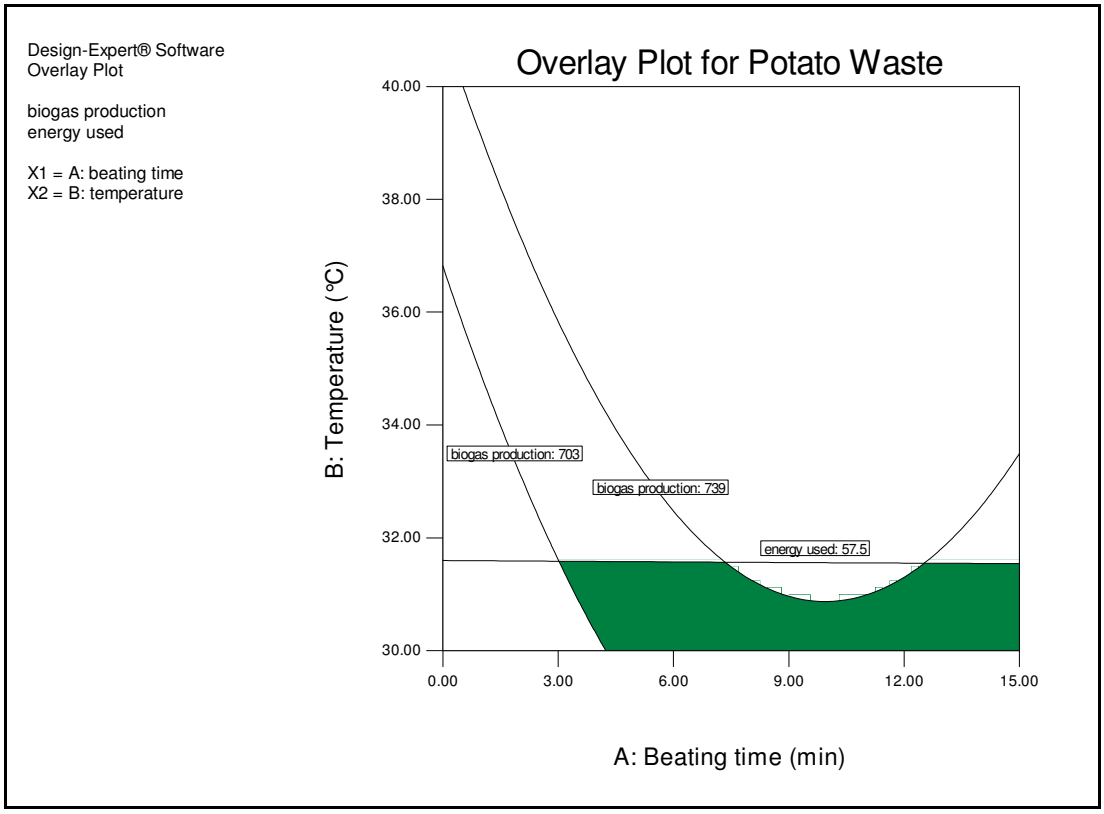


Figure 6-23: The feasible solution in green shaded area for second optimization criterion.

