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Development and Evaluation of Methods for Assessing the Efficiency of Biogas Plants

Dissertation

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Contents

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Abbreviations

AD	anaerobic digestion
adE	anaerobically degradable energy
AMP	Automatic methane potential test
BFT	Bergedorf fermentation test
BGP	biogas plant (as source for inoculum)
BP	biogas plant
BMP	biochemical methane potential test
CE	conversion efficiency
CHP	combined heat and power
CH_4	methane
CON	concentrated fodder
CV	coefficient of variation
DE	Germany
DM	dry matter
DMS	dried maize silage
EBR	energy balance residual
EEG	Renwable Energy Source Act
EFOM	energy of fermentable organic dry matter
EU	European Union
EUD	Eudiometer
FID	flame ionization detector
FOM	fermentable organic dry matter
FW	food waste
GC	gas chromatopgraphy
GCV	gross calorific value

Abbreviations

GS	grass silage
H	heat
HAY	hay
HBT	Hohenheim biogas yield test
HRT	hydraulic retention time
ODM	organic dry matter
ODMBR	organic dry matter balance residual
OLR	organic loading rate
on-site SMY	on-site measured specific methane yield
KTBL	Association for Technology and Structures in Agriculture
LRD	2.5 m^3 laboratory reactor (as source for inoculum)
LRS	400 L laboratory reactor (as source for inoculum)
LM	liquid manure
LSD	post-hoc Fishers least significant differences
MCC	microcrystalline cellulose
MS	maize silage
NH_3-N / NH_4+-N	ammonium
P	Power
RNG	renewable natural gas
SE	standard error
SM	solid manure
SMP	specific methane potential
TE	trace elements
tE	total energy
TGF	triglyceride fodder
TKN	total kjeldahl nitrogen
TP	total phosphorus
UN	United Nations

US	United States
VFA	volatile fatty acids
VS	volatile solid
WWP7	waste treatment plant 7d degassing
WWP14	waste treatment plant 14d degassing
YE	yield efficiency

1 Introduction

1.1 Renewable Energy

The high emission of greenhouse gasses worldwide leads in global warming and its well-known consequences such as a sea level rise in the range of 0.26-0.93 meter in total with an increase in average temperature more than 1.5 °C, resulting to the flooding of millions of homes [1]. For this reason, the Kyoto protocol was signed by 191 states of the United Nations (UN) in 1997. This protocol determined legal bindings for a reduction of greenhouse gas emission [2]. Based on the Kyoto protocol, in 2014 the states of the EU decided to reduce their greenhouse gas emission by more than 40% compared to 1990, as well as to obtain 32% of the produced energy from renewable energy sources, both goals are supposed to be achieved by 2030 [3,4]. In December 2020, the EU decided to increase the goal to 55% less greenhouse gas emission compared to 1990 in 2030 and greenhouse gas neutrality till 2050. The success and the measures of the countries are controlled by the European climate law [5]. Overall, renewable energy generation results in less greenhouse gas emissions by cloosing the cycle of greenhouse gases and carbon [4]. However, in 2016, around 81% of the worldwide primary energy production came from the use of oil, coal and gas fossil fuels [6].

The situation in Germany is similar. In 2019, only 14.8% of the primary energy was produced using renewable energy sources, while the target is to reach 30% by 2030. Nowadays, the main part of the primary energy production from renewable energy sources in Germany is done by using bioenergy (51%) as well as by the use of biological waste (7%) [7,8]. A renewable energy technology using both sources is anaerobic digestion.

1.2 Anaerobic digestion

In the anaerobic digestion process, biomass is used as the feedstock and is converted into biogas. This microbial anaerobic digestion is a complex process carried out by diverse microbial communities and involves four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis [9]. The microbial communities of all steps have different favorable conditions and are inhibited by different impact, e.g. the pH-value, temperature, volatile fatty acids (VFA), trace elements, nutrients or ammonium concentration. In the first step, hydrolysis, the complex structured molecules like fat, carbohydrates and proteins are degraded into organic components like amino acids, sugar and fatty acids [10]. The degradation is done by enzymes, emitted from anaerobic bacteria [11]. These organic components are further degraded into short-chain VFAs (e.g. acetic, propionic and butyric acids), carbon dioxide and hydrogen as well as small amounts

