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DIGESTION OF CORN AND AMMONIA REMOVAL IN A LAB SCALE DIGESTER

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Thesis Abstract

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This research was done as an internal project for developing in-house knowledge for PROCES-Groningen B.V. The project is related to bio-digestion and factors affecting the process. The bio-digestion process is taken into account which includes the digesting of corn and ammonia removal which occur after digestion. The aims of this research are to analyze parameters affecting bio-digestion and provide the framework for a construction of a better bio-digester.

The digestion of corn analysis was done with thermophilic and mesophilic digesters where the gas production, pH, volatile fatty acids content and lignin content was analyzed. The ammonia removal was done with air stripping method where both flocculated and drain digested pre-treated chicken manure was used. The varying amount of air volume was also examined with the air stripping method experiments.

The result of this research will provide a framework for the construction of a better bio-digester. These results will also give a detailed analysis of digestion of corn and better way of removing ammonia which will provide the background for further research. This result will also provide more information about how other future research might be directed.

Key words
bio-digestion, digestion of corn, mesophilic, thermophilic, ammonia removal

FOREWORD

I wish to use this opportunity to thank all persons that have made this thesis a success in any way possible. I wish to show my appreciation to the Almighty GOD for his blessings and knowledge to be able to finish this thesis.

My profound gratitude goes to my parents, PROCES-Groningen B.V staff for their support and their help during the writing of this thesis. I will also like to say a big thank you to my supervisor in PROCES, Mr. Han Bannings for his words of encouragement and for being very helpful during my first weeks working for their company.

I will like to thank all lecturers that have taught me at Central Ostrobothnia University of Applied Sciences in the department of chemistry and technology. My appreciation goes to my thesis supervisor, Jana Holm, the principal lecturer of my department, Staffan Borg and my language lecturer, Esko Johnson and all friends, colleagues, lecturer that I cannot mention.

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1 INTRODUCTION

With the increasing energy demand around the world and the need to protect the environment, there is a need to find an alternative source of energy source. The major source of global energy is fossil fuels that comprises of oil, natural gas and coal which accounts for 95% of the world's total energy demands. Fossil fuel is a non-renewable source of energy which implies that it cannot be created again once it used up. It is formed from the remains of dead plants and animals buried deep in the earth's core millions of years ago.

The global consign is that as the population of the world increases, the demand for energy will increase and at a certain point there will be no more fossil fuel left. The fact that energy from fossil fuel causes pollution, global warming, acid rain which affects the environment and causes an imbalance in the ecosystem is a major global issue.

The only alternative is to use renewable sources of energy. Renewable sources of energy implies to natural source of energy which is replenished naturally at a faster rate than consumption. The renewable energy sources such as wind, solar radiation, geothermal and biomass. This type of energy source provides less or no emissions compare to fossil fuel.

Biomass is a type of renewable source of energy which produces energy from waste from plants, animals and humans. This type of energy source can help to reduce waste landfill problem because the waste can be made useful to produce biogas and the substrate can be used as fertilizer.

Biomass energy comes from the sun through the process of photosynthesis. This process occurs in plants where the chlorophyll converts the carbon dioxide from the air and water from the ground into carbohydrates using the sun's energy. The different types of plants used for bio-mass energy production such as trees, grasses, other crops (corn, sorghum), oil

plants (soyabeans, sunflowers), biomass residue from forestry, agriculture and municipal waste.

Bio-gas is produced from inside a bio-digester which will be the major focus of this thesis. The production and factors that affect bio-gas production are analyzed which include the bio-digestion process and the removal of toxic compounds from the process. There are several toxic compounds like ammonia, aromatic compounds, cyanide, heavy metals, hydrogen sulphide, etc during the digestion process that can inhibit the system but this project will be focused on removal of ammonia from the digestion process.

The digestion of corn stover research entails the composition of corn stover and the comparison of the digestion of thermophilic and mesophilic bacteria. The gas production and pH values, volatile fatty acids contents and the lignin content analysis were fully analyzed.

The ammonia removal which takes place after digestion will be researched because there are several ways of ammonia removal in a bio-digester. The air stripping method of ammonia will be the major focus of this research and it will consider the air volume, the rate of ammonia removal and the theory behind the air stripping method.

This project was done in PROCES-Groningen B.V. which is a chemical engineering consultancy and is working for the objective of carrying out research in the optimization of the treatment of organic wastes, based on bio-digestion. The target was to reduce as much as possible the amount of organic solids and transform this into biogas.

The result of this research is internal and it is done for developing in-house knowledge of the company. This project will give a detailed analysis of digestion of corn and better way of removing ammonia which will provide the background for more research. The result will also provide more information and will dictate how other future research will be directed.

2 BACKGROUND

2.1 Biodigester

Bio-digester is a waste management system that converts organic wastes (manure, sewage, municipal waste, green waste, energy crops and biomass) into a nutrient rich liquid fertilizer and biogas (methane and carbon dioxide), a renewable source of electrical and heat energy. By preventing methane from being released into the atmosphere, it helps to reduce emissions that can cause climate change. (AIDG 2009; Henk 2009, 3.)

Bio-digesters provide clean and renewable energy thereby reducing greenhouse gas emission. They help to convert waste into high quality organic fertilizer which helps to improve crop yields and thus can digest a wide variety of organic wastes which include animal manure, crop stalks, straw, slaughterhouse wastes, biodegradable garbage and wastewater. (AIDG 2009.)

Bio-digesting of organic wastes are divided into two based on their use of oxygen. The bio-digester which makes use of oxygen is known as aerobic digester while the bio-digester which doesn't make use of air is known as anaerobic digester.

2.2 Introduction to aerobic digester process

Aerobic digestion of organic matter (municipal waste and sewage) is a natural biological degradation and purification process in the presence of air (oxygen) allows bacteria to break down and digest the waste. The organic matters are broken down into carbon dioxide (CO_2), water (H_2O), nitrates, sulphates and biomass (microorganisms). The final metabolic waste products are used to provide the bacteria with energy for growth and reproduction. (Seafish 2005; Water management 2009.)

For example: formaldehyde being digested in an aerobic digester

$CH_2O + O_2 \rightarrow CO_2 + H_20 + Cells$

Aerobic bacteria are very efficient in breaking down waste products and a portion of the produced energy is used for synthesis and growth of new bacteria. It produces lower BOD (biochemical oxygen demand) concentrations in supernatant liquor. It produces an odorless, humus-like, biologically stable end product. Aerobic digesters are easy to operate and require a low capital cost.

Aerobic digester has a high power cost which is associated with supply of the required oxygen and it doesn't produce the useful by-product methane. The digestion process is greatly affected by temperature, location, geometry of the tank, type of mixing device and type of tank material. (Henk & Banning 2006, 9.)

2.3 Introduction to anaerobic digester process

Anaerobic digestion is a natural biological process that is carried out in a number of steps by several types of microorganisms (bacteria) that breaks down organic matters in an environment which requires little or no oxygen (Davies 2006; Cheshire 2006.). Anaerobic digester can digest most organic matters including waste paper, grass clippings, leftover food, industrial effluents, sewage and animal waste. (Davies 2006; Henk & Banning 2006, 11.)

The end-product of anaerobic digestion is biogas (consists of methane (50%–80%), carbon dioxide (20%–50%), and trace levels of other gases such as hydrogen, carbon monoxide, nitrogen, oxygen, and hydrogen sulfide). The solid residue from the process is called the digestate which is used as a soil conditioner to fertilize land while the liquid filtrate is used as a liquid fertilizer.

The formation of biogas from organic matter is given in the chemical equation below

$$C_cH_hO_oN_nS_s + yH_2O \rightarrow xCH_4 + nNH_3 + sH_2S + (c\text{-}x)\ CO_2$$

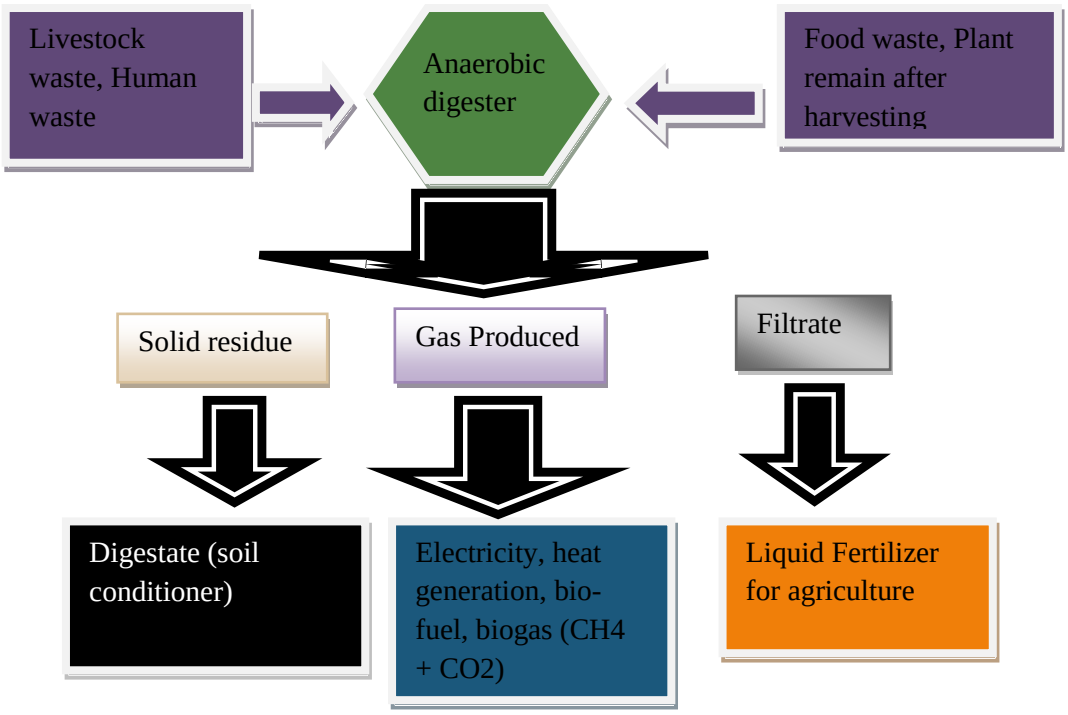
The products include, for example, the following:

Carbohydrates, $C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$

Fats, $C_{12}H_{24}O + 3H_2O \rightarrow 4.5CO_2 + 7.5CH_4$

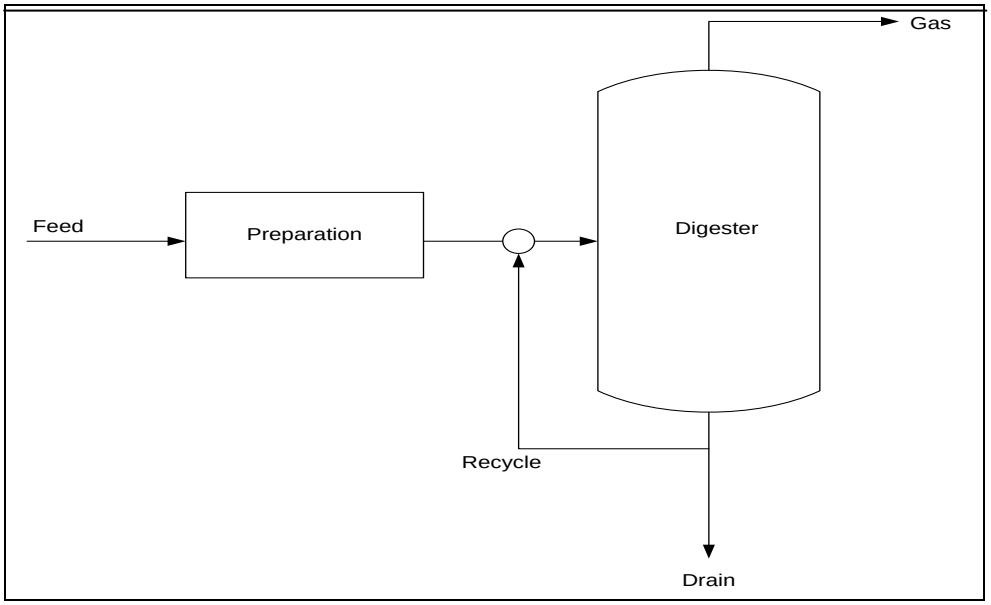
Proteins, $C_{13}H_{25}O_7N_3S + 6H_2O \rightarrow 6.5CO_2 + 6.5CH_4 + 3NH_3 + H_2S$

(Henk 2009, 7; Miel 2008, 11.)



