COURSE:

METHODOLOGY FOR PRODUCING, PRESENTING AND MANAGING TECHNICAL WORKS

4th Grade Year

Assignment nr. 1

Technical Report on Energy generation from animal farm waste

Lecturer: Jorge Cerqueiro Pequeño

Student: Alexej Vnukov

Vigo, April 2019

0. ABSTRACT

For the desired expansion of renewable energies on the basis of biomass, the energetic use of liquid slurry as an agricultural waste material is an attractive option. Compared to the use of renewable raw materials, it does not compete with food production and has the potential to reduce greenhouse gas emissions relatively cheaply. In Germany, the manure bonus for renewable raw materials in biogas plants has therefore been granted since the beginning of 2009 if the proportion of manure is at least 30% of the fresh substrate mass used. This incentive can lead to an increase in the use of manure.

Table of contents

1. Introduction

Fossil fuels are the main source of energy for the world. Energy consumption will continue to increase in the future. While it is unclear how long fossil fuels will last, so much is clear that they are limited. As the easily accessible resources of fossil fuels are increasingly exhausted, the price of oil reaches new highs almost every year. Unconventional sources, such as tar sands and oil shale, are becoming economically interesting. Biofuels have been predicted to be a future alternative energy source and are already being used as an energy source in the fast-growing transport sector (an average annual increase of 3% is expected over the next twenty years, largely due to growing mobility in China and India). Transport represents 20% of global primary energy use and 70% of all liquid fuels. However, currently only bioethanol, biodiesel and regenerative diesel are produced on an industrial scale. Biofuels are produced from vegetable biomass consisting of carbohydrates (starch, sucrose, cellulose, and hemicellulose), protein, fats, oils, nucleic acids (DNA, RNA) and lignin. The relative composition of these components depends not only on the plant species but also on the part of the plant from which they originate. For example, trees contain more lignocellulose than cereals and fruits and seeds contain more starch and protein than stems. On average, more than 70% of the total plant biomass is lignocellulose. Of the plant biomass, protein, starch, sucrose and lipids are relatively easily degradable, whereas lignocellulose is not. Humans are not able to digest cellulose or lignin, which is why they depend mainly on starch, lipids and protein as food. Until recently, biofuels were largely produced from easily degradable starch, sucrose (bioethanol) and fats (biodiesel and regenerative diesel), which also serve humans as food (first generation biofuels). This competition (fuel versus food) has a negative socio-economic impact, which is why the main focus is now on the production of biofuels from the lignocellulosic part of plants (second-generation biofuels). However, second-generation biofuels are currently in a pre-commercial phase, and if they meet the 2015-2020 targets at all, there are still significant technical barriers to the chemical transformation of biomass. Biofuels that can be produced from biomass through biological processes include biogas (methane), bioethanol (ethanol), biodiesel or regenerative diesel (diesel-like compounds),

butanol, methanol and hydrogen. In addition, electricity can be generated from biomass using biofuel cells. In the following, the production and use of these energy sources are compared, bytheir energy efficiency and the feasibility of their use compared and the limited availability of biomass as a general source for biofuel production discussed in detail.

2. Excrements from animal farming

Figure 1: Mass animal husbandry [6]

Manure from animal husbandry mainly occurs in agriculture, the terms farm manure or farmyard manure are also used for this organic material. The raw materials for these biomass fractions are manure, which is more or less solid and the liquid urine. Depending on the type of housing of the animals, both raw materials may accumulate together with the bedding material (usually straw or wood shavings), this is known as solid manure. If excrement and urine accumulate together without other additives (except for water, e.g. in the case of split floor cultivation), the resulting mixture is called liquid manure. In modern housing concepts, water is normally added to these excrements for transport and cleaning purposes, the resulting mixture is then called full slurry. This solid slurry may also

contain other components (e.g. feed waste) or may be added (e.g. straw, kitchen, garden waste and leaves).

Figure 2: Animal farm waste [4]

The quantity and composition of the excrement vary significantly depending on the feed and other variables. For example, with the same dry matter content (DM percentage), the excrements of cattle are more viscous than those of pigs and in particular chickens; this is due, among other things, to the different digestive systems or the different types of feedstuffs that are usually fed to these farm animals. However, there may also be considerable differences within the same species. For example, cattle manure is thinner in summer when grass is fed than in winter when dry hay and silage are fed. Pig manure is also thinner when feeding liquid feed (e.g. whey, thick stillage) than when feeding dry feed (e.g. silage maize). Full slurry is thus a heterogeneous mixture of liquids of different origin, which may contain a wide variety of solids. The liquid consists mainly of water and dissolved salts as well as organic acids and other soluble components. The solids can be divided into three categories according to their physical behaviour.