of lactic acid and alcohols. This step is called acidogenesis. In the next step, the acetogenesis, the VFAs are degraded into acetic acid, hydrogen and carbon dioxide, the educts of the methanogenesis. The products of acidogenesis and acetogenesis are converted to methane and carbon dioxide, the so-called biogas, via acetoclastic or hydrogenotrophic methanogenesis by different anaerobic archaea [10,12]. The biogas can be easily stored at the BP or as biomethane in the gas grid and flexibly burned by a combined heat power (CHP) unit to produce power and heat according to demand. This flexibility is a great advantage of biogas as renewable source for power production compared to other renewable energy sources like wind or solar, which are dependent on the weather. If there is no sun and wind, the power and heat requirements are higher than the production. In this time, biogas plants can produce a high amount of electricity to get a high price at the spot market by using the gas stored in gas roofs and tanks or by producing just-in-time biogas by a feeding strategy. In contrast, biogas plants can reduce their electricity production during periods of high energy production from wind and solar plants and low prices at spot market. In this way, biogas can generate high revenues as well as a great impact on the stability of the power grid [13–15]. Another benefit of the anaerobic digestion is the local generation of power and heat. It creates jobs in rural areas and even enables villages to become independent in energy production (bioenergy village). It furthermore increases the value of feedstocks such as manure, food waste, the wastes of food production, landscape conservation material and energy crops [16]. The agricultural waste will be by business as usual only used as fertilizer. In the biogas plant, this material can be used firstly for energy production and secondly as fertilizer. This bioeconomic process also reduces uncontrolled emission of methane and other gases [17]. To achieve the main goal – lower greenhouse gas emission – high efficiency and a low methane emission are obligatory as the greenhouse gas effect of methane is 25 times higher compared to the effect of carbon dioxide measured over the period of 100 years [18,19].

1.2.1 Biogas sector worldwide

The number of BPs worldwide has increased strongly, but the expansion differs between the countries depending on the promotion by their government.

In developing countries all over the world, biogas is mainly produced with manure and waste at small scale BPs to gain heat or light for household use like cooking with the great advantage of reducing the demand of wood and charcoal for cooking [20]. Anyways, in more and more countries such as China, India or Vietnam, agricultural BPs are installed to get a higher value from manure and other organic waste as well as to produce more energy from renewable energy

sources to reduce the greenhouse gas emissions [16]. However, the biogas sector in these countries is growing slowly due to several reason like cultural taboos regarding the use of animal feces, lack of trust in the technology, lack of water and sufficient feedstock, cold temperature, low heat utilization, high installation cost, low fertilizer cost, low efficiency due to the implementation of mostly low cost biogas plants, corruption and lack of process monitoring, maintenance, education, funding and adequate information [20,21]. The number of BPs also slowly increased in industrialized countries like the US and member states of the EU. In the US, 2,100 BPs are already installed, annually producing 1.03 TWh power. However, there is an overall potential of 41.2 TWh power, a high potential for further BPs. Overall, more than 50% of the BPs in the US use wastewater as feedstock while only 250 are using livestock manure [16]. A underutilized potential in the US is food waste as a substrate, although it is becoming more popular because of the banning of landfills for food processors in some states of the US [22]. However, the support of federal US political system for the biogas production differs in each state. Most states in the US do not have any electric incentives or CO_2 certificates supporting the biogas sector like the EU, resulting in uneconomic operation [23]. Furthermore, unlike Germany, none of the state have a law on pasteurization of food waste.

The EU countries also show an increasing production of BPs. Nevertheless, there is a huge difference between the market-leading countries with guaranteed feed-in tariff (France, Italy and Germany) and other countries [24]. A total of 19,943 BPs and 725 biomethane plants were built in the EU until the end of 2019, with an annual biogas production of 167 TWh and an annual biomethane production of 26 TWh, respectively [25]. Most BPs use agricultural products, whereas less than 9% of the BPs use sources like food waste. This feedstock is mainly used only in few countries, e.g. Switzerland [26]. In addition to feedstocks, there are also differences in the goal of the biogas sectors in Europe, e.g. the Swedish government supports the production of biomethane for using in the automotive industry according to a low electrical price and a surplus of hydropower electricity in Sweden as well as a lack of access to a natural gas pipeline, while the German government supports the production of power and heat by the EEG [27]. Overall, Germany is the market leader in Europe with more than 50% of the total European BPs and producing around 50% of the European biogas [24].