GRAPH 1.General overview of anaerobic digestion (Waste solutions 2008)

The next flow diagram shows how an anaerobic digester works. Sometimes it is necessary to pre-treat the feed before going inside the digester. The gas is produced by the methanogenic bacteria inside the digester. It is necessary to recycle part of the drain to maintain high the content of micro-organisms in the digester.



GRAPH 2. Scheme of an anaerobic digester

The anaerobic digester is well known as a treatment process for sludge that contains large amounts of solids. These solids require relatively long digestion periods, which allow the slow bacterial processes of hydrolysis and solubilization of the solids. Once solubilized, the resulting complex organic compounds are degraded to simple organic compounds, mostly volatile acids and alcohols, methane, new bacterial cells and variety of simple inorganic compounds such as carbon dioxide and hydrogen gas. (Henk 2009, 12.)

The amount of biogas and the quality of digestates obtained will vary according to the amount of organic waste fed to the digester and the temperature influences the rate of gas production and decomposition. Sewage and manure yield less biogas as the animal which produced it has already taken out some of the energy content. (Henk 2009, 13.)

There are three basic types of anaerobic digestion processes which are determined by different species of bacteria that survive at different temperature ranges which are psychrophilic digestion (bacteria), mesophilic digestion (bacteria) and thermophilic digestion (bacteria).

Psychrophilic digestion takes place at a temperature range of 5-20ºC. Due to this low temperature the organic matter digestion and methane production is relatively low. This type of digestion is limited to small scale operations such as septic tanks and it takes more than 100 days to complete. The main micro-organisms present are called psychrophilic. (Gerardi 2003, 147.)

Mesophilic digestion takes place at a temperature range of 20-40ºC, although the best temperature is between 30-35°C. Mesophilic digestion can take a month or two to complete. It is the most commonly used process for anaerobic digestion, in particular municipal and industrial wastewater treatment. Decomposition of the volatile suspended solids (VSS) is around 40% over a retention time of 15 to 40 days at a temperature of 30 to 40^{o}C, which requires larger digestion tanks. (Gerardi 2003, 148.)

Two of the major advantages of this process are, firstly that there are more mesophiles in nature than thermophiles and psychrophiles but the biogas production tends to be less. The second advantage is that it is also less expensive to maintain a mesophilic digester compared to thermophilic digester.

Thermophilic digestion takes place in a temperature range of 50-60ºC. The rate of digestion and methane production is very fast while the destruction of pathogens is achieved. At high temperature, the number of thermophilic methane forming bacteria is limited and the bacterial growth is slow. The bacterial population experiences a higher endogenous death rate which is due to the bacteria being very sensitive to fluctuations in digester temperature. (Gerardi 2003, 148; Mari Jose 2009, 32.)

Thermophilic digestion helps in increasing volatile solid reduction for greater bio-energy conversion, which produces increased pathogen destruction for improved bio-solids quality. Thermophilic bacteria have faster reaction rates with short retention times and greater capacity for a given volume. This digestion also helps to improve the ability to remove water from the digested bio-solids. (Gerardi 2003, 148; Mari Jose 2009, 32.)

Thermophilic digestion has its own disadvantages, which can cause more intense odor from the bio-solids resulting from a higher volatile fatty acid (VFA) content. High energy is required for heating solids and maintaining the digesters at high temperature. This high temperature also causes greater thermal stress on concrete digesters (Gerardi 2003, 148; Mari Jose 2009, 32.). The anaerobic digestion process takes place stage by stage which are hydrolysis stage, acidogenesis stage, acetogenesis stage and methanogenesis stage.

2.3.1 Hydrolysis stage in an anaerobic digester process

Hydrolysis is the process whereby a complex compound is spitted into simple organic molecules by using water to split the chemical bonds between the substances. This is the first stage in an anaerobic digestion and it is achieved by the breaking down of insoluble organic polymers such as carbohydrates, cellulose, proteins and fats into liquid by enzymes produced by hydrolytic bacteria. (Gerardi 2003, 51; Henk 2009, 8.)

The hydrolysis stage determines the rate of the gas production in an anaerobic digester because microorganisms can only use soluble organic matter. These can pass through their cellular wall so the breaking down of organic polymers into soluble matter is crucial for the micro-organisms. This process depends on the process temperature, the size of the

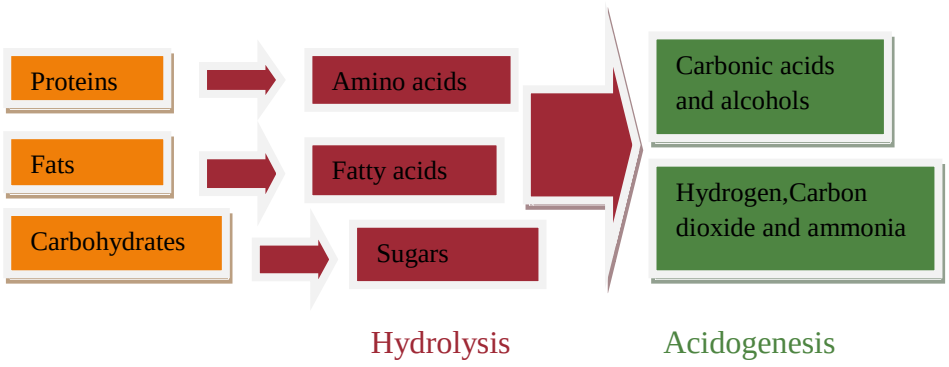
particles, pH, the concentration of the NH_4^+, hydraulic retention time and the composition of the substrate (lignin, carbohydrates, fat, and proteins percentage). (Gerardi 2003, 52.)

Carbohydrates, proteins and fats are hydrolyzed to sugars, which are decomposed further to form carbon dioxide, hydrogen, ammonia and organic acids. Proteins have a high source of carbon, energy and amino acids which have a high nutrition value.
Hydrolysis stage decomposition end-products are given below
Complex carbohydrates → simple sugars
Complex fats (lipids) → fatty acids
Complex proteins → amino acids

At the end of this stage, the gas concentrations may rise to levels of 80 per cent carbon dioxide and 20 per cent hydrogen. (Mari Jose 2009, 23.)

2.3.2 Acidogenesis stage in an anaerobic digester process

The second stage of the anaerobic digestion process and the soluble compounds that was produced in the hydrolysis stage is further broken down through fermentation by enzymes, bacteria, yeasts or molds in the absence of oxygen (Gerardi 2003, 55.). The decomposition of the end-products from the hydrolysis stage results into the production of carbon dioxide, alcohols, hydrogen gas, organic acids, some organic-nitrogen compounds and some organic-sulfur compounds (Gerardi 2003, 57.). Graph 3 illustrates the acidogenesis stage in an anaerobic digester process.



GRAPH 3. View of the acidogenesis stage (Adapted from Instablogs Network 2005)

2.3.3 Acetogenesis stage in an anaerobic digester process

The third stage of the anaerobic process where the products form the fermentation or acid forming stage is further digested to produce carbon dioxide, hydrogen and acetic acid. This process is carried out by the acetogenic bacteria although some product such as hydrogen and acetic acid from the acid forming stage can be utilized directly in the methane forming stage (methanogenesis). (Gerardi 2003, 56; Henk 2009, 8.)

Some other products such as ethanol, volatile fatty acids and aromatic compounds must be converted by the acetogenic bacteria into simpler products (acetate and hydrogen). At the end of this stage carbon dioxide and hydrogen concentrations begin to decrease (Gerardi 2003, 55). The chemical reaction below illustrates the acetogenesis stage in an anaerobic digestion process.

$CH_3CH_2OH + H_20 \rightarrow CH_3COOH^- + H^+ + 2H_2$ (carbohydrate)

ethanol water acetate

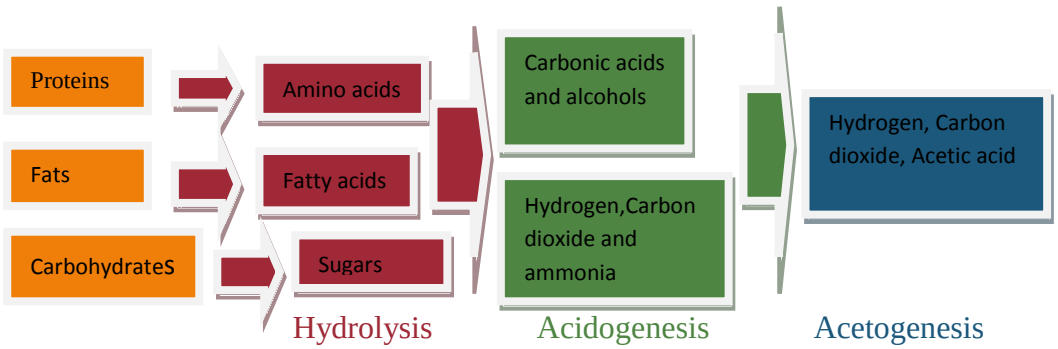
$CH_3CH_2C00H^- + H_20 \rightarrow CH_3COOH^- + HCO_3^- + H^+ + 3H_2$ (fatty acids)

propionate water acetate

$CH_3CH\ (NH_2)\ COOH + 3H_20 \rightarrow CH_3COOH^- + HCO_3^- + NH_4 + H^+ + 2H_2$ (amino acids)

alanine water acetate

(Gerardi 2003, 26.)



GRAPH 4. View of the acetogenesis stage (Adapted from Instablogs Network 2005)

2.3.4 Methanogenesis stage in anaerobic digester process

This is the final stage in the anaerobic digestion process where methane and carbon dioxide are formed by methanogenic bacteria. The methane formed is mostly from acetate and carbon dioxide/hydrogen, but it is also formed from other organic compounds such as formate, methylamines. Methanogenic bacteria break down acids, and a slightly alkaline solution is achieved from the overall process because the formation of ammonia from the amino groups i.e. from proteins and amino acids. (Gerardi 2003, 57.)

Other compounds such as acids, alcohol that are not converted by the methanogenic bacteria accumulate in the digester supernatant which is responsible for the relatively high organic strength of the supernatant (Mari Jose 2009, 30.). Close relationship is required between the acetogenic bacteria and the methanogenic bacteria during the final stage of the anaerobic process. Due to the fact that the conversion of the fermentation products by the acetogens is thermodynamically only if the hydrogen concentration is kept sufficiently low. (Mari Jose 2009, 36.)

The chemical reaction equation below illustrates the conversion of methanol and acetate into methane.