- Suspended particles that remain more or less in suspension (e.g. certain excrement particles, bacteria, cellulose fibres).

- Floating solids which, due to their low density or the gas bubbles they produce, can accumulate on the surface and form a floating layer (e.g. straw, roughage residues).

- Sediments that accumulate at the bottom of the collection container as a result of sedimentation (e.g. unwanted sand particles, but also organic material).

Excrements from livestock farming are usually used on farms untreated as fertiliser and spread in this form on farmland; in the case of area-adapted livestock farming, the aim is to recycle the nutrients contained therein and thus close the internal nutrient cycles. In the case of non-adapted animal husbandry, such use on the farm's own land may not be possible, as there may then be a surplus of nutrients on the land used for the production of the animals; this implies the risk of nitrogen leaching in groundwater and surface water. Different treatment options are possible for the treatment that may then be necessary for transport to more distant arable land and for improving the application properties (e.g. minimisation of smell, improved distribution capability, reduction of water content). For example, chicken excrements can be dried, composted or pelletised and pig excrements can be separated by solid-liquid separation. Such agricultural substrates (i.e. slurry, manure) are typical substrates that can be used for biogas production in agriculture. They are relatively easy to ferment from a technical point of view. However, there may be problems with chicken excrements due to the relatively high nitrogen content. This leads to the formation of high NHC 4 concentrations during anaerobic treatment, which can inhibit the fermentation process. In Germany, liquid manure and slurry are already partly used for biogas production. However, since such agricultural substrates - unlike municipal or industrial organically contaminated waste and waste water - do not necessarily have to be treated (anaerobically) and can therefore be applied to the fields without additional (aerobic and/or anaerobic) treatment (i.e. after simple interim storage and consequently without additional costs), anaerobic fermentation only takes place if

this is economically viable (e.g. in Germany on the basis of the Renewable Energy Sources Law). An additional advantage of biogas production from the environmental and climate protection point of view is that the use of excrements from animal husbandry in biogas plants can significantly reduce the often strong release of greenhouse gases from the storage of this group of substances (i.e. positive contribution to climate protection); the same applies to the odorous substances that are degraded to biogas in biogas plants (i.e. fermented slurry "stinks" much less). In the case of thermophilic process variants, hygienisation of the material can also be achieved to a certain extent. [1] (2009): Energie aus Biomasse, p. 301-303; [2] (2016): Energie aus Biomasse, p. 158

3. Thermo-chemical transformation (burning)

For biogenic solid fuels (e.g. wood, straw), direct combustion in furnaces is still by far the most important energy conversion process and procedure. Incineration plants are used to produce heat. This thermal energy can be used as secondary energy (e.g. steam, which can then be further converted into electrical energy), as final energy (e.g. district heating) or as useable energy. Combustion is the complete oxidation of a (biogenic) (solid)-fuel by releasing energy. This produces off-gases and ash. Against this background, the technical aspects related to the direct thermal conversion of biogenic solid fuels will be discussed below. The focus of this part is on the description of combustion plant technology. In addition, the possibilities of electricity generation - both within the framework of mono-combustion of biogenic solid fuels and in co-incineration (i.e. the joint thermal use of solid biomass and fossil solid fuels such as hard coal) - or combined heat and power generation (CHP) are addressed. [1] (2009): Energie aus Biomasse, p. 375; [2] (2016): Energie aus Biomasse, p. 646

4.1 Production and use of biogas

The generation of biogas from residues, by-products and waste on the one hand and renewable raw materials on the other hand is an option for biomass conversion which has gained considerable market importance in recent years. Biogas and the resulting bio-methane is characterized by a relatively simple production and use of the through high flexibility with regard to possible usage options in the energy system i.e. use in the heat, electricity and fuel markets is possible.

Figure 3: Example of a biogas plant [7]

In the following, the biochemical basics of anaerobic digestion for the production of biogas are described. In view of the resulting requirements and boundary conditions for a process engineering implementation, selected application examples will be presented. With the aim of using biomass as efficiently as possible, the material and/or energetic utilisation concepts of the other fermentation products will be explained in addition to the options for using biogas or biomethane. [8]

4.2 Anaerobic degradation

During methane formation, microorganisms decompose organic substances in an oxygen-free environment, releasing biogas. This is a gas mixture saturated with water vapour, which essentially consists of methane (CH_4) and carbon dioxide (CO_2). Other components besides steam are trace gases such as nitrogen, oxygen, hydrogen, hydrogen sulphide and ammonia.