1.2.2 Biogas sector in Germany

The German biogas sector is well developed and supported by the renewable Energy Source Act (EEG). In the year 2020 around 8,950 BPs with an installed capacity of 6.2 GW were in operation[8]. Overall, 29.4 TWh are produced annually, with an assumed technical potential of

almost 60 TWh [8,28]. Most of the BPs are agricultural and have been built during the last twenty years as a result of the high feed-in tariffs and the premiums guaranteed by the EEG. The Electricity Feed-in Act in 1991 guaranteed the grid feed-in of renewably produced energies [29]. In 2004, a bonus for those BPs using energy crops was established, valid for twenty years [30]. The EEG 2009 expanded the feed-in composition by adding the use of more than 30% manure [31]. The EEG 2009 also includes a premium for sale of the generated heat, which results in a higher efficiency of the BPs and thus in a more economic operation.

In 2012, 2017 and 2021 the EEG then reduced the feed-in compensation as well as the premiums, e.g. the use of energy crops is no longer rewarded by a premium. Nowadays, new BPs only receive an additional premium feed-in compensation for feeding more than 80% manure or landscape conservation material. At the same time, the constraints for the BPs increase, e.g. a hydraulic retention time of more than 150 days is required for BPs built after 2016 and for secondary digesters built after 2011 [32]. Thus, these laws result in a minor expansion of BPs [8]. Most of the existing BPs are going to lose their feed-in compensation during the next few years. It is possible for them to take part in a tendering procedure to get a feed-in compensation for ten more years, but it will be much lower than before (2021: maximum 18.4 ct/kW). Additionally, to take part numerous requirements must be met to participate in the tendering procedure: For example, less than 40% of the feedstock are allowed to consist of maize and the fed-in compensation will only paid for 45% of the installed power capacity to support the flexible production of biogas plants. For providing the additional electricity, the biogas plants will receive 65 € per kW installed power and per year [33]. However, based on these conditions, economic operation is only possible for agricultural BPs that have a highly efficient conversion process and high heat utilization.

Besides agricultural biogas plants, there are also BPs which use sewage sludge, bio organic industrial waste and food waste as substrate. These substrates are important because of their potential to use waste to generate a higher value product such as power, heat and later as biofertilizer, resulting in a closed cycle loop usage of carbon and nutrient as well as in long-term conservation of the carbon and nutrients on agricultural land. This results in a high ecological benefit compared to other technologies like combustion of organic material. Unlike agricultural BPs, these biogas plants can earn some money in addition to the EEG by collecting the waste such as food waste [34]. That’s why it is an interesting alternative concept for some BPs to use food waste as feedstock. However, for using food waste as feedstock, stricter rules have to be established. In Europe, a separation of food waste from plastic and other garbage is necessary. To meet epidemiological and phytohygienic concerns, pretreatment by

pasteurization at more than 70 °C for minimum 60 minutes or a thermophilic digester operation temperature of more than 50 °C is required [35]. 4.2% of the total input material in German BPs is food waste [36], which is an easily degradable substrate. Yet, it is very inhomogeneous and the composition depends strongly on the feedstocks. Therefore, prediction of the methane potential and determination of the efficiency is more difficult compared to agricultural feedstocks [37].

1.3 Efficiency analysis

A high efficiency is very important for an economic operation of a biogas plant, especially without the high feed-in compensation, e.g. by the EEG 2004 [30] and the EEG 2009 [31], as discussed before. Until today, only a few studies have been conducted systematically determined the efficiency of full-scale BPs. Many problems are reported when doing so. To investigate the efficiency, the system boundary, a method to determine the input and output potential and a mass balance must be defined [38,39].

The system boundary can be chosen depending on the main topic of the investigation. For example, to determine the efficiency of the complete BP which feed-in electricity, the system boundary should include the CHP units, the electricity and heat grid up to the selling point as well as the digester. In this example, the output includes the used power, the used heat and the residual potential, while the input is the feedstock potential. In contrast, for checking the efficiency of the biological system (biological efficiency), the system boundary does not include the CHP unit, but primarily the digester. Here, the input is similar to before, but the output is the methane produced [39].