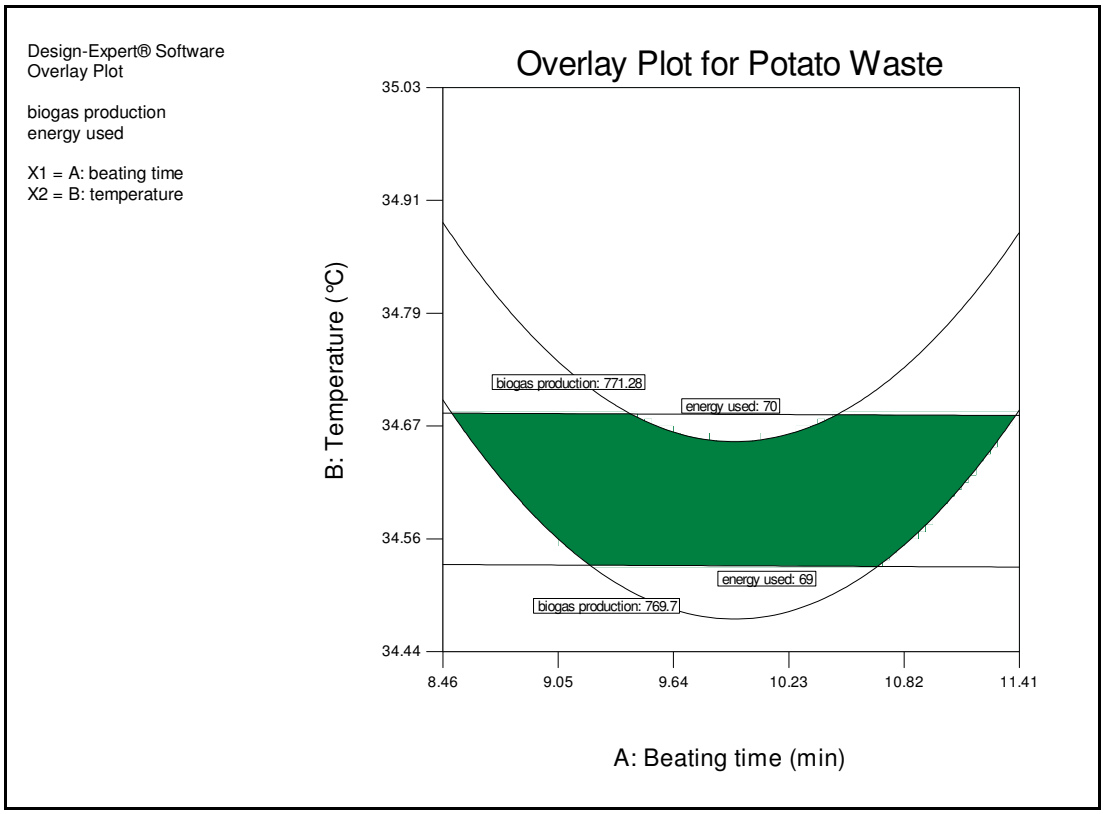


Figure 6-24: The feasible solution in green shaded area for third optimization criterion.