This biogas is naturally produced by anaerobic microorganisms in moors, sediments, soils and rumen of ruminants. But such microbial methane formation also occurs in anthropological systems such as solid manure deposits, slurry pits or domestic waste landfills. In biogas and sewage gas plants, these anaerobic fermentation processes are technically applied and an energetically usable biogas is produced with the highest possible efficiency.

This anaerobic degradation of organic material is realized by a complex network of microbial communities (biocenosis) in which the microorganisms are in different relationships and dependencies to each other. The different phylogenetic groups show individual activities and growth rates. As a consequence, the rate of total degradation is determined by the microbiological group with the lowest total activity. The diversity of microorganisms decreases over the stages of anaerobic degradation and thus their specialization increases.

- When using stackable or puncture-resistant substrates, the hydrolysis is often the speed-determining step. Above all cellulose and hemicellulose, which are frequently found in plant substrates, can only be hydrolyzed comparatively slowly.

- In the case of lignocellulose, degradation is further complicated. An anaerobic degradation of lignin is not known and the degradable substances cellulose and hemicellulose are built into a lignin skeleton and therefore difficult to access for hydrolytic bacteria.

- If large amounts of easily degradable compounds are involved (e.g. in waste water from distilleries or dairies, in kitchen waste, in some renewable raw materials), acetoclastic methane formation may become the determining step for the rate, as the growth rates of syntrophic bacteria and methane formers are lower compared to fermenters.

During substrate degradation, active biomass is newly formed by the reproduction of microorganisms. The proportion of the substrate that is converted into microorganism biomass is quantified very differently. For the individual groups involved in degradation, the figures vary between 3 and 10 %. In the following, the different interdependent metabolic steps of anaerobic digestion are described in more detail. [2] (2016): Energie aus Biomasse, p. 1610-1613

4.2.1 Hydrolysis

In a first step, hydrolysis, the fermentation substrate, which consists of complex polymeric compounds (e.g. carbohydrates, fats, proteins), is broken down by hydrolytic bacteria into its oligomeric and finally di- and monomeric units (e.g. sugars, fatty acids, glycerol, amino acids). Hydrolytic bacteria form exoenzymes from the group of hydrolases (e.g. amylases, lipases, proteases, cellulases, hemicellulases), which are enriched on the membrane outside of the bacterial cell. These are partially released into the environment as large enzyme complexes (cellulosomes). The bacterial production of adhesion proteins supports hydrolysis. [2] (2016): Energie aus Biomasse, p. 1612

4.2.2 Acidogenesis

In a second step, the water-soluble hydrolysis products in the cell interior of the bacteria are fermented essentially with the formation of various low-molecular organic acids (mainly acetic acid, propionic acid, n-butyric acid, lactic acid), alcohols, carbon dioxide and hydrogen. The fermentations do not always result in a direct degradation of the substrates up to the final fermentation product; thus microbial chain extensions can also temporarily form e.g. butyric acid from acetic acid or valeric acid from propionic acid. This leads to a meandering rather than linear metabolic process during anaerobic fermentation. The diversity of bacterial

fermenters is high and can contain several thousand different facultative and strictly anaerobic species, mainly from the classes Clostridia, Bacteroidia, Gammaproteobacteria, Actinobacteria and Bacilli. [2] (2016): Energie aus Biomasse, p. 1612

4.2.3 Acetogenesis (acetate formation)

In the third step, the products of the acidogenesis are converted to acetate. If alcohols or organic acids such as short-chain fatty acids (e.g. propionic acid, n-butyric acid) are used as substrates, hydrogen, carbon dioxide and other C1 compounds are also produced. For the activity of acetogenic bacteria low hydrogen partial pressures is essential, since the degradation process is only thermodynamically possible under these conditions. In order to maintain such low hydrogen partial pressures, the bacteria are therefore closely related to hydrogen-consuming microorganisms. It is assumed that instead of the direct so-called interspecies hydrogen transfer, hydrogen can also be transferred from one cell to another in the form of formate. This dependence between the microorganisms is called syntrophy. Syntrophic partners of acetogenic bacteria can be, for example, sulfate-reducing bacteria or methanogenic archaea. A special form of acetogenesis is the formation of acetate from hydrogen and carbon dioxide. This is the reverse reaction of syntrophic acetate oxidation, which is part of an alternative route of methane formation from acetate.