The input and output values as well as the potential have to be measured and determined by different methods. In the case of Germany, most BPs feed into the electricity grid, while the heat is sold to customers such as private households. The sold power and heat are measured by a calibrated power and heat meter. Thus, the values can be used as outputs for the efficiency analysis. Other outputs like produced gas, power, heat or the mass of digestate are more difficult to determine, as accurate measurement devices are often lacking at most BPs. Calculation of these parameters based on other parameters like the sold power seems to be necessary [40].

For the biological efficiency analysis, the mass of the feedstock and the methane potential of the feedstock are the main input parameters. Most biogas operators in Germany note the feedstock mass on a daily basis. Moreover, according to German law, they have to weight them on a frequently calibrated scale [30]. Beyond that, the methane potential of the feedstock cannot be determined by an online measurement device. Several laboratory methods are available to

determine the methane potential, for instance, the calculation based on organic dry matter, calorific value, biochemical methane potential or on fermentable organic dry matter according to Weißbach [41–43]. Anyway, most of those methods are rarely used today and a comparison of all the methods is still missing. Most studies also only report the measurement accuracy in the laboratory and only few studies like Mönch-Tegeder et al. [44] report about the accuracy of one of these methods, namely the biochemical methane potential test (BMP) at full-scale biogas plants.

1.4 Biochemical methane potential test

The BMP is a batch-test and the most common method to determine the methane potential of substrates and the residual methane potential of digestate as well as to design a BP. It has been used for several years [45]. To evaluate the results, it is important to know the accuracy of this method. Thus, different guidelines have been developed to achieve a high accuracy [46-48]. The VDI 4630 [46] is the most common guideline in Germany and describes the preparation of the inoculum, the different digestion systems for the BMP, the experimental conditions and the evaluation of the results in detail. For the digestion system, some details of the procedure are pointed out, e.g. mixing at least once a day. Certain restrictions are mentioned for the inoculum, like the use of an inoculum from a source like wastewater treatment, laboratory anaerobic digester or a biogas plant. Also, the gas production of the inoculum is limited. Only 20% of the biogas should be produced by the inoculum itself in a test and at the same time the inoculum-to-substrate ratio (ISR) based on organic dry matter should be at least 2:1 in order to ensure sufficient buffer capacity of the mixture. For substrates, it is mandatory to determine the dry matter (DM) and organic dry matter (ODM) and calculate results based on ODM, including subtraction of the inoculum potential, correction to standard pressure and temperature values (273.15 K, 1013.3 hPa) and use of a positive control such as standard substrate like cellulose, hay or concentrated fodder. Furthermore, at least three replicates are mandatory for BMP of a substrate and the experiment must be conducted for three consecutive days generating less than 0.5% of the total production per day. In the case of Hohenheim biogas yield test, a retention time of at least 35 days is required, thus satisfying the restriction. The residual methane potential determination is also described in VDI 4630 [49] and VdLUFA [50]. For both, no inoculum is added and the retention time is fixed to 60 days.

Beside German guideline, European guidelines are also being developed. These guidelines are similar in certain points, but also have some differences. Angelidaki et al. [51] suggest taking an inoculum fed with a wide range of substrate and degassing for 2-5 days. Different to

the VDI 4630 [49], Angelidaki et al. (2009) [51] also recommend verifying the inoculum activity by testing with different acids as substrate as well as calculating the rate of hydroxylation from the later experiments. Only bottles with 0.1 to 2.0 L and the headspace rinsing by N_2/CO_2 80/20% are suggested as digestion system. Both are more restricted in comparison to VDI 4630 [49], which describe various possible digestion systems. However, the ISR is not clearly described. The concentration should vary between 5-100% until a stable process can be found [47].

For a European interlaboratory test, Holliger et al. (2016) developed also a guideline. It differs from the other regulations in specifying quality criteria for inoculum, e.g. volatile fatty acid concentration smaller than 1.0 g L^{-1} or ammonium concentration smaller than 2.5 g L^{-1}. Also, a sieving of the inoculum and sieving and grinding of the substrate are recommended. The ISR depends on the substrate, but is usually between 2 and 4, but at least above 1. Furthermore, unlike other studies, Holliger et al. (2016) suggest a reactor volume larger than 400 mL [52].

All those aspects affect the results. In order to investigate and to reduce the influence of these aspects, several interlaboratory tests were carried out and a coefficient of variation (CV) between 8-17% was reported [45,48,53,54]. However, clear reasons for this CV couldn't be determined.