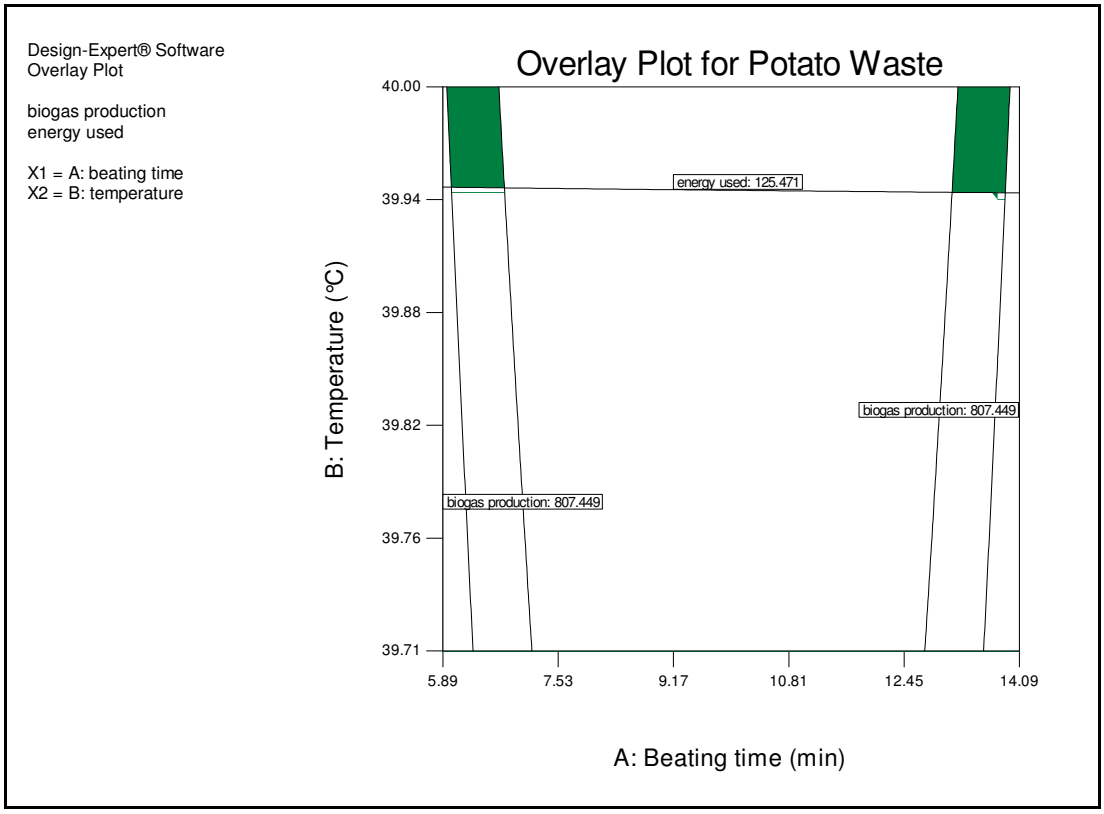


Figure 6-25: The feasible solution in green shaded area for fourth optimization criterion.

Chapter 7

CONCLUSION

7.1 Conclusion

In this study a new mechanical pre-treatment method to enhance the performance of the anaerobic digestion of lignocellulosic materials has been explored employing a Hollander Beater device. Attributable to the Hollander beater device the name "beating treatment" has been given to this new method of mechanical treatment. Three different lignocellulosic materials named maize silage; fresh grass and potato-waste have been used as a main substrate in this experimental research. Digester sludge was used as the inoculum. In order to investigate the effect of the treatment on the lignocellulosic materials a number of experiments before and after treatment have been conducted using an OVAT approach. Results indicate that there is a significant improvement in performance of anaerobic co-digestion of each substrate, in terms of the yield of biogas production. The findings of this part of study can be summarized in the following:

- Beating treatment as a new pre-treatment technique is effective and accelerates the degradability for lignocellulosic material. However, prolonging beating time does not always improve the biogas yield
- Beating treatment achieved an improvement of 25.4% of biogas yield from maize silage, after 20 minutes in comparison with untreated sample, and about 15.7% and 15.1% of biogas yield increment after 60 minutes and 180 minutes of beating treatment respectively.
- The CH_4 yield from maize silage was in the range of 320 - 416.9 mL/g VS.
- An increment of 178.9% of energy in terms of methane can be achieved after 20 minutes of beating time.
- Beating treatment achieved an improvement of 43.1% of biogas yield from fresh grass after 5 minutes beating treatment in comparison with an untreated sample, and about 35.2% and 28.8% of biogas yield increment after 15 minutes and 40 minutes of beating treatment respectively.

- The analysis indicates that CH_4 yield from fresh grass was in the range of 354.6 - 478.7 ml/g VS.
- An increment of 363% of energy in terms of methane can be achieved after 5 minutes of beating time from AD of fresh grass.
- Beating treatment achieved an improvement of 33.9% of biogas yield from potato waste after 5 minutes beating treatment in comparison with untreated sample, and about 25.4%, 18.8% and 11.7% of biogas yield increment after 15 minutes, 35 minutes and 60 minutes of beating treatment respectively.
- The analysis indicates that CH_4 yield from potato waste was in range of 338.7 - 551 ml/g VS.
- An increment of 830.2% of energy in terms of methane from potato waste can be achieved after 5 minutes of beating time.
- Regression analysis, indicates that there is a 3rd order polynomial relationship between the biogas production and degree of beating, also indicates that the 15 days of retention time can be suggested as an increment in the productivity which is afterwards insignificant.
- A combined pre-treatment and co-digestion strategy is a successful method to enhance the biogas production.

In addition, the design of experiment DOE and response surface methodology (RSM) were employed to optimise anaerobic digestion processes after beating treatment. Two different lignocellulosic materials anaerobically digested with digester sludge after beating treatment and also the effects of the two most important factors (temperature and beating time) on the biogas production and energy consumption have been investigated.

The findings of this part of study can be summarized in the following:

- RSM is an effective tool to optimize anaerobic digestion of maize silage, and potato waste or any lignocellulosic materials combined with beating treatment.
- Both factors (temperature and beating time) have a significant effect on the overall AD process.