The diversity of syntrophically living bacteria is less than that of acidogenesis. Thus different representatives of the synergistales, syntrophobacterales, clostridiales and Thermoanaerobacteriales are identified as abundant acetogens. [2] (2016): Energie aus Biomasse, p. 1612

4.2.4 Methanogenesis

In the last step methane is finally produced by the activity of specialized strictly anaerobic microorganisms from the group of Euryarchaeota, the methanogenic archaea. The methanogenic organisms are divided into three groups, the hydrogenotrophs, methylotrophs and acetotrophs, according to the metabolic physiology of their substrates.

- In the hydrogenotrophic process, carbon dioxide is reduced using hydrogen. The methane formers compete with other hydrogen-using microorganisms (e.g. sulfate reducers).

- Methylotrophic methanogenesis uses methylated compounds (e.g. methanol) as substrate.

- In acetoclastic methanogenesis, acetate is split directly to form methane and carbon dioxide.

Acetate can also be degraded to methane and carbon dioxide by syntrophic acetate oxidation. First, both methyl and carboxyl groups of the acetate are oxidized to carbon dioxide (CO_2) by bacterial syntrophic acetate oxidizers to form hydrogen. This reaction is thermodynamically unfavourable. However, it can occur in combination with hydrogenotrophic methanogenesis. The entire process then becomes exergonic. Which of the metabolic pathways to methane formation predominates in biogas production depends on the particular process conditions.
Six different orders of methanogenic archaea are possible:
Methanobacteriales, Methanococcales, Methanocellales, Methanomicrobiales, Methanosarcinales and Methanopyrales. Most known methane formers are able to use the latter two pathways (hydrogenotrophic and methylotrophic methanogenesis) for methane formation, while only a few use the acetoclastic pathways. Acetoclastic methanogenesis is performed by Methanosarcina at high and by Methanosaeta at low acetate concentrations. Both belong to the methanosarcinales order. Methanosaetaceae is the only known family whose members can only catalyse acetoclastic methanogenesis. In methanogenic microorganisms, a large number of novel coenzymes involved in redox reactions or the transfer of C_1 units have been identified. One of these is the coenzyme F_{420}, which is responsible for the autofluorescence of methanogenic archaea after excitation with 420 nm light. [2] (2016): Energie aus Biomasse, p. 1612
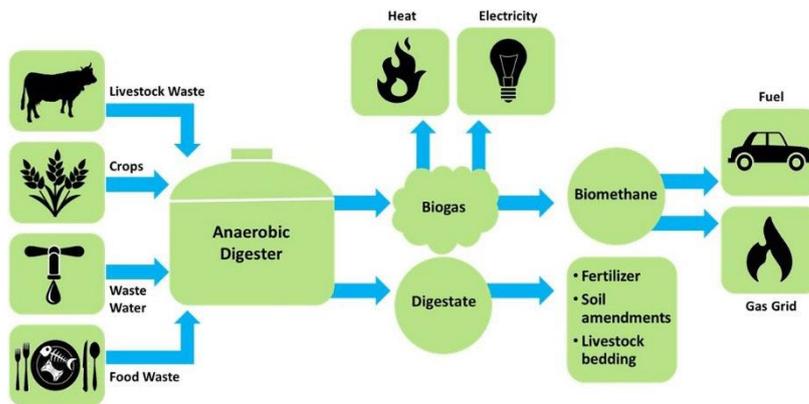
5.1 Biogas

Figure 4: Biogas production [5]

Biogas is a gas mixture that consists of approximately half to a maximum of two thirds methane (CH_4) and from about one third to at most one half of carbon dioxide (CO_2) as well as various trace gases.

Gas properties. For the combustion of biogas with 60 % methane 5.71 m^3_{air}/m^3_{gas} are required. The flame migration velocity of this mixture is 0.25 m/s maximum.