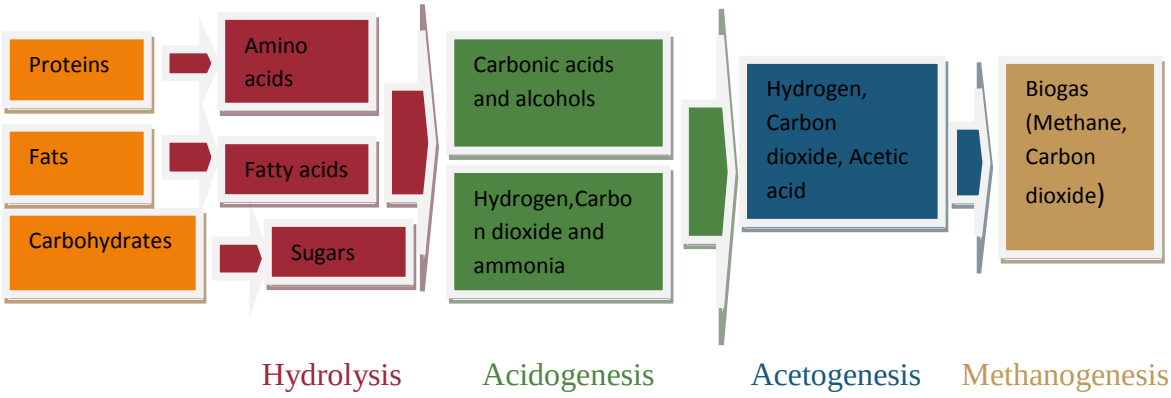
$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$

methanol methane water

$CH_3COOH + H_20 \rightarrow HCO_3^- + CH_4$

acetate water methane

(Gerardi 2003, 39.)



GRAPH 5. View of the Methanogenesis stage (Adapted from Instablogs Network 2005)

2.4 Influence of environmental and control parameters

In an anaerobic digester various important parameters affect the rate of the different stages of the digestion process, i.e. pH, alkalinity, temperature and retention times. These parameters usually influence the rate of production of the major end products. This can also cause several unwanted products, production of toxic compounds and cause digester failure.

2.4.1 Effect of temperature on the anaerobic digestion process

Temperature is one of the most essential factors that affect bacteria activity within an anaerobic digester because it influences the speed of anaerobic digestion. There are three temperature ranges which anaerobic microorganisms can perform optimally: psychrophilic (below 25°C), mesophilic (25-40°C) and thermophilic (45-60°C). (Gerardi 2003, 89.)

Bacteria are sensitive to temperature changes because it affects their biological activity so an increase in temperature increases enzymatic activity while a decrease in temperature decreases enzymatic activity. Due to this factor of temperature on enzymatic activity, sludge retention time should be increased with decreasing temperature in a digester. (Gerardi 2003, 90.)

Methane forming bacteria are greatly affected by fluctuations in temperature which inhibit the production of methane. The production of methane and the destruction of volatile solids are greater at higher temperature which is faster in thermophilic digesters than in mesophilic digesters. Acetate forming bacteria and methane forming bacteria are sensitive to temperature changes, but hydrolytic bacteria are less sensitive to temperature changes. (Mari Jose 2009, 37; Gerardi 2003, 90.)

An increase in temperature in a digester has some benefits which include an increase in solubility of organic compounds, enhanced biological and chemical reaction rates, and an increase in death rate of pathogens under thermophilic conditions. It is important to maintain a stable operating temperature in a digester, since frequent fluctuations in

temperature affect the bacteria, especially the methane forming bacteria. To avoid digester failure temperature changes should be as minimal as possible, i.e. < 1°C/day for thermopiles and 2-3°C/day for mesophiles. (Gerardi 2003, 91.)

2.4.2 Effect of pH and alkalinity on anaerobic digestion process

The pH is one of the variables used to diagnose anaerobic systems which affects different chemical equilibriums and can shift the equilibrium to produce certain components which affect the digestion process. The value of the pH determines the production of biogas and its composition from a digester because if the pH is lower than 6 then the biogas produced is poor in methane. For an effective and efficiently functioning digester, a pH of 6.8-7.2 is ideally, but it is best when the pH is within 7.0-7.2. (Gerardi 2003, 99.)

The optimal working pH ranges of different groups of bacteria which are in the anaerobic digestion process are listed below:

Acid forming bacteria: pH between 7.2-7.4
Acetogenic bacteria: pH between 7.0-7.2
Methanogenic bacteria: pH between 6.5 -7.5

Alkalinity is important for pH control because it serves as a buffer which prevents a rapid change in the pH. High alkalinity concentration in a digester is an indication of digester stability while a decrease in alkalinity is an indicator of impending digester failure. A decrease in alkalinity can be caused by the inability of the methane forming bacteria to convert all the organic acids into methane which accumulates in the digester. Low alkalinity also causes the discharge of organic acids by a slug to the digester and the presence of wastes inhibits the activity of methane forming bacteria. (Gerardi 2003, 100.)

Alkalinity and pH in an anaerobic digester can be adjusted using several ways by adding of dilute water or neutralizing substances, for example milk of lime (CaO, $Ca(OH)_2$), sodium carbonate (Na_2CO_3), caustic soda solution (NaOH). The adjustment can also be done by the continuous removal of the acids, emptying and restarting the fermentation process and

stopping the substrate supply so that the methanogenic bacteria are able to degrade the acid. (Gerardi 2003, 101- 103.)

2.4.3 The impact of retention times on anaerobic digester process

Retention times in a digester are divided into two, which are solid retention time (SRT) and hydraulic retention time (HRT). Hydraulic retention time (HRT) is the time that sludge or wastewater is in an anaerobic digester. The hydraulic retention time in an anaerobic digester helps to control the conversion of volatile solids into gaseous products. High or low HRT values do not increase or decrease the rate of the conversion of volatile solids into gaseous products. (Gerardi 2003, 87.)

Solid retention time is the average time that bacteria (solids) are in an anaerobic digester. The typical solid retention time in an anaerobic digester must be longer than 12 days because at retention time of less than 10 days, significant washout of methane forming bacteria occurs. (Gerardi 2003, 87.)

High solid retention values may be achieved by increasing the digester's volume and by increasing the concentration of the bacteria (solids) in the anaerobic bio-digester. The high retention time in an anaerobic digester helps to maximize removal capacity and reduces required digester volume. It provides a buffer capacity for protection against the effect of shock loadings and toxic compounds while also permitting biological acclimation to toxic substances in wastewaters and sludge. (Gerardi 2003, 87.)

2.5 Toxics and inhibitors in an anaerobic digester

Anaerobic digestion is inhibited by the presence of toxic substances which can hinder the digestion process. This toxic substance may be created as sub-product from the metabolic activity of the micro-organisms or it might be in the feed of the digester.

The effect of toxicity in a digester can be reduced by the micro-organism either by the micro-organism repairing the damaged enzyme system in order to adjust to the toxic waste or by the micro-organism growing a relatively large population of bacteria that are capable of producing enzyme systems necessary to degrade the toxic compounds. (Gerardi 2003, 105.)

Indication of toxicity in an anaerobic digester can be rapid or slow depending on the type of toxicity and the concentration of the toxic substance. There are several ways of indicating toxicity in an anaerobic digester which can be observed by the disappearance of methane and hydrogen production. Toxicity can also be noticed by an increase in volatile acid concentration, a decrease in alkalinity and pH values in an anaerobic digester. (Gerardi 2003, 107.)

Anaerobic digesters have different and numerous wastes that cause toxicity in the digester, but the most common type of toxic compounds are ammonia (information can be found on pages 29 about ammonia toxicity), hydrogen sulfide and volatile acids. (Gerardi 2003, 105.)

2.5.1 Hydrogen sulphide as a toxic compound in an anaerobic digester

Soluble sulfur (HS^-) is needed by bacteria cell for growth nutrient but excessive concentration of hydrogen sulfide (H_2S) is toxic to the anaerobic digestion process. The methane forming bacteria is the most sensitive to hydrogen sulfide than acidogenic and acetogenic bacteria. The reduction of sulfate and the broken down of compounds like proteins and amino acids produces hydrogen sulphide. Many proteins contain sulfur in a thiol-group (-SH) which is released during the digestion of amino acids. (Gerardi 2003, 108.)

Methanogenic bacteria complete with sulfate reducing bacteria whenever there are sulfates in the system for the same substrates (acetate and hydrogen). Sulfate reducing bacteria have thermodynamic and kinetic advantages over methanogenic bacteria. The effect of this

competition will determine the amount of methane and hydrogen sulfide in the biogas produced. (Mari Jose 2009, 13.)

Hydrogen sulfide in an anaerobic digester is most toxic in the non ionic form where inhibition is helped by low pH and low temperatures. Free hydrogen sulfide can be removed by the rapid production of biogas (methane, carbon dioxide) and hydrogen in an anaerobic digester. The reduction of soluble hydrogen sulfide can be achieved by various ways which include scrubbing and re-circulating digester biogas, diluting the sulfides, precipitating the sulfide as a metal salt and separating and treating the sulfate or sulfide waste stream. (Gerardi 2003, 109.)

2.5.2 Volatile fatty acids as a toxic compound in an anaerobic digester

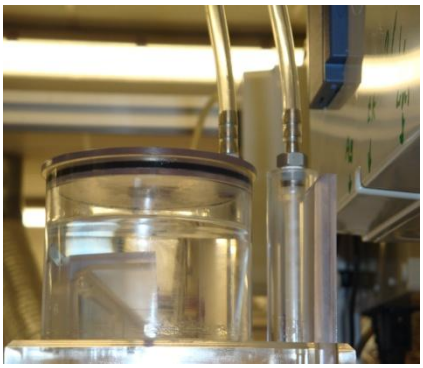
Volatile short chain acids with 1-3 carbon units for example acetate and propionate cause a reduction in concentration of alkalinity and pH at high concentration. The most toxic of short chain volatile acids is propionate, which is toxic at concentration less than 5 mg/l in an anaerobic digester. (Gerardi 2003, 114.)

Long chain volatile acids with 8-18 carbon units for example capric and oleic acid are able to dissolve in the cell walls of the bacteria where they inhibit the activity of the bacteria even at a low concentration. This is due the long-chain fatty acids having almost identical chemical composition and structure to the lipid components in the cell wall. Lauric acid is the most toxic and causes toxicity at concentration of greater than 500 g/l in an anaerobic digester. (Gerardi 2003, 115.)

Volatile fatty acids toxicity occurs between the methane forming bacteria and the acid forming bacteria. Increase in the concentration of volatile acid implies that the process is unstable and consequently the biogas production will decrease. This effect can be corrected by adding an alkaline compound. (Gerardi 2003, 115.)

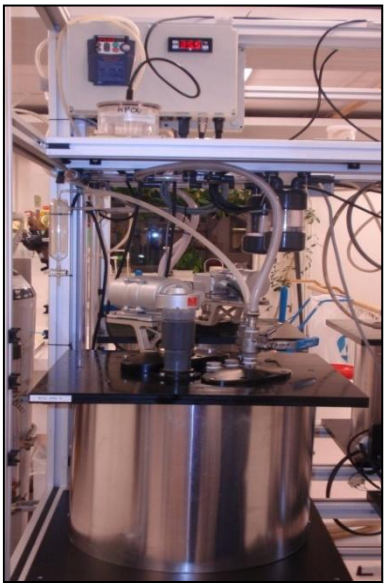
2.6 PROCES B.V Groningen bio-digesters in use

At PROCES B.V, there are 12 anaerobic mesophilic and thermophilic digesters which comprises of one 200 liters, five 20 liters and six 1 liter.



GRAPH 6. The “klapper” of a digester

The digester is fed and drained periodically. The gas production is measured by the “klapper”, a measuring apparatus. The klapper is surrounded by silicon oil and when the klapper is filled up with gas, it turns (meaning: klaps). The device has a magnet on top and during the ‘klapping’; this magnet passes a sensor in the lid. This gives an electrical pulse, which is collected and counted by the computer, running specific software, called Labview. The measuring device is calibrated, so the gas volume in a specific time frame is known.



GRAPH 7. A 20 litre digester.