- Beating time factor has no effect on the energy consumption, which indicates and supports that beating treatment is cost effective. This confirms that beating treatment technique will lead to a quantum leap in the field of bio-energy.
- For the potato-waste substrate, the model indicates that more than 10 minutes beating will be insignificant in terms of productivity.
- For the maize silage substrate, the model indicates that more than 31 minutes beating will be insignificant in terms of productivity.
- Ten adequate mathematical models have been developed for AD of maize silage and AD of potato-waste process. These models can be used for successful prediction or optimization analysis.

7.2 Thesis contribution

As part of the contribution of this thesis to energy improvement, beating treatment was introduced as a new mechanical treatment technique for lignocellulosic materials as a way of accelerating the hydrolysis process during anaerobic digestion. This also verifies the success of DOE as a method of predicting and optimizing anaerobic digestion of lignocellulosic materials after beating treatment.

Unlike previous researches, this research has estimated and included energy requirement, which is a cost indicator of the AD process, as a response for optimization. This research also achieved a decrease in the retention time of anaerobic digestion after beating treatment. The effects of each of the parameters on responses were identified, and this enabled the determination of parameters settings that would lead to optimal outcomes.

7.3 Future work

For further improvement and developmental needs to this process, some other critical analyses will need to be carried out on the following;

Application of beating treatment to other lignocellulosic materials that time has never permitted to work on in this study.

Investigation of the effect of gap between the drum and bedplate of the Hollander beater that shows variable factors and the use of RSM technique. Further investigation should also be conducted to determine the effect of beating treatment on the microstructure and particle size by using advanced and modern equipment such as particle size analyser names mastersizer 3000.

Effects of other parameters, such as pH, N/C ratio, sludge quantity and VFA, should also be investigated using RSM. Techniques such as box-behnken design can be used instead of composite design to investigate effect of interaction between factors.

The same work can be replicated using Taguchi optimization technique to achieve comprehension analysis. Artificial intelligence techniques, such as Advanced Neural Network, Fuzzy Logic and Genetic Algorithms, can also be applied to investigate the effect of factors on AD of lignocellulosic materials after beating treatment.

Publication

1) Ayad K. Mohamed, F. Alfarjani, K. Benyounis, T. Prescott, A. Olabi "Application of mechanical pre-treatment to produce methane from maize", proceedings of ECOS2011 conference, pg. 3595 – 3602 Novi Sad, Serbia
2) F. Alfarjani, Ayad. K. Mohamed, K. Benyounis, T. Prescott, A. Olabi "Mechanical Pre-treatment to Enhance Anaerobic Digestion Process: Overview" 2011, proceedings of ECOS2011, pg. 3573 – 3582, Novi Sad, Serbia
3) Ayad. K. M. Aboderheeba, F. Alfarjani, A. Olabi, the relationship between degree of beating and biogas production from maize silage anaerobically digested after beating treatment, proceedings of SEEP2012 conference, pg. 107 –112, DCU, Dublin, Ireland
4) Ayad. K. M. Aboderheeba, F. Alfarjani, A. Olabi, "Beating Treatment to Enhance Digestibility of Fresh Gras", proceedings of GCGW2012 conference, pg. 260 – 268, Istanbul Technical University, Turkey.
5) F. Alfarjani, Ayad. K. M. Aboderheeba, K. Benyounis, A. Olabi "Modeling Anaerobic Digestion Process for Grass Silage After Beating Treatment Using Design Of Experiment (DOE)", proceedings of GCGW2012 conference, pg. 281 – 289, Istanbul Technical University, Turkey
6) Ayad K. M. Aboderheeba, Fatma A. Alfarjani, K. Y. Benyounis, A. G. Olabi, "new mechanical treatment to enhance digestibility of lignocellulosic materilas for biogas improvment" under preparation for journal submission.
7) Paper titled "Beating Treatment to Enhance Digestibility fresh grass" Which is published in GCGW2012 has been selected to be publish in "International Journal of Global worming
8) Ayad K. M. Aboderheeba, Fatma A. Alfarjani, K. Y. Benyounis, A. G. Olabi, "Accelerate Hydrolysis Stage to Improve Productivity of Biogas from Potato waste using the New Beating Treatment" has been submit to the journal.
9) poster titled "Beating Treatment to Enhance Digestibility of Lignocellulosic Biomass (Maize silage): Novel approach", has been published in the Faculty Research Day (FRD), on 12th of September 2012, in Dublin City University

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Appendixes

Appendix A

This Appendix contains the relevant equations which have been used to calculate volume of biogas

Volume of biogas for each sample (***Y***):

$$Y = \sum_{i=1}^{n} Xi$$

Where:

Xi= volume reading deference (VRD)

n = number of reading

VRD = Final Volume Reading (FVR) – Initial Volume Reading (IVR)

Volume of biogas for each condition:

$$\acute{Y} = \frac{\sum_{i=1}^{n} Yi}{n}$$

Where:

n = number of samples

Yi = volume of biogas for each sample

Notes:

The contribution of sludge in biogas production is eliminated for each collection.