There is a risk of explosion if an explosive biogas/air mixture and an ignition source are present. A methane/air mixture with a methane content of between 5 and 15 % by volume is explosive; a CO_2 content of for example 35 % narrows these limits to 5 to 12 % by volume. There is a particular risk of explosion in closed and poorly ventilated rooms into which the biogas can escape. Biogas can contain disturbing components (water, hydrogen sulphide, ammonia and carbon dioxide as well as various trace elements), the elimination of which can expand the possible uses. These individual gas components are briefly discussed below. In addition, the operation of the fermenter (e.g. charging, use of agitators) can lead to additional, but time-limited, fluctuations of the quantity and quality of gas.
[2] (2016): Energie aus Biomasse, p. 1722

5.1.1 Methane (CH4)

Methane is a colourless and odourless gas whose density is lower than that of air. It is particularly flammable in mixtures with air and burns with a bluish, non-sooty flame. The calorific value is 35.89 [MJ/m^3]. The critical temperature for the

liquefaction of methane is 161.5 °C. Above this temperature there is no liquefaction even at very high pressures. This means that long-term storage in the smallest possible space (Liquefied Natural Gas) for later use is only possible at very low temperatures. [2] (2016): Energie aus Biomasse, p. 1723

5.1.2 Carbon dioxide (CO2)

Carbon dioxide is an inert component of biogas. The solubility of CO2 in condensate and the resulting formation of carbonic acid lead to acidification and thus to corrosiveness of the condensate. However, CO2 elimination is not absolutely necessary for the thermal utilisation of the gas. However, in some applications (e.g. fuel for motor vehicles, feeding into the natural gas network) the carbon dioxide must be removed for quality assurance or volume reduction. [2] (2016): Energie aus Biomasse, p. 1723

5.1.3 Water (H2O)

Water is also a component of biogas. Depending on the temperature, different amounts of water can be contained in the biogas in the form of water vapour. The condensate produced during cooling can be converted into cause blockages in the pipes and promote corrosion, as certain biogas components dissolve in the condensate and only then they have a particularly corrosive effect. The lines should therefore be laid with a gradient in the direction of a steam trap. The remaining water vapour does not affect many possible applications (e.g. use in a CHP unit). The amount of condensate increases with increasing gas pressure. The stronger this rises, the more aggressive the condensates are, since the solubility equilibria also shift to the corrosive products dissociated in water. [2] (2016): Energie aus Biomasse, p. 1723

5.1.4 Hydrogen sulphide (H2S)

Hydrogen sulphide is already effective at low contents in the biogas (up to 2 000 ppm) corrosive to copper and copper compounds. For gas discharge only plastic or stainless steel pipes should therefore be used. For use of biogas containing

H_2S as fuel, corrosion-resistant material (e.g. stainless steel) must also be used for the chimney system. In addition, the energetic use of a gas containing H_2S for SO_x-formation and thus for emissions whose release to the atmosphere is legally limited in many countries. At the same time, the accidental inhalation of biogas containing H_2S is dangerous, since a content of 1,000 ppm H_2S and more can be fatal for humans. [2] (2016): Energie aus Biomasse, p. 1724

5.1.5 Nitrogen and nitrogen compounds

Elementary nitrogen in biogas may have entered the plant in the form of air as a component of the starting material. In this case, the additional oxygen introduced is immediately converted by facultative aerobic organisms. In general, the simultaneous presence of nitrogen and oxygen indicates the entry of false air, which may have entered the gas chamber of the plant or the gas pipeline. On the other hand, nitrogen-containing compounds can occur in biogas, since nitrogen compounds released during bacterial degradation from proteins or nucleic acids are converted to ammonium in the reductive environment of a biogas plant. The ammonium dissolved in the liquid phase is again in equilibrium with gaseous ammonia. In the pH value range between 7.0 and 7.6, in which biogas formation preferably takes place, this equilibrium is very sensitive to changes in the pH value. An increase of the pH value by a few tenths of a unit already significantly increases the ammonia content in the biogas. [2] (2016): Energie aus Biomasse, p. 1724

5.1.6 Trace elements

Depending on the input substrate, higher hydrocarbons, chlorine and fluorine compounds, organic sulphur compounds or siloxanes may also be present in the biogas.

6.1 Gas utilisation

Biogas can be used energetically by a variety of different possibilities. The main variants are for the provision of heat, electricity and fuel.

6.1.1 Heat supply

Over a wide range of composition, biogas can easily be used in most biogas-compatible industrial combustion plants. In the case of existing oil burners, the burner must be converted to a two-material system.