The digester is fitted with a tube on the top of the lid where the feed goes in and another tube on the bottom to take out the drain. In the lid there are also two pipe connections where the produced gas is released and depending on the combination of the valves which determines the biogas outlet for example to the klapper. The digester is connected to a gas bag and is used when the digester is drained and fed so that the amount that is taken out can be replaced by the gas that is inside the gas bag. This operation is made to keep air out of the system and to maintain gas composition. The digester has a mixer, and the rounds per minute (rpm) are controlled by a frequency controller. There is also a heating system consisting of tracing connected to a temperature indicator and controller. The temperature indicator displays the temperature at all times.

GRAPH 8. Biocon 1- 6 mesophilic digesters

The 1 litre mesophilic digesters are Biocon 1- 6 respectively because they are six in number. The Biocon 1- 6 is made up of 1 liter erlenmeyer flask which contains the sludge and a magnet which is mounted on a magnetic stirrer which enables it to mix the sludge. The digesters are placed in a water bath which is connected to a heating device which maintains the temperature at 37°C. The top of the flask contains a gas stopper with a valve which connects to a calibrated gas holder where the gas production is collected. The gas holder is placed in an outside tank which will collect the water as the digester produces gas. The gas produced increases while the gas holder volume will decrease.

The gas holder contains water, and it is connected to the erlenmeyer flask so that the gas produced, bubbles through the water into the gas holder .The gas holder cross cut is 166 cm^2. The water displaced by the gas produced can be measured directly from the gas

holder by measuring the differences in the height of the water column. An empty gas-washing bottle which is connected to each erlenmeyer collects foam if there is any foam produced. A dropping funnel is connected to the outside tank which ensures that the water level in the tank is constant.

The standard operating procedure for the feeding, draining and data processing of a bio-digester can be found in the appendices 1-7.

3 COMPARISON OF THE THERMOPHILIC AND MESOPHILIC DIGESTION OF CORN

3.1 Introduction to corn digestion in an anaerobic digester

Corn stover is a plant biomass where the carbohydrate polymers (cellulose and hemicellulose) are tightly bounded to the lignin by hydrogen and covalent bonds. This complex structure provides a primary protective barrier that prevents cell destruction by chemical or biological methods, leading to lower digestion rate and biogas yield. This is the main reason why corn stover is usually not used alone as sole feedstock for biogas production. (Henk 2009, 44.)

Corn stover is compost of mainly of lignin, cellulose, and hemicellulose which account for 78.3% of the total dry matter of corn stover and are the main carbon sources for anaerobic micro-organisms or bacteria. The cellulose and hemicellulose are prevented by lignin from reacting with water which causes swelling. Before corn stover can be used as a raw material, the lignin covalent bond with the cellulose and hemicellulose must be removed in order to render the cellulose and hemicellulose fractions accessible for fermentation. (Fakirov & Bhattacharyya 2007, 618; Henk & Banning 2006, 45.)

Lignin is found in the cell wall between the cellulose, hemicellulose and the pectin components. It is due to the covalent cross linking between the hemicellulose and the cellulose via ester and ether linkages that confers mechanical strength to the cell wall and by extension to the plant as a whole. (Henk 2009, 45.)

The lignin is the non-carbohydrate constituent of wood, which binds to cellulose fibers to harden and strengthen the cell walls of plants and with the hemicellulose, to help in binding the cells together and direct water flow. It is one of the most abundant natural polymers, constitutes one-fourth to one-third of the total dry weight of trees where it is

concentrated in the cell walls making it the main constituent of the wood tissue. (McCrady 1991.)

Lignification is a process whereby the cellulose walls of the wood become impregnated with lignin, which greatly increases the strength and hardness of the cell and also gives the necessary rigidity to the tree. It is essential to woody plants in order that they stand erect. (Henk 2009, 45.)

Cellulose is an odorless, tasteless organic compound with the formula $(C_6H_{10}O_5)n$. It is made of repeat units of the monomer glucose. Due to the fact that cellulose is built out of a sugar monomer, it is called a polysaccharide. The mechanical strength and chemical stability of cellulose occurs as a result of the ability of cellulose chains to bond with hydrogen resulting in the formation of fibres (micro fibrils). This complex carbohydrate is the main constituent of the cell wall in most plants. It can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature. Cellulose has many uses as an anti-cake agent, emulsifier, stabilizer, dispersing agent, thickener, and gelling agent and its most important use is the ability to hold onto water. Cellulose is an un-branched or linear polysaccharide polymer which is chiral, hydrophilic, insoluble in water and most organic solvents. It is the most common organic on earth making up to 33% of all plant matter. Cellulose molecules bind strongly to each other. They are broken down by a process called cellulolysis where the cellulose is broken down into smaller polysaccharides called cellodextrins or into glucose units completely. (Henk 2009, 47; Henk & Banning 2006, 44.)

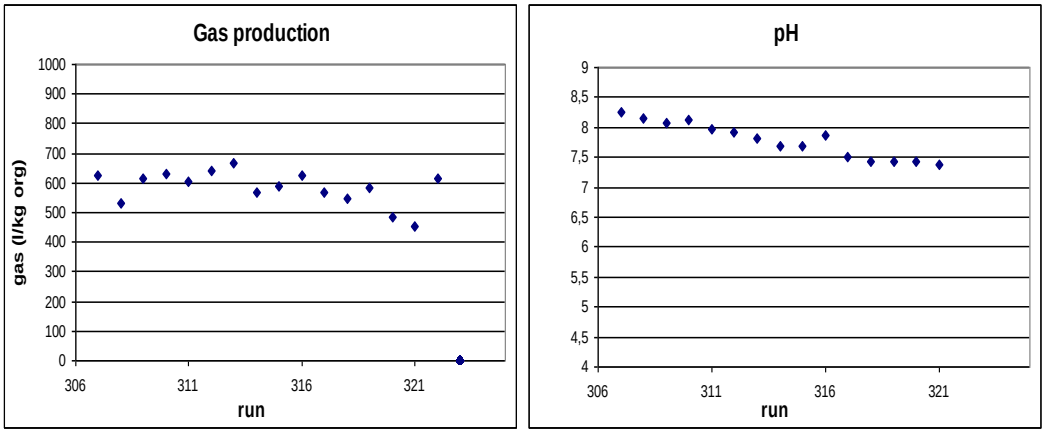
Hemicellulose is a branched polymer which can contain different sugar monomers present in almost all plant cell walls along with cellulose. The branched chain of hemicellulose molecule binds to other carbohydrates (e.g. pectins) together with cellulose micro fibrils to form a network of cross-linking fibres. This polysaccharide with less than 150 polymer units of various sugars has a random, amorphous structure with little strength and it is easily hydrolyzed by dilute acid, base or myriad hemicellulose enzymes. Hemicellulose contains many different sugar monomers but xylose is always present in the largest

amount, followed by mannose which present as a polymer or in combination with D-glucose as glucomann. Hemicellulose contains mainly the D-pentose sugars, and at times small amounts of L-sugars which are used in pulp industry to provide tensile and strength. (Hocking 1998, 460.)

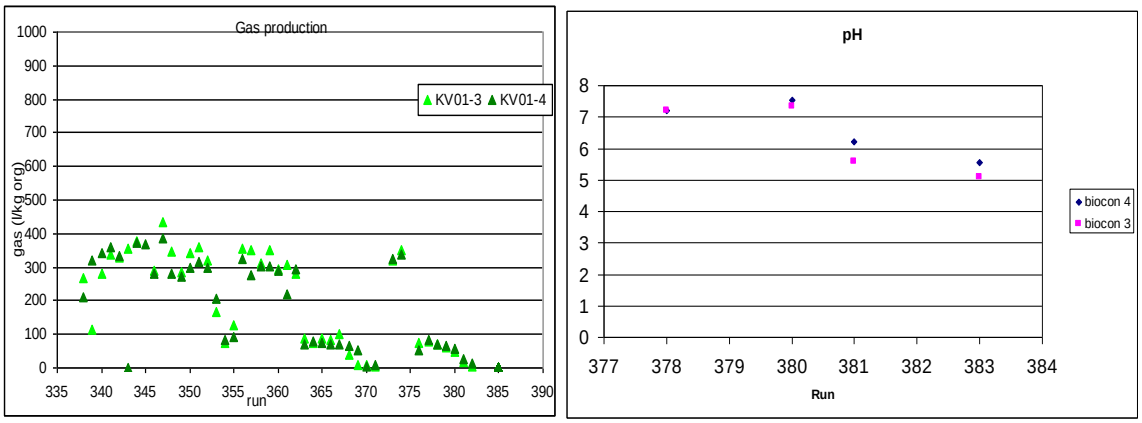
This analysis looks at the digestion of corn stover without pre-treatment in thermophilic and mesophilic digesters so as to have more information and possibly find better ways of digesting corn stover. The mesophilic digesters used in this analysis consists of two 1 liter digesters which are called Biocon 3 and 4 respectively while the thermophilic digester used is the 20 liters digester called the KV 26.2. This analysis will compare the gas production, lignin content after digestion, pH values and volatile fatty acids content in both thermophilic and mesophilic digesters respectively.

3.2 Gas production and pH after corn digestion

The graph below shows the gas production from the digesters measured at 2 days interval per week and at 3 days interval during the weekend.



GRAPH 9. Corn stover in a thermophilic digester



GRAPH 10. Corn stover in a mesophilic digester

The graph 9 illustrates the gas production and pH graph for the thermophilic digester i.e. KV 26.2 and the run is for 17 runs. From the graph above, the gas production was found to never drop below 400 l/kg organic and the highest gas production was close to 700 l/kg organic. The pH was decreasing from the range of 8.5 - 7.8 and at 7.5 it's becoming stable.

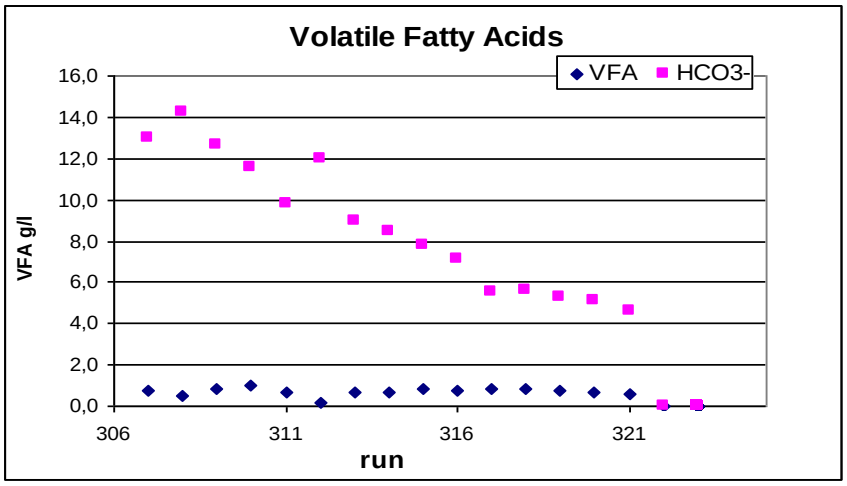
The graph 10 displays the gas production for the Biocon 3 and 4 digesters which was measured for 35 runs while the pH measurement was measured at intervals. The gas production highest volume was around 400 l/kg organic and the lowest gas production can be seen as zero at run 370 and 382 respectively, because at this point there was digester failure. The pH value was found not to be stable and it was below the optimal operation pH of mesophilic bacteria.

It can be seen that in the thermophilic digester the pH was stable at a pH of 7.3, while in the mesophilic digester there was no stability in pH. This instability in pH means that the mesophilic digester is more liable to stop working because the optimal working pH value in a digester is in the range of 6.8 - 7.2 while the thermophilic digester will be performing optimally.