Appendix B

Energy analysis of biogas produced from maize silage anaerobcally digested with sludge.

The TS of the total amount of substrate (maize silage) is calculated using following formula:

$$X_{total} = \frac{1500\ (X_a)}{a} \tag{5.1}$$

Where;

X_a: the value of TS in 13g of wet substrate (maize silage in this case),

a: amount of untreated sample of substrate (13g maize silage),

X_{total}: the TS of total substrate (1500g maize silage) has been treated.

$$X_{total} = \frac{1500\ (4.47)}{13} = 515.8\ g$$

Volatile solid VS of the total maize silage has been treated (1500g) is 496.7g.

The total biogas (Y) expected from total untreated substrate is given by formula:

$$Y = \bar{x}_{total} \times b \tag{5.2}$$

Where:

Y: the total biogas expected from the total VS,

$\bar{x}_{total}$: VS of the TS for total amount of substrate (1500g maize silage)

b: the amount of biogas produced from 1g of VS,

Y = 496.7 X 634.6 = 315.2 litter

- The total biogas production (Y_1) from total VS of 1500g (after 20 minutes beating) can be calculated using equation (5.2) regarding Y to be Y_1 in this case.

Y_1 = 494.7 X 795.7 = 393.6 litter

The amount of increment of biogas production ($\acute{Y}_1$) after 20 minutes beating can be calculated as:

$$\acute{Y}_1 = Y_1 - Y \tag{5.3}$$

$\acute{Y}_1$ = 393.6 – 315.2 = 78.4 liter

- The total biogas expected (Y_2) from total dry matter of 1500g (after 60 minutes beating) can be calculated using equation (5.2) regarding Y to be Y_2 in this case**.**

Y_2 = 494.7 X 734.1 = 363.2 litter

The amount of increment of biogas expected ($\acute{Y}_2$) after 60 minutes beating can be calculated as:

$$\acute{Y}_2 = Y_2 - Y \tag{5.4}$$

$\acute{Y}_2$ = 363.2 – 315.2 = 48 liter

- The total biogas expected (Y_3) from total dry matter of 1500g (after 180 minutes beating) can be calculated using equation (5.2) regarding Y to be Y_3 in this case.

Y_3 = 496.7 X 730.2 = 361.2 litter

The amount of increment of biogas production ($\acute{Y}_3$) after 180 minutes beating can be as:

$$\acute{Y}_3 = Y_3 - Y \tag{5.5}$$

$\acute{Y}_3 = 361.2 - 315.2 = 46$ litre of biogas

The energy content of the increment of biogas was calculated based on a value of 9810 Wh/Nm^3. The electricity used to achieve treatment for each level was measured. 0.147kWh was consumed for 20 minutes beating, 0.381kWh for 60 minutes beating and 0.986Kwh was consumed for 180 minutes. Table app_a.1 illustrates the amount of energy content in the increment of biogas after three different level of beating. Also it shows the incremental rate in percentage can be obtained through applying the beating treatment to maize silage. It was found that first level of treatment has a positive energy balance. while second level of treatment (60 minutes beating) and third level of treatment (180 minutes beating) have negative energy balance.

Table app_a.1: Energy analysis.

Beating Time	Increment of Biogas (l/kg VS)	CH_4 %	Content of Energy produced (EP) (Kwh/l)	Electricity Used (UE) - (Kwh)	% Energy balance of (UE) Vs. (EP)
20 mins	78.4	53	0.41	0.147	35.85
60 mins	48	55	0.26	0.381	146.4
180 mins	46	54	0.24	0.986	410.8

Appendix C

Energy analysis of biogas produced from fresh grass anaerobcally digested with sludge.