Also, plants originally intended for other fuels (e.g. natural gas) can often be adapted to biogas. Usually only the burner nozzles and/or the actual burner need to be modified. If biogas containing H_2S is also used, a corrosion-resistant material must also be used for the chimney system (e.g. stainless steel). In this case, more corrosion-resistant cast iron boilers are preferable to non-ferrous metal boilers. The same applies analogously to gas condensing boilers.

In industrial furnaces, the combustion air supply can be controlled using continuous monitoring of the biogas calorific value to ensure optimum combustion. In practice, however, the biogas composition fluctuates only slightly if the fermentation reactor is operated stably. The firing system is also usually regulated in such a way that safe operation is ensured even with fluctuating composition.

6.1.2 Use in combustion engines

Biogas can be used in stationary and mobile combustion engines and converted into mechanical energy. The most commonly used spark ignition engines (gas Otto engines) are those in which the flammable air-gas mixture is ignited with one spark. In the case of compression-ignition engines (diesel engines), in addition to biogas, the use of an additional fuel with a low ignition temperature is required. Diesel gas engines are so-called dual fuel engines. The air-gas mixture is sucked in by the engine, compressed and ignited by injecting approx. 8 to 10 % diesel fuel. Alternatively, many new engines can also use biogenic fuels such as vegetable oil or biodiesel as ignition oil. The gas mixture used in a gas engine must be anti-knock. The knock resistance of a gas during combustion in gas engines is indicated by the methane number, which is approximately comparable to the octane number for petrol. The methane number is the percentage by volume of methane in a methane-hydrogen mixture which, under standard

conditions, has the same knocking characteristics in a test engine as the gas mixture to be tested. It is defined by the following two cornerstones.

- Methane by definition has a methane number of 100 and is anti-knock.
- Hydrogen by definition has a methane number of 0 and is knock resistant.

6.1.3 Vehicle fuel

Natural gas - and so methane - can also be used as a vehicle fuel in the form of CNG (compressed natural gas). Currently, there are vehicles available on the market that can run on CNG as standard, from cars to buses or trucks. For these vehicles to have an acceptable radius of action, the gas must be compressed to 200 to 250 bar.

Due to this high compression, prior treatment of the biogas is absolutely necessary, since compression of the gas components that cannot be used for energy purposes (e.g. carbon dioxide), for example, would involve a generally unacceptable amount of economic effort. At the same time, further cleaning is necessary.

Water vapour has to be removed as well as hydrogen sulphide. If the biogas meets the natural gas specifications after such treatment, any CNG-compatible vehicle can also be operated with treated biogas without any problems. Such a treatment of the biogas to natural gas quality also has the advantage that the biomethane can be fed into the existing natural gas network. Since it is chemically identical to natural gas and can therefore be taken from any existing CNG filling station or refueled by the corresponding vehicles.

6.1.4 Feeding into natural gas networks

A flexible option for the use of biogas is the upgrading of biogas to natural gas quality with subsequent feeding into the existing natural gas network. This allows all natural gas applications with biogas or biomethane to be accessed (i.e. heat market, power generation, mobility sector, material use, for example in the chemical industry).

6.1.5 Further possibilities

Biogas can also be used for lighting, cooking and cooling. These fields of application are generally used in micro-plants (e.g. in households in India or China). Local biogas networks can also be set up in addition to generating electricity to supply heat and cooking gas. Particularly when used as cooking gas, however, it is important to note that biogas may contain higher levels of hydrogen sulphide, which are hazardous to health. For this reason, the gas should be desulphurised beforehand when used in a closed kitchen.

7. BIBLIOGRAPHICAL AND DOCUMENTAL REFERENCES

[1] Kaltschmitt, Martin / Hartmann, Hans / Hofbauer, Hermann (2009): Energie aus Biomasse

[2] Kaltschmitt, Martin / Hartmann, Hans / Hofbauer, Hermann (2016): Energie aus Biomasse

[3] Tippkötter, Nils (2016): Grundlagen der biochemischen Umwandlung

[4] https://modernfarmer.com/2014/08/manure-usa/

[5] https://www.eesi.org/papers/view/fact-sheet-biogasconverting-waste-to-energy

[6] https://www.br.de/

[7]https://www.werra-rundschau.de/lokales/wanfried/biogasanlage-bei-wanfried-soll-erweitert-werden-10690880.html

[8] https://www.heizsparer.de/energie/gas/biogas/was-ist-biogas

Vigo, 29 of April 2019

The Engineer international degree environmental engineering
Alexej Vnukov

APPENDIX /APPENDICES