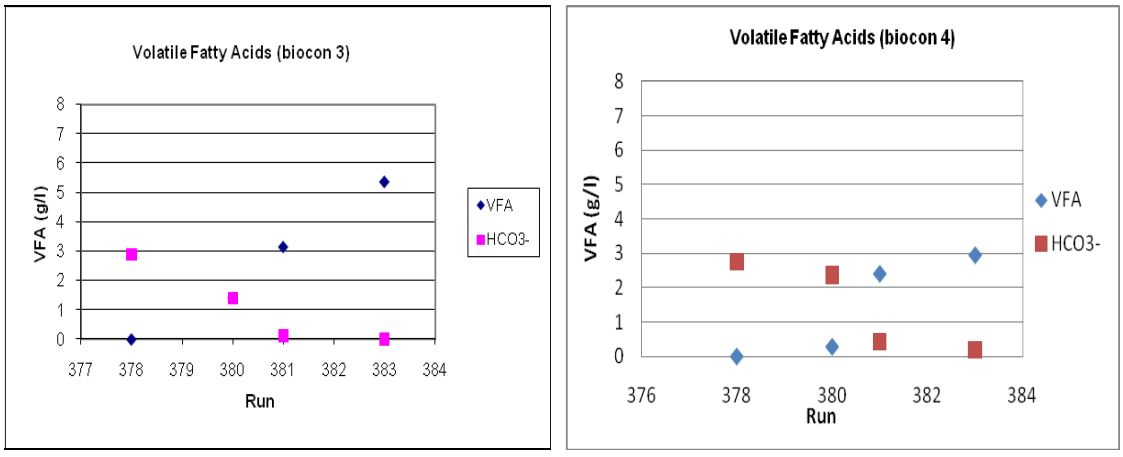
The gas production in the thermophilic digester was approximately 700 l/kg organic compared to around 450 l/kg of organic from the mesophilic. The gas production from the thermophilic digester is more than the gas production from the mesophilic digester.

3.3 Volatile fatty acids content after corn digestion

The volatile fatty was measured in comparison with the bicarbonate (HCO_3^-). The volatile fatty acids and the bicarbonate were interrelated because the differences between the amount of volatile fatty acid and bicarbonate must be wide; the wider the difference between the two compounds, the more stable the digester.



GRAPH 11. Volatile fatty acids in a thermophilic digester



GRAPH 12. Volatile fatty acids in a mesophilic digester

The production of volatile fatty acids and bicarbonate both occur during the digestion of carbohydrate, proteins and fats. The bicarbonate normally occurs as a result of ammonia combining with carbon dioxide in the digester.

Volatile fatty acid toxicity occurs between the methane forming bacteria and the acid forming bacteria. Increase in the concentration of volatile acid implies that the process is unstable and consequently the biogas production will decrease.

From Graph 11 illustrating the thermophilic volatile fatty acids in a thermophilic digester, the volatile fatty acids and the bicarbonate from the thermophilic digester show a large difference at the beginning. After some runs it starts to decrease but since the margin of the difference is still acceptable, which implies that the system is stable.

Graph 12 illustrating the mesophilic volatile fatty acids in a mesophilic digester show at the beginning there is a wide margin of differences between volatile fatty acids and bicarbonate in both Biocon 3 and 4. At run no. 380, the difference between the VFA and bicarbonate is zero in the Biocon 3, which implies that the system has failed (the digester has stopped working).

In the Biocon 4, there must have been a point where the VFA and the bicarbonate margin is zero. Looking at the graph at run no. 381, the VFA value has gone down while the bicarbonate value has increase. This implies that there was system failure at run no. 380 and run no. 381.

The thermophilic digester has a wider VFA to bicarbonate margin difference and the system is very unlikely to fail or stop working while in the mesophilic digester the margin difference is zero and there had been system failure. The thermophilic digester is more stable compared to the mesophilic digester.

3.4 Lignin content analysis before and after corn digestion

Before corn stover can be used as a raw material, the lignin which is covalent cross linked with the hemicellulose and the cellulose via ester and ether linkages must be removed. This analysis will take a look at the amount of lignin before digestion and the amount after digestion in thermophilic digester. The mesophilic digester lignin content could not be analyzed due to time constrain. (McCrady 1991.)

The procedure for lignin measurement involves the material being dried to a moisture content of less than 10%. The material was grounded and sieved into a fine fraction and coarser ones. The fine fraction was used to measure the moisture and ash content. The extractable in the material (fine fraction) was determined by extracting with water and alcohol. The material was hydrolyzed with 74% sulfuric acid for one hour at 30ºC after which it was filtered to determine insoluble lignin. The material was dried and weighed then calcine the material for ash determination. Dry the filtrate to determine the weight of the other components and determine the protein content of the sample. (PROCES 2009, 10.)

TABLE 1. Data from lignin analysis

Material analyzed	solids wt%	ashes wt%	extractives wt%	proteins wt%	lignin wt%	cellulose wt%
Heartleaves corn	91.6	4.3	15.21	6.68	10.2	67.91
Heartleaves corn after digestion	93.27	6.23	10	7.27	24.7	58.03

The lignin measurement of the KV26.2 shows an increase in lignin content after digestion. Based on the organic material, the lignin, cellulose and hemicellulose are in a ratio, so if the lignin content increases then cellulose and hemicellulose should decrease. The lignin from the Biocon 3 and 4 should be identical to the results from KV26.2 because the materials after sieving are similar.

The Biocon 3 and 4 have gone through digester failure twice while the KV26.1 is performing optimally may be due to the fact that the Biocon 3 and 4, are being drained from the top while the KV26.1 is being drained from the bottom. The draining of Biocon 3 and 4 from the top causes the accumulation of corn and lignin in the digester sludge. The draining of the KV26.1 from the bottom reduces the accumulation of corn and also reduces the amount of lignin in the sludge of the digester. It is a known fact that bacteria are very sensitive to lignin in the digester sludge.

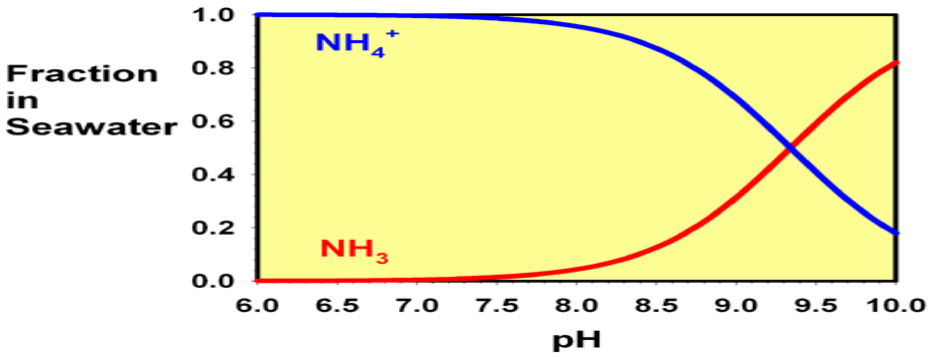
4 AMMONIA REMOVAL FROM A MESOPHILIC DIGESTER

4.1 Ammonia toxicity in an anaerobic digester

Ammonia is a toxic compound and at levels in excess of 1500 mg/l causes digester failure (Gerardi 2003, 108). During the anaerobic digestion process of organic nitrogen compounds such as amino acids and proteins, nitrogen is reduced into ammonium ions (NH_4^+) or ammonical-nitrogen (NH_4^+-N). The reduced nitrogen can exist in two forms, ammonium ion (NH_4^+) and free ammonia (NH_3). Free ammonia is toxic while ammonium ions are an important nutrient for bacteria growth although an excessive concentration can limit growth. (Gerardi 2003, 107.)

The two forms of reduced ammonia amount are determined by the pH of the anaerobic digester. The two forms are in relatively equal amounts at pH of 9.3. With increasing pH, the amount of free ammonia increases while the amount of ammonium ions decreases vice versa. At pH of 7, free ammonia is approximately 0.5% of the total reduced nitrogen (Gerardi 2003, 107). This is illustrated by the chemical equation and graph 13 showing the ammonia to ammonium ratio as a function of pH respectively.

$$NH_4^+ \leftrightarrow NH_3 + H^+$$



GRAPH 13. The ammonia to ammonium ratio as a function of pH (Reefkeeping magazine 2008.)

In addition to pH, the quantity of free ammonium ion depends on the concentration of the substrate, the digester temperature and the carbon to nitrogen ratio. The effect of ammonia and ammonium ions on an anaerobic digester process is shown in Table 2.

TABLE 2. The effect of ammonia and ammonium ions on an anaerobic digester process. (Gerardi 2003, 107.)

Ammonium and dissolved ammonia	Effect
50 – 200 mg/l	beneficial
200 – 1000 mg/l	no adverse effect
1500 – 3000 mg/l	inhibitory at pH > 7

As to selecting a counter ion of the formed ammonium there are various possibilities: acetate, propionate, lactate, carbonate, bicarbonate, chloride, sulphate and phosphate.
Based on the fact that during digestion a high concentration of carbon dioxide is formed, the main counter ion is carbonate. Ammonium carbonate is extremely soluble in water (320 g/l), so there is often a high concentration of ammonium and carbonate and far less ammonium carbonate as a solid. There are several ways of reducing the ammonium content in an anaerobic digester which include reducing the protein content of the digester feed, stripping of ammonia and formation of struvite. (Henk 2009, 44; Mari Jose 2009, 34.)

On a standard feed the protein content is around 25%. In the case of a digester of high content on protein on the feed, the percentage can be reduced by diluting using corn, sugar, meaning ingredients with high content on carbohydrates. (Mari Jose 2009, 61.)

The formation of struvite involves using magnesium phosphate to precipitate the ammonium from the digester. This precipitation contain compound of magnesium ammonium phosphate hex hydrate ($MgNH_4PO_4 \cdot 6H_2O$), commonly called struvite. Struvite is composed of equimolecular concentrations of magnesium (Mg^{+2}), ammonium (NH_4^+), and phosphate (PO_4^{-3}). (Mari Jose 2009, 61.)

4.2 Air stripping methods of ammonnia removal

Stripping is a physicochemical process wherein a liquid mixture is contacted with a gas to remove a volatile component by mass transfer from the liquid to the gas phase (Henley and Seader, 1998.). Air stripping is a good method for the removal and recovery of valuable ammonia from wastewater and sludge.

There are two methods that may be employed for the removal of the ammonia from the sludge by means of air stripping. The first involves the rising of the pH to a figure of approximately 12. This is referred as a "pH driven". The second involves increasing the temperature of the sludge to approximately 65°C to 70°C. This is referred as "thermally driven". (Etxeberria 2009, 34.)

The ammonia removal from an anaerobic digester through pH driven air stripping is achieved by adjusting the pH. This is normally achieved by adding lime or caustic soda. The addition of lime or caustic soda not only increases the pH but causes the precipitation of certain salts and larger organic molecules, thus decreasing residual chemical oxygen demand (COD). (Etxeberria 2009, 35.)

The thermally driven air stripping method of ammonia removal is achieved by raising the temperature of the system. Inside the digester there are many free molecules of NH_4^+, CO_3^{-2} and also the molecules $(NH_4)_2CO_3$. The decomposition temperature of ammonium carbonate is 58°C, meaning at temperatures above 58°C ammonium carbonate will decompose to NH_3 (g) + CO_2 (g). This process involves raising the temperature of a solution containing ammonium carbonate in water or sludge to approximately 65°C to 70°C, so that the ammonium carbonate will decompose and the formed NH_3 (g) is taken out immediately. (Etxeberria 2009, 35.)