The TS of the total amount of substrate (grass) used in this experiment calculated using equation 5.1.

$$X_{total} = \frac{1000\ (2.13)}{13} = 163.9\ g$$

The Volatile solid VS of the total amount of substrate (grass) (1000g) is 148g.

The total biogas (Y) expected from total untreated substrate (grass) is given by equation 5.2.

$$Y = 148 \times 669.1 = 99 \text{ litter of biogas}$$

- The total biogas production (Y_1) from total VS of 1000g (after 5 minutes beating) can be calculated using equation (5.2) regarding Y to be Y_1 in this case.

$$Y_1 = 157.4 \times 957.4 = 150.7 \text{ litter of biogas}$$

The amount of increment of biogas production ($\acute{Y}_1$) after 5 minutes beating can be calculated using equation 5.3:

$$\acute{Y}_1 = 150.7 - 99 = 51.7 \text{ litter of biogas}$$

- The total biogas expected (Y_2) from total VS of 1000g (after 15 minutes beating) can be calculated using equation (5.2) regarding Y to be Y_2 in this case.

$$Y_2 = 156.5x\ 904.8 = 141.6 \text{ litter of biogas}$$

The amount of increment of biogas expected ($\acute{Y}_2$) after 15 minutes beating can be calculated equation 5.4:

$$\acute{Y}_2 = 141.6 - 99 = 42.6 \text{ litter of biogas}$$

- The total biogas expected (Y_3) from total VS of 1000g (after 40 minutes beating) can be calculated using equation (5.2) regarding Y to be Y_3 in this case.

$$Y_3 = 155.4 \times 861.5 = 133.9 \text{ litter of biogas}$$

The amount of increment of biogas production ($\acute{Y}_3$) after 40 minutes beating can be calculated using equation 5.5:

$$\acute{Y}_3 = 133.9 - 99 = 34.9 \text{ liter of biogas}$$

The energy content of the increment of biogas was calculated based on a value of 9810 Wh/Nm^3. The electricity used to achieve treatment for each level was measured. 0.054 KWH was consumed for 5 minutes beating, 0.11 KWH for 15 minutes beating and 0.233 KWH was consumed for 40 minutes. Table app_b.1 illustrates the amount of energy content in the increment of biogas after three different level of beating. Also it shows the incremental rate in percentage can be obtained through applying the beating treatment to grass. It was found that first and second level of treatment have a positive energy balance., while third level of treatment (40 minutes beating) have negative energy balance.

Table app_b.1: energy analysis.

beating time	increment of biogas (l/x_{total} VS)	CH4 (%)	content of energy produced [EP] (Kwh/l)	electricity used [EU] (Kwh)	% energy balance of [EU] Vs. [EP]
5 minutes	51.7	50	0.25	0.054	21.6
15 minutes	42.6	51	0.21	0.11	52.4
40 minutes	34.9	52	0.18	0.233	129.4

Appendix D

Wet sieving analysis for potato waste substrate:

The aim of this analysis is to estimate the particle size of substrate after different levels of beating treatment. 5 different sizes of sieves have been used for this analysis. The procedure of the analysis as following:

1. Dry beaker of 200ml was weighed and recorded.
2. About 200ml pulp were collected randomly from the beating bath and collected into beaker.
3. Then the beaker with sample was weighed and recorded.
4. Net wet weight of each sample was measured by subtracting the empty beaker weight from the original value.
5. Dry sieve was weighed and recorded.
6. The sample was poured into the sieve and after the water content as well as the small particle size was drained out, then the sieve with the remaining substrate were weighed and noted.
7. The quantity of substrate left over, can be calculated by subtracting the value obtained in step 5 above from that of step 6
8. The remaining substrate can be calculated through the ratio of value of substrate remaining and that of sample weight and in percentage, it is worked out through multiplying by 100.

The Tables app_d.1- app_d.20 below showed detailed illustration of the analysis of particle size measurement and calculation for all different levels of beating treatment, while Table app_d.21 showing the average value of wet sieve analysis.

- First level of beating treatment (5 minutes beating time)

Table app_d.1.

Sieve 4 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	112.2	362.7	458.6	459.8	250.5	1.2	0.5
2	112.3	361.3	458.8	459.6	249	0.8	0.3
Average							0.4

Table app_d.2.