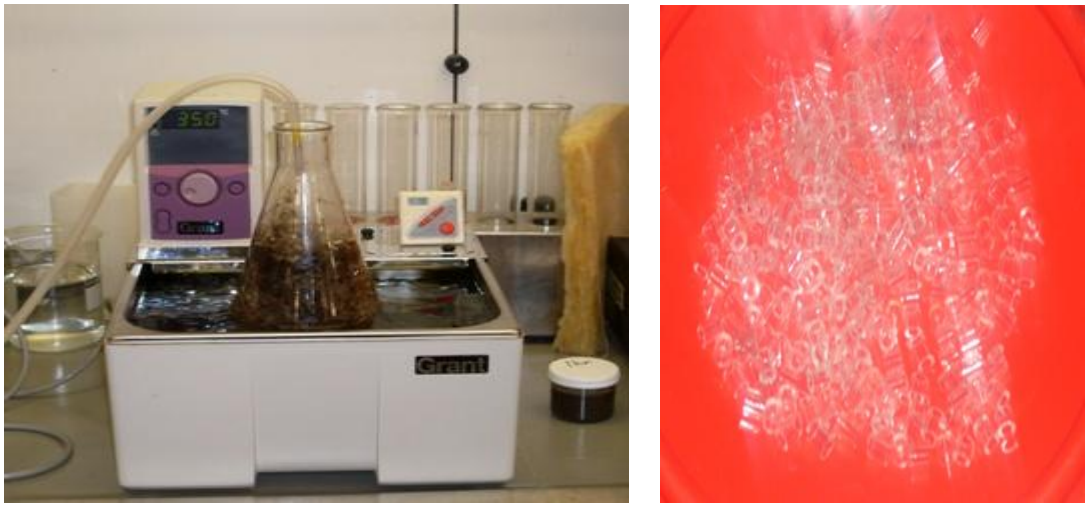
Air stripping is usually operated in a packed tower to get high efficiency due to its large mass transfer area. Packed towers in air stripping usually causes scaling and fouling in the packing due to the reactions between CO_2 in air and some metal ions in sludge. For a low volatile compound such as ammonia with a small Henry's law constant, the stripping process is effective only if the stripping condition is well optimized. (Xuejun, Fuping, Qinghua, Tiantao & Jinxin 2009, 985.)

The stripping efficiency and the mass transfer coefficient increase swiftly at a critical value for the air flow rate. For an effective air stripping of ammonia, temperature greater 25°C and an air flow rate greater than 1.4 l/s should be used. (Xuejun et al 2009.)

4.3 Air stripping experiments of a mesophilic digester

The stripping experiment is done with an erlenmeyer flask which contain sludge and small glass fragments which are filled up in the erlenmeyer flask. A small tube is placed in the middle of the erlenmeyer which is connected to a pipe which is then connected to an air pump. The setup of the erlenmeyer is then placed inside a stirred thermostatic water bath which contains a heating rod to raise the temperature of the water bath. There is a temperature sensor connected to the heating rod where the temperature is displayed and can also be adjusted by using a control knob.

The small glass fragments are used in this experiment to increase the surface contact between the air and the sludge. The idea is to use the normal mesophilic digester's temperature (35°C) and bubble air through the sludge which will evaporate ammonia and carbon dioxide.



GRAPH 14. Left: the experiment apparatus setup. Right: glass filaments

The stripping process is based on the equilibrium between the gas and liquid phase and solubility of the solute determines the liquid-to-gas ratio that is why a low solubility of the solute is desired. (Xuejun et al 2009, 985.)

Based on the fact that during digestion a lot of carbon dioxide and ammonium are formed, a counter ion is produced such as acetate, lactate, carbonate, bicarbonate, phosphate, etc. one of the major counter ion is carbonate. Since ammonium carbonate is extremely soluble in water (320 g/l), so there is a lot of ammonium carbonate in liquid than as a solid. (Henk 2009, 33.)

The amount of ammonia and ammonium in a solution is pH dependant which can is showed in graph 13 in the ammonia toxicity section. The air which is applied into the Erlenmeyer causes the ammonia and carbon dioxide to be evaporated based on Henry's law but the equilibrium will shift so as to balance the ammonia to ammonium ratio in the liquid or sludge according to Le Châtelier's principle. (Henk 2009, 44; Xuejun et al 2009, 986.)

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

This equilibrium balance causes the ammonium carbonate or ammonium bicarbonate produced to dissociate thereby producing more carbon dioxide and water. In aqueous solution like in the digester, bicarbonate exists in equilibrium with the carbon dioxide and water produced which depends on the pK_a and the pK_{a1} values respectively. (Henk 2009, 45.)

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$ $\quad K_a = 5.61 \cdot 10^{-11}$; $pK_{a1} = 10.25$ at 25ºC

$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ $\quad K_{a1} = 4.30 \cdot 10^{-7}$; $pK_a = 6.36$ at 25ºC

The final equation is illustrated below which is the dissociation of ammonium carbonate or ammonium bicarbonate.

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O$$

$$NH_4HCO_3 \rightarrow NH_3 + H_2O + CO_2$$

The dependency of pH determines the concentration of ammonia to ammonium in a solution. The pK_a and pK_{a1} value determines the bicarbonate to carbon dioxide and water formation. This implies that at any pH and at different values of pK_a and pK_{a1}, the composition of ammonia, ammonium, bicarbonate, carbon dioxide and water varies respectively. (Henk 2009, 45.)

Air stripping method of ammonia removal from an anaerobic digester was started by first performing trial experiments with ammonium carbonate. The ammonium carbonate used was prepared in 1 litre of water.

The calculation for the preparation of the solution of ammonium carbonate is given below:
The molar mass of ammonium carbonate $(NH_4)_2CO_3 = (14 \cdot 2) + (4(1) \cdot 2) + 12 + (16 \cdot 3)$

$= 96$ g/mol

The mole molar mass of ammonia $(NH_3) = (2 \cdot 14) + (2 \cdot 3(1))$

$= 34$ g/mol

Equation of reaction: $(NH_4)_2CO_3 \rightarrow 2NH_3 + H_2O + CO_2$

To get the number of mole fraction of ammonia in the ammonium carbonate

The number of moles of solute ÷ the total number of moles in a solution

34 g/mol ÷ 96 g/mol = 0.3542 mol% of ammonia

To get the actual amount of ammonia in ammonium carbonate of 12 g

12 g of ammonium carbonate · 0.3542 mol% of ammonia

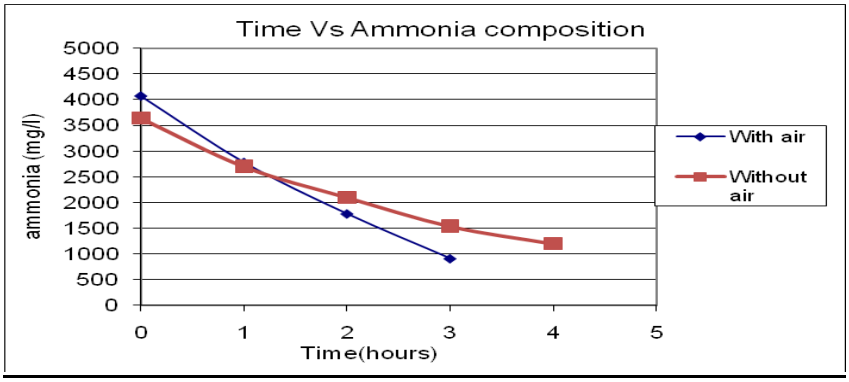
= 4.25 g of ammonia in 12 g of ammonium carbonate in 1l of water

Unfortunately this ammonium carbonate contains also ammonium bicarbonate and ammonium carbamate:

$NH_4HCO_3 \rightarrow NH_3 + H_2O + CO_2$

$NH_2OCONH_4 \rightarrow 2NH_3 + CO_2$

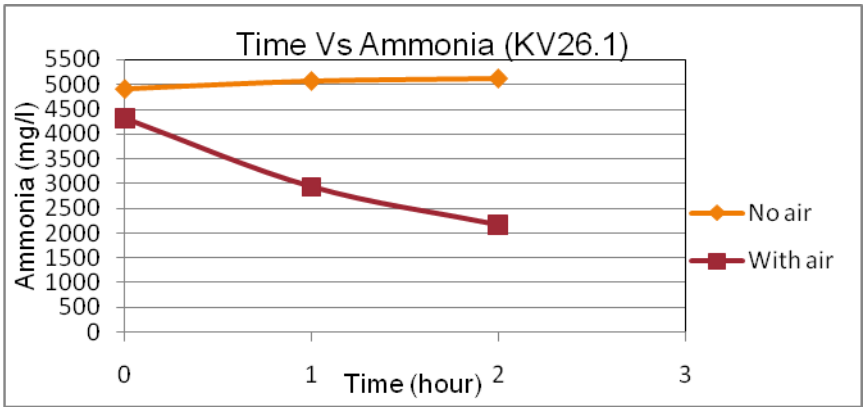
This is why the ammonia measured is lower than the theoretical value of ammonia (Henk 2009, 41). The measured ammonia was 4070 mg/l used for the reaction with air and 3640 mg/l was measured for the reaction without air.



GRAPH 15. Trials with ammonium carbonate

As can be seen from Graph 15 illustrating trials with ammonium carbonate, the reaction with air after 3 hrs reduce ammonia from 4070 mg/l to 910 mg/l. The experiment done without air shows that ammonia was reduced from 3640 mg/l to 1200 mg/l in 4 hours.

The air stripping method of ammonia removal in an anaerobic digester was analyzed with the drain of the KV26.1digester. The KV 26.1 is a 20 litres mesophilic digester that is fed with pre-treated chicken manure. The target was to see if it is possible to reduce of ammonia in the drain by using the air stripping method.

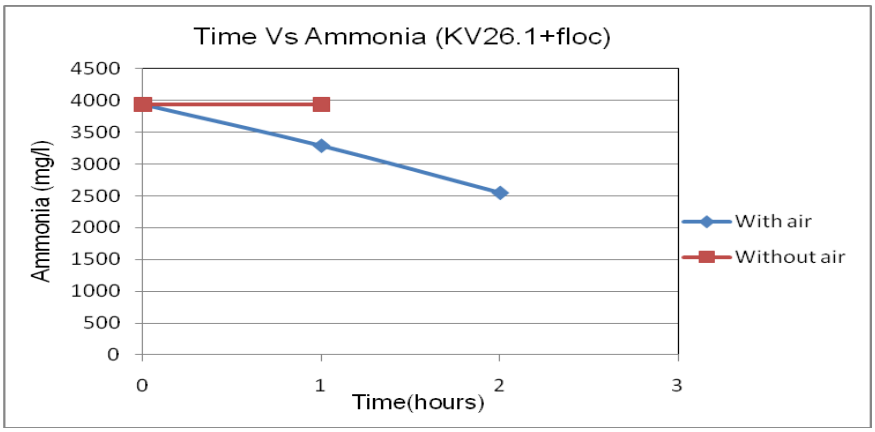


GRAPH 16.Experiment with drain of KV26.1

From the graph 16 illustrating the experiment with drain of KV26.1, it can be seen that the ammonia content in the drain without air and at a temperature of 35°C did not reduce after

2 hours. The experiment with air of the drain and at a temperature of 35°C showed a 50% reduction of the ammonia content started with.

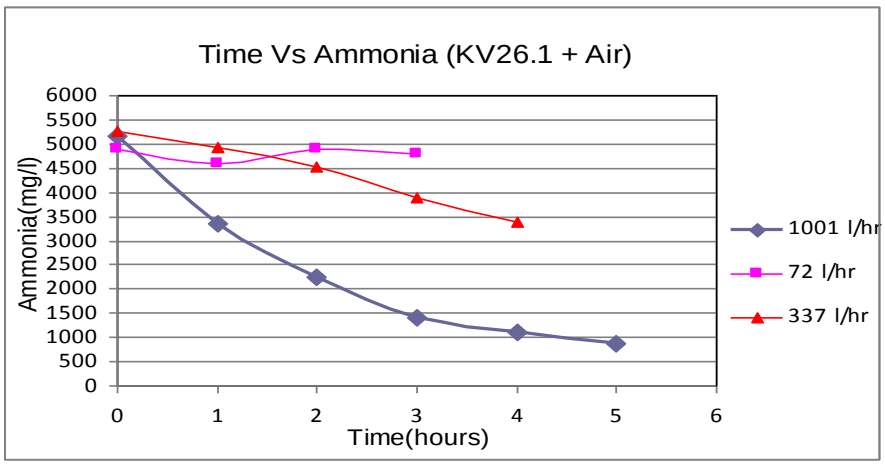
The drain of the KV 26.1 digester was used for this experiment of air stripping of ammonia from an anaerobic digester. The drain was flocculated and the clear spill was treated with the air stripping method to reduce the ammonia content.



GRAPH 17. Flocculated drain of KV26.1

The ammonia content in the flocculated drain without air stripping, but at a temperature of 35°C did not reduce the ammonia content after 1 hour. The ammonia content in the flocculated drain with air stripping from Graph 17 shows a reduction from 4000 mg/l to 2550 mg/l in 2 hours. This reduction in ammonia is not as fast if compared to the drain without flocculants which is about 50% reduction in 2 hours.

This experiment was done with the drain of KV 26.1 digester without flocculation or addition of any substance using air stripping method while the amount of air is varied so as to see the effect of air volume on the ammonia reduction.



GRAPH 18. Experiment of KV26.1 with varying air volume

Graph 18 illustrating the ammonia content removal while varying the volume of air used indicates that the amount of air used influences the rate of ammonia removal. The fastest rate of ammonia removal was found using 1001 l/hr of air and in 5 hours the ammonia level achieved was 860 mg/l. There was no reduction in ammonia content with an air volume of 72 l/hr after 3 hours.

In some of the trials there was a formation of foam that could pass to the washing bottle if it was not stopped in time. To solve this problem anti-foaming agent was added, but it needs to be taken into account that some anti-foaming only function with some drains, meaning they are specific.

5 CONCLUSIONS

This study focuses on two parameters which are the digestion of corn and ammonia removal after digestion from a bio-digester which was done in PROCES laboratory. The digestion of corn was done with mesophilic and thermophilic digesters while the ammonia removal was done with the mesophilic digesters only.

The digestion of corn was analyzed with a 20 l thermophilic digester and 2 one litre mesophilic digesters. The analyses were done based on the pH values, gas production, volatile fatty acids and lignin contents after digestion of the corn with 1-2 months of data collection and processing.

The ammonia removal was done with the air stripping method after the digestion of pre-treated chicken manure from the mesophilic digester. The air stripping experiment was started with ammonium carbonate dissolved in one litre of water to check the effectiveness of the process. The digested drain from KV26.1was treated with the air stripping method to see the effect on the ammonia content. The flocculated drain after digestion from the KV26.1 was used to analyze the reduction of ammonia using the air stripping method. The variation of the air volume in the air stripping of ammonia experiment was also undertaken where the digested drain was used.

The analysis of parameters such as pH and gas production, lignin content and volatile fatty acid from thermophilic and mesophilic digestion of corn had shown that the thermophilic digester was performing better. The stability of the thermophilic digester in terms of volatile fatty acids, gas production and pH compared to the instability of the mesophilic digester. Although the lignin from both digesters was at the same level, but the mesophilic digester had experience system failure twice.

The pH stability in the thermophilic digester thus indicated better performance of the bacteria inside the digester while the instability in pH of the mesophilic digester indicated that the digester was prone to system failure. The gas production from the thermophilic digester is more than the gas production from the mesophilic digester.

The thermophilic digester had a wider VFA to bicarbonate margin difference and the system was very unlikely to fail or stop working while in the mesophilic digester the margin difference was zero that had caused system failure.

The KV26.1 was performing better than the Biocon 3 and 4 which can be explained by the fact that the Biocon 3 and 4 respectively had gone through system failure twice. The KV26.2 did not experience any system failure and from indications looks very stable.

The thermpohilic digester had better capacity and ability to digest corn stover than the mesophilic digester.

Air stripping of ammonia was done with air, which under standard conditions should have been other gases such as nitrogen, biogas but due to time constraints and lack of adequate planning other gases could not be used.

From the experiment concluded, it has been seen that air stripping of ammonia is very effective and the fact that the drain can be used directly without having to flocculate makes it more cost effective. The reduction of ammonia was much faster in1000 l/hr than in 337 l/hr. The pH values remain constant during and after air stripping of ammonia which indicates that the bacteria will be able to survive after the air stripping method.

The various experiments that were done with the digestion of corn were time consuming because of the amount of months it took to collate the various data. The digestion failure of the Biocon 3 and 4 also make the data collate slow. Various factors made the analysis of lignin very slow because the after digestion analysis was postponed several times due to summer heat, holidays which make the analysis of the mesophilic digester impossible to do.

This research was done independently which really helps to boost my confidence and my ability to conduct research. It also gave me a chance to analyze the digestion process and think like a process engineer should, because a process engineer must have a good understanding of the process and the ability to reduce complications in the system while making sure that the system is running optimally.

This project gave me the opportunity to learn how food waste, plant waste, animal waste even human waste can be put to beneficial use to generate biogas, which can be used to produce electricity, or used for cooking. The exposure to various samples collection, several analysis methods and data recording procedures have enhance my studies in the area of analysis, experimental research and above all to the field of science which will be useful for me in future challenges.

More research is needed in the comparism of the mesophilic and thermophilic digestion of corn. The gas production and pH, the rate of digestion of lignin and volatile fatty acids analysis must be done with digesters of equal volume so as to get a better comparison data.

Further research is required to understand the various parameters that affect air stripping of ammonia. The optimal air volume to be used in ammonia stripping should also be considered in future research.

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Standard operating procedure for the feeding and draining of bio-digesters.

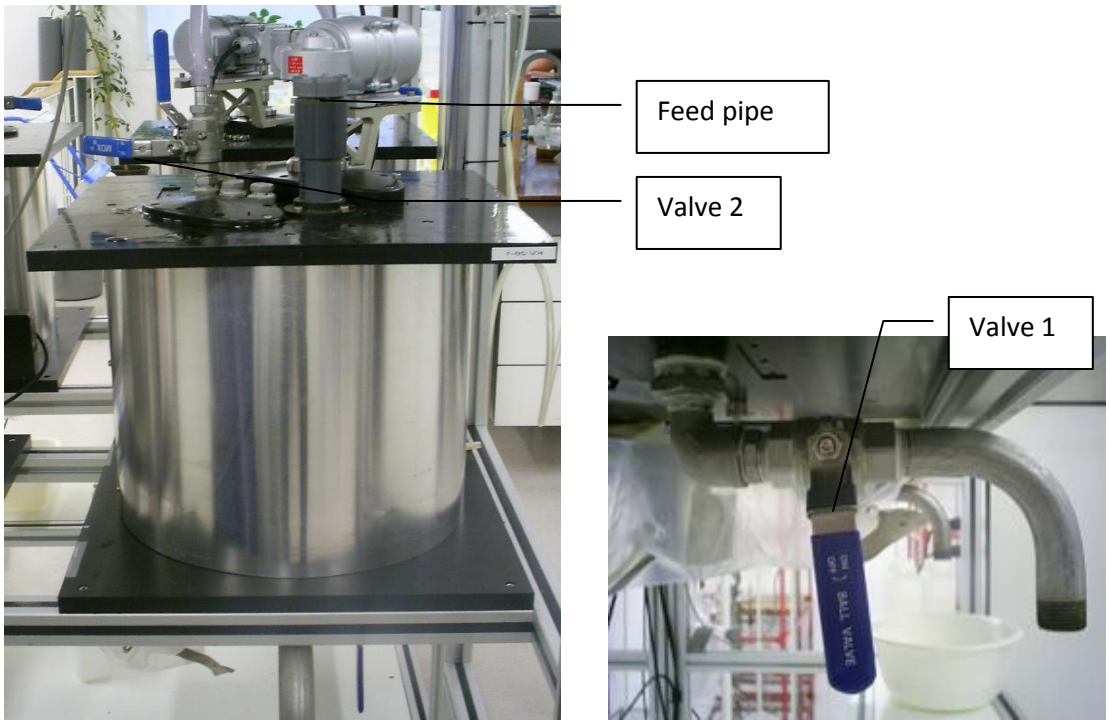
The main idea behind this procedure is that the digesters are operated in such a way that it resembles a continuous fed digester with a constant volume, on average, as much as possible. A run is one cycle of feeding and draining. It is started with the addition of the feed and ends with the removal of the spill from the digester.

The operating procedure for feeding a digester is started by opening the data sheet of the digester to be fed after which the number of days the coming run is going to last is filled in the correct field. The number of days the run *after the coming run* is going to last is fill in the correct field and if necessary, update the feed batch drop down list with the purple button. Print the run list using the blue button. (If desired, fill in all known run data first or do it later by hand).

Prepare the feed according to the run list and write down the exact amount of feed prepared on the run list. Stop the run on the data logger and drain the digester by opening the valve 2 on top of the digester. Close the exit gas valve of the back flush system and drain by means of the valve 1 at the bottom of the digester. Fill in the exact amount of drain on the run list.

Prepare a sample, put the digester name, run number and date on the sample pot. Open the feed pipe on top of the digester and feed the digester making sure that valve 2 is (still) open (drain).Open the feed pipe and put a funnel in the feed pipe and pour the feed in. Flush with the calculated amount of water and add excess of spill from the drain.

Close the feed pipe and the gas back flush valve on top of the digester. Open the exit gas valve of the gas back flush system and fill in the new run number in the datalogger. Start the run on the datalogger; write down the start time on the run list. Clean all used equipment, including the digester frame, digester and all used materials. Put all run list data in the PIMS data base. This can be done at once if all data is known or in multiple sessions. The drained volume must be written down on the run list of the *ended run.* (Miel 2008, 10)



Graph 19:Left: photograph of a KV26 series digester. Right: detail: 1.5" drain valve and pipe.

The digesters are operated in a semi-continuous way. During a run, the feed is transferred to spill (or digestate). It is unknown how long it takes. Therefore, it is assumed that $0 < t_{Rransfer} < t_{Run}$.

From this assumption follows that at the start of a certain run, the digester volume is $V_{pre\ feeding}$ and at the end of the run the digester volume is $V_{pre\ feeding} + V_{feed,}$ V_{feed} being transferred to digestate.

The *average digester volume* is then $V_{average} = (2V_{pre\ feeding} + V_{feed})/2$.

The drain volume is calculated by using this Formula: $V\ drain = V_{run,\ n-1} - V_{pre\ run,\ n}$

During feeding and draining the level of the digester is kept on an average of 20 liters. If the feed for one day is 0.7 liter, the digester must be at a level of 20- (0.7/2) = 19.65 liter *before* the feed is added.

After the feed is added the level will be (19.65 + 0.7) = 20.35 liter.

The amount that needs to be drained depends on the amount of feed of the next run. If the digester has been fed for one day, and will be fed again for one day, 0.7 liters is drained. The digester is then back at 19.65 liter. After feeding the next run the level will be 20.35 liter again.

In case of the digester being fed for two days, the *level* has to go down to 19,3ltr. So an extra 0.35 liter has to be drained, giving a total of (0.7 + 0.35) = 1.05 liter.

After the feeding the level in the digester will be (19.3 + 1.4) = 20.7 liter.

In the case that the new run is also for two days, 1.4 liter can be drained and added again.

When again the feed is for one day, (20.7 – 19.65) = 1.05 liter has to drained.

In the weekend three days feed has to be added (= 2.1 liter). The digester must be drained to a level of 18.95 liter. With the feed the level during the run will be (18.95 + 2.1) = 21.05 liter.

After the weekend one needs to drain (21.05 – 19.65) = 1.4 liter in the case of a one day run.