Sieve 2 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	112.1	363.1	412.9	416.6	251	3.7	1.5
2	112.3	361.6	413.6	417.8	249.3	4.2	1.7
Average							1.6

Table app_d.3.

Sieve 1 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	112	362.7	391.6	402.2	250.7	10.6	4.2
2	112	363.6	391.9	402.9	251.6	11	4.4
Average							4.3

Table app_d.4.

Sieve 0.8 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	112.1	360.9	338	352.6	248.8	14.6	5.9
2	112	362.2	338.9	354	250.2	15.1	6.0
Average							6.0

Table app_d.5.

Sieve 0.355 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	111.6	367	316.2	331.9	255.4	15.7	6.2
2	111.9	368.1	316.5	332.6	256.2	16.1	6.3
Average							6.3

- Second level of beating treatment (15 minutes beating time)

Table app_d.6.

Sieve 4 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	117.5	365.5	459.5	461.3	248	1.8	0.7
2	117.4	367.2	457.8	461.5	249.8	3.7	1.5
Average							1.1

Table app_d.7.

Sieve 2 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
	117.4	368.5	410.9	420.8	251.1	9.9	3.9
	117.5	369	411.7	420.9	251.5	9.2	3.7
Average							3.8

Table app_d.8.

Sieve 1 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	117.5	363.8	391.2	407.3	246.3	16.1	6.5
2	117.6	352.9	392.6	407.5	235.3	14.9	6.3
Average							6.4

Table app_d.9.

Sieve 0.8 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	117.3	368.9	338.4	356.7	251.6	18.3	7.3
2	117.6	364.9	338.7	357.8	247.3	19.1	7.7
Average							7.5

Table app_d.10.

Sieve 0.355 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	117.5	358.7	316.8	336.9	241.2	20.1	8.3
2	117.5	348.6	315.6	335.9	231.1	20.3	8.8
Average							8.6

- Third level of beating treatment (35 minutes of beating time)

Table app_d.11.

Sieve 4 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	113.8	371.8	458.5	460.1	258	1.6	0.6
2	113.7	370.1	458.9	461	256.4	2.1	0.8
Average							0.7

Table app_d.12.

Sieve 2 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	113.3	366.6	409.6	417	253.3	7.4	2.9
2	114.2	367.5	412.4	419.5	253.3	7.1	2.8
Average							2.9

Table app_d.13.

Sieve 1 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	113.9	372.1	390.1	403.2	258.2	13.1	5.1
2	114.3	372.1	392.4	404.3	257.8	11.9	4.6
Average							4.9

Table app_d.14.

Sieve 0.8 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	113.9	364.8	337.6	355.2	250.9	17.6	7.0
2	113.9	363.5	338.7	353.8	249.6	15.1	6.0
Average							6.5

Table app_d.15.

Sieve 0.355 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	113.7	360.3	315.2	333.4	246.6	18.2	7.4
2	113.9	363	315.1	334.2	249.1	19.1	7.7
Average							7.6

- Fourth level of beating treatment (60 minutes of beating time)

Table app_d.16.

Sieve 4 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	112.2	362.7	458.6	459.5	250.5	0.9	0.4
2	112.3	361.3	458.8	459.6	249	0.8	0.3
Average							0.35

Table app_d.17.

Sieve 2 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	112.1	363.1	412.9	416.6	251	3.7	1.5
2	112.3	361.6	413.6	417.8	249.3	4.2	1.7
Average							1.6

Table app_d.18.

Sieve 1 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	112	362.7	391.6	402.2	250.7	10.6	4.2
2	112	363.6	391.9	402.9	251.6	11	4.4
Average							4.3

Table app_d.19.

Sieve 0.8 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	112.1	360.9	338	352.6	248.8	14.6	5.9
2	112	362.2	338.9	354	250.2	15.1	6.0
Average							6.0

Table app_d.20.