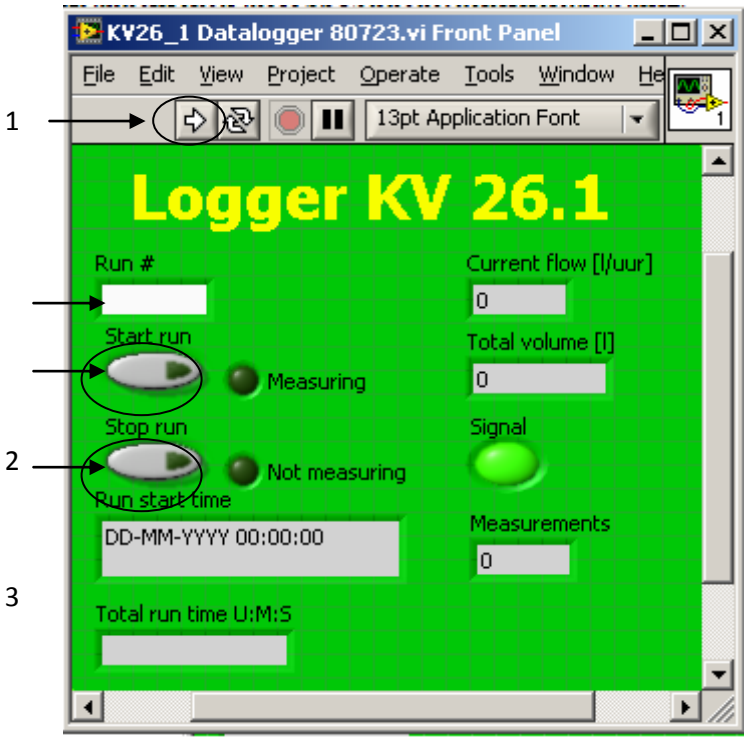
In the case of a two days run (21.05 – 19.3) = 1.75 liter.

The weight of the spill is equal to the weight of the feed, minus the weight of the produced biogas. By adding and removing the same amounts, the digester will stay at a constant level prior to the start of the run. (Miel 2008, 23)

The PIMMS data loggers system is a programme in LabView, a graphical programming interface. Instead of using for example visual basic, the programmer ‘draws’ a program using icons and lines.

The data loggers are placed on the lab-computer, which is connected to the Lab-Jack. The labjack receives signals from the tumbler gas measurements. The gas is bubbling in to the ‘hollow dice’ and makes it flip over to the other side and back. Through a magnet, a switch is activated and a signal is send to the Lab-Jack.

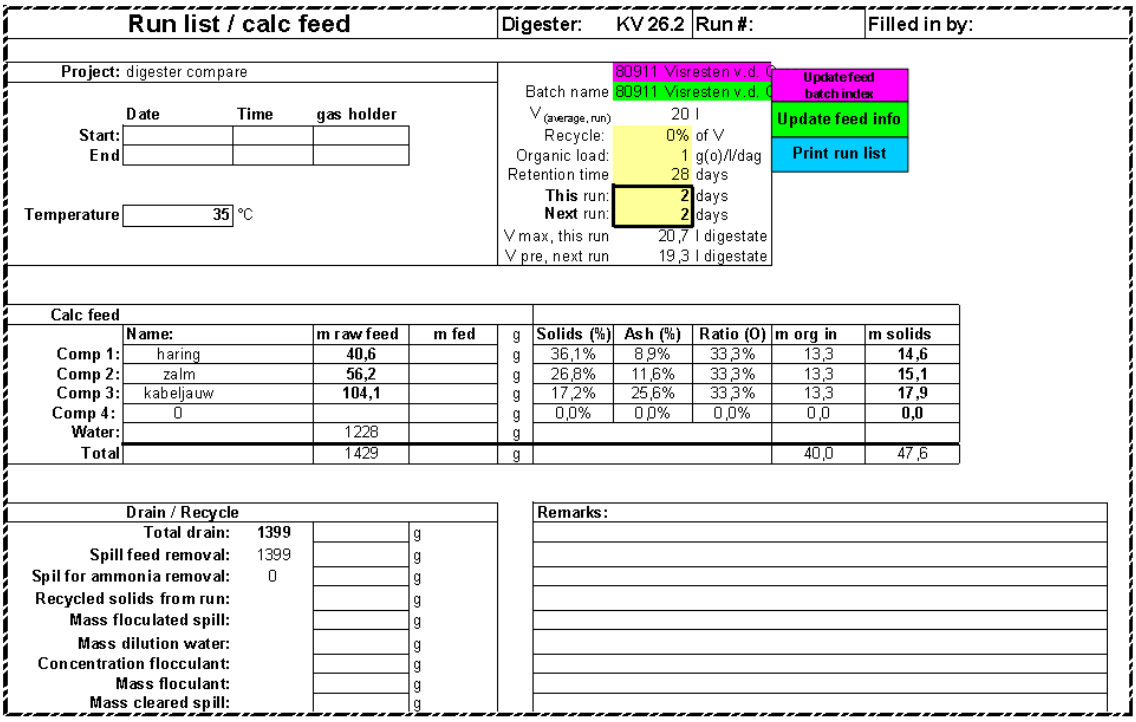
The data logger ‘counts’ the number of switches and the time between two pulses is a measure for the flow rate.



GRAPH 20. A view of data logger

The data logger is started by pushing the white ‘play’ [1] button in the head section of the screen. When the data logger is activated, the white play button is black then the data logger is now waiting to be started.

Fill in the run number in the white text box [2] with ditto name then push the ‘start run’ button [3]; the logger starts logging. The data logger displays the run start time, the current flow, the total gas volume and the total number of measurements. When the run ends, press the stop-button [4] on the data logger and write the total gas production down on the run list.



Run list / calc feed | Digester: KV 26.2 | Run #: | Filled in by:

Project: digester compare

	Date	Time	gas holder
Start:			
End			

Temperature 35 °C

	80911 Visresten v. d. G	Updatefeed batch index
Batch name	80911 Visresten v. d. G	Update feed info
$V_{(average, run)}$	20 l	Print run list
Recycle:	0% of V	
Organic load:	1 g(o)/l/dag	
Retention time	28 days	
This run:	2 days	
Next run:	2 days	
V max, this run	20,7 l digestate	
V pre, next run	19,3 l digestate	

Calc feed

	Name:	m raw feed	m fed		Solids (%)	Ash (%)	Ratio (O)	m org in	m solids
Comp 1:	haring	**40,6**		g	36,1%	8,9%	33,3%	13,3	**14,6**
Comp 2:	zalm	**56,2**		g	26,8%	11,6%	33,3%	13,3	**15,1**
Comp 3:	kabeljauw	**104,1**		g	17,2%	25,6%	33,3%	13,3	**17,9**
Comp 4:	0			g	0,0%	0,0%	0,0%	0,0	**0,0**
Water:		1228		g					
Total		1429		g				40,0	47,6

Drain / Recycle

Total drain:	1399		g
Spill feed removal:	1399		g
Spil for ammonia removal:	0		g
Recycled solids from run:			g
Mass floculated spill:			g
Mass dilution water:			g
Concentration flocculant:			g
Mass floculant:			g
Mass cleared spill:			g

Remarks:

GRAPH 21. Example of a run list

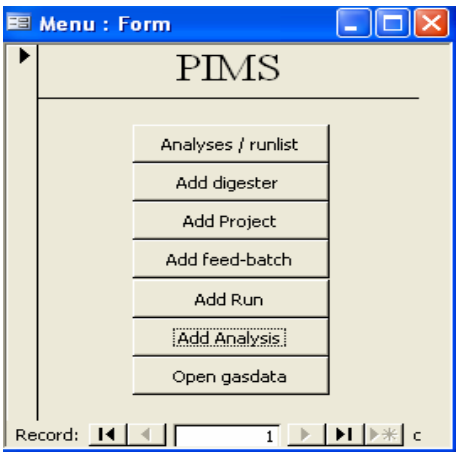
The fields THIS RUN and NEXT run contain the number of days of the runs. These numbers are required to maintain the average digester volume of 20 litres (or any given volume). *Care must be taken to fill them in carefully!!!*

'The magenta and green button are 'tools' to select the feed-batch. The magenta button activates a macro that imports a list of feed batches from the PIMS data base. In the magenta field on the run list, a drop down menu allows you to select the desired feed batch. This batch is linked to the green field. The green button updates the characteristics for calculating the amount of feed. The blue button prints page 1 on the run list sheets, containing just the run list and not the complete list of feed batches, somewhat to the right (scroll).In the calculation of 'spill for feed removal', there is a correction for conversion of organics to biogas. It is assumed that on average 75% if the organics of the feed is transferred to biogas. This amount is subtracted from the amount to be drained.

Data input procedures of the PIMS database is important so as to ensure no data is lost. When a project is running, every run will produce data. This data is transferred in the data base for storing and analysis. Analysis occurs by means of the data sheets in Excel.

A digester test is defined by the following characteristics which are digester name (for example KV26.1), run number (165), project name (Biocon) and feed Batch (Standard Feed). This information allows Excel to extract all the required data from this digester and this project in order to analyze the data. This information is also displayed on the run list. Besides this, also gas production and the exact amount of feed is filled in every run. Analysis data is stored in the analysis map. All this data has to be transferred to the data base.

The procedure of storing analysis is to start the PIMS data base by activating the short cut on the desk top then MS-Access will make one or two notes: click “open” and if required, ‘next”, “yes” or anything that gives you full access. The menu appears then press the button “analysis / runlist”; the form opens.



GRAPH 22. View of the start menu of the PIMS data base.

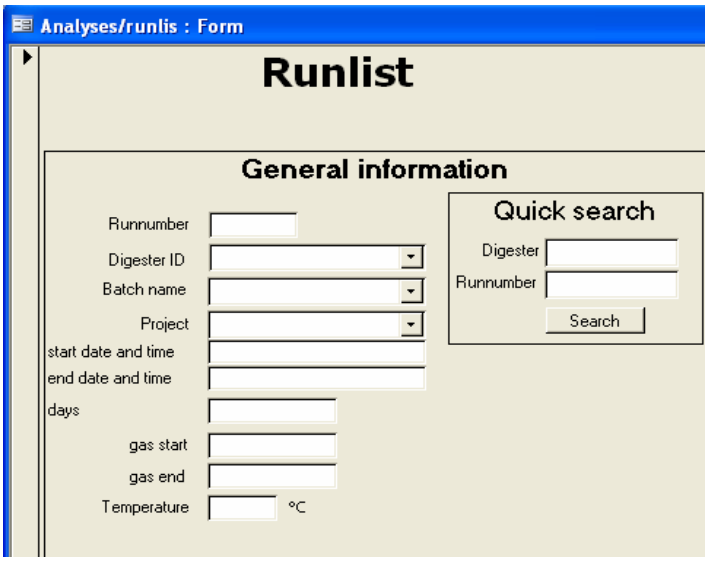
From here, there are two possibilities; which are “add a new run” or “add data to an existing run”.

The “add new run” is started by the form opening a standard to make a new run. To make sure the run does not exist yet, first the digester name and run number should be filled in ‘quick search’. If another run is displayed than the filled in run number, the run does not exist.

The run number is filled and the pull down menu is used to select the digester. The pull down menu is used to select the feed batch and to select the project name. After which the rest of the data (run and/or analyses) is filled in.

The left column contains all data from the run list. The middle column contains all data from the analysis sheet. On the top right section, there is room for remarks, either from the run list or the analysis sheet. These details contain all the key information to recognize a run. The rest of the data is to monitor digester performance.

When ready, click on the ‘new record’ button to update the database. Very often, not all data is filled in at once, so when a run already exists, a second run should not be added, otherwise the system will not function properly.



GRAPH 23. View of part of the runlist/analysis form.

If a run already exists, the digester name and run number can be filled in “quick search” and if the run exists, it will appear on the form so the remainder of information can be filled added. . (Miel 2008, 15)