Sieve 0.355 mm							
Sample No.	beaker weight	beaker + sample weight	sieve weight	sieve + sample weight	sample weight	Substrate Remaining (SR)	% of SR
1	111.6	367	316.2	331.9	255.4	15.7	6.2
2	111.9	368.1	316.5	332.6	256.2	16.1	6.3
Average							6.3

Table app_d.21 showing the average value of wet sieve analysis.

beating time	4 mm	2 mm	1 mm	0.8 mm	0.355 mm
5 min	4.4	6.9	8.7	9.8	9.8
15 min	1.1	3.8	6.4	7.5	8.6
35 min	0.7	2.9	4.9	6.5	7.6
60 min	0.4	1.6	4.3	6	6.3

Appendix E

Energy analysis of biogas produced from potato waste anaerobcally digested with sludge.

Equations 5.1 – 5.5 have been used to evaluate the economic feasibility at lab scale of beating treatment for potato waste as renewable energy resource.

The TS of the total amount of substrate (potato waste) used in this experiment calculated using equation 5.1.

$$X_{total} = \frac{1500\ (3.57)}{15} = 357\ g$$

The Volatile solid VS of the total amount of substrate (1500g) is 326.3g.

The total biogas (Y) expected from total untreated substrate potato waste) is given by equation 5.2.

$$Y = 326.3 \text{ x } 667.3 = 217.7 \text{ litre of biogas}$$

- The total biogas production (Y_1) from total VS of 1500g (after 5 minutes beating) can be calculated using equation (5.2) regarding Y to be Y_1 in this case.

$$Y_1 = 334.2 \text{ x } 893.6 = 298.6 \text{ litre of biogas}$$

The amount of increment of biogas production ($\acute{Y}_1$) after 5 minutes beating can be calculated using equation 5.3:

$$\acute{Y}_1 = 298.6 - 217.7 = 80.9 \text{ liter of biogas}$$

- The total biogas expected (Y_2) from total VS of 1500g (after 15 minutes beating) can be calculated using equation (5.2) regarding Y to be Y_2 in this case.

$$Y_2 = 333.4\text{x } 836.5 = 278.9 \text{ litre of biogas}$$

The amount of increment of biogas expected ($\acute{Y}_2$) after 15 minutes beating time can be calculated equation 5.4:

$$\acute{Y}_2 = 278.9 - 217.7 = 61.2 \text{ liter of biogas}$$

- The total biogas expected (Y_3) from total VS of 1500g (after 35 minutes beating) can be calculated using equation (5.2) regarding Y to be Y_3 in this case.

$$Y_3 = 339.2 \times 793 = 269 \text{ litre of biogas}$$

The amount of increment of biogas production ($\acute{Y}_3$) after 35 minutes beating time can be calculated using equation 5.5:

$$\acute{Y}_3 = 269 - 217.7 = 51.3 \text{ liter of biogas}$$

- The total biogas expected (Y_4) from total VS of 1500g (after 60 minutes beating) can be calculated using equation (5.2) regarding Y to be Y_4 in this case.

$$Y_4 = 338.4 \times 745.2 = 252.8 \text{ litre of biogas}$$

The amount of increment of biogas production ($\acute{Y}_4$) after 60 minutes beating time can be calculated using equation 5.5:

$$\acute{Y}_4 = 252.8 - 217.7 = 25.1 \text{ liter of biogas}$$

The energy content of the increment of biogas was calculated based on a value of 9810 Wh/Nm^3. The electricity used to achieve treatment for each level was measured. 0.043 KWH was consumed for 5 minutes beating, 0.095 KWH for 15 minutes beating, 0.193 KWH for 35 minutes beating and 0.318 KWH was consumed for 60 minutes. Table app_d.1 illustrates the amount of energy content in the increment of biogas after three different level of beating. Also it shows the incremental rate in percentage can be obtained through applying the beating treatment to grass. It was found that first and second level of treatment have a positive energy balance., while third level of treatment (40 minutes beating) have negative energy balance (see Table app_d.1).

Table app_d.1: energy analysis (potato waste).

beating time	increment of biogas (l/x_{total} VS)	CH4 (%)	content of energy produced [EP] (Kwh/l)	electricity used [EU] (Kwh)	% energy balance of [EU] Vs. [EP]
5 minutes	80.9	51	0.40	0.043	10.8
15 minutes	61.2	50	0.30	0.095	31.7
35 minutes	51.3	52	0.26	0.193	74.2
60 minutes	35.1	50	0.17	0.318	187.1