Most research studies in the field of accuracy of the biochemical potential test has focused on the inoculum, which differs in each laboratory. All those studies found variations between different inocula, which are also depend on the substrate used. The coefficient of variation differs between 2-128% depending on the inoculum used to determine the specific methane yield of different substrates [54,55].

1.5 Objectives of the study

The biogas sector worldwide is strongly dependent on the promotion by governments on account of the high production costs of biogas compared to cost of crude oil, which is also promoted strongly. The biogas sector in Germany was well supported by the EEG. Consequently, it has developed and grown fast over the past twenty years. Nowadays, the growth has stopped because of the reduction of the feed-in tariffs and the bonus payments by the EEG 2012, EEG 2017 and EEG 2021. Therefore, lower production costs are essential not only in several countries worldwide but also in Germany to secure the future growth of the biogas sector. Higher efficiency can lead to lower production costs and thus economic

operation. To reach this goal, it is necessary to determine an accurate standard method for the estimation of the efficiency of a BP.

The novel approach and objectives of this thesis are to define a method for estimating the biological efficiency of full-scale BPs through a defined system boundary and to use different methods to determine the specific methane potential (SMP) of the substrates and the digestate. Other objectives are to determine the accuracy of the developed method, to compare the methods for determining the SMP and evaluate their informative value as well as determining the accuracy of the most common method to estimate the SMP, the biochemical methane potential.

For this purpose, the biological efficiency of 33 German was investigated and the biological efficiencies of these BPs is calculated based on the most commonly used methods for determining the methane potential of substrates and digestate.

On the example of the most commonly used method, the biochemical methane potential test, two BPs in different countries (Germany and the US) are investigated. The objective of this research is to investigate the method on these two biogas plants and show the accuracy as well as the problems by determining the efficiency for BP using food waste as substrate and on international biogas plant. Based on this study, the effects of different regulations of states on the structure and the biological yield efficiency of the BPs is investigated. In addition, the accuracy of feeding the inhomogeneous substrate food waste is studied.

Finally, the determination of the accuracy of the biochemical methane potential test is done based on two special impacts, the impacts of the used inoculum and of the digestion system.

The following three subtasks are defined:

Comparison of biological efficiency assessment methods and their application to agricultural full-scale biogas plants

Following the changes in the EEG and the resulting lower income due to feed-in tariffs and bonus payments, the focus in the German biogas sector is placed on the efficiency of agricultural BPs. Aside from Germany, the biogas sector is not subsidized in many countries. As a result, expansion does not take place due to the missing economic viability. Economic operation of BP is only possible if a high efficiency and thus low production costs are achieved. However, a standard method for determining the biological efficiency of a BP is still missing in the literature as well as a description of the parameters that influence the accuracy of the method, such as the field-site data quality. The objective of this subtask is to fill this gap.

To achieve this objective, the method for the biological efficiency analysis must be defined, including system boundaries, the input and the output variables as well as a mass and energy balance. Afterwards, the accuracy of the method and the resulting mass and energy balance as well as the meaning and accuracy of the methods for determining the methane potential are investigated.

Efficiency of biogas plants using food waste in Germany and the United States of America

In addition to agricultural BPs, food waste is a common and valuable substrate. In total, 4.2% of the input material of the BPs in Germany is food waste. For some BPs, this is an opportunity to become independent from the EEG. However, regulations in the EU are much stricter than for agricultural plants. In the US, food waste is not a common substrate, but it is coming into focus due to landfill bans for food processors. Furthermore, Food waste is an inhomogeneous material, making it challenging to determine the methane potential.

The objective of this subtask is to apply the developed method at two biogas plant feeding food waste as well as on one international biogas plant. To get an idea how to explain the results of the efficiency analysis, a comparison of both countries is drawn – containing the setups of the BPs as well as the current feed-in tariffs and the current bonus in both countries. Additional factors on the measurement accuracy of the BP in the US and the impact of feeding inhomogeneous material such as food waste as substrate are investigated.

Influence of inoculum and digestion system on the biochemical methane potential test

The biochemical potential test is the most common test for the determination of the SMP. This method has been used for several years to calculate the setup of a BP. In order to ensure a high accuracy of this test, many different guidelines have specified the properties of the inoculum, the digestion system and the calculation. Nevertheless, several interlaboratory tests showed a coefficient of variation of around 8-17% even when the same guideline was used. Previous detailed research on the effects of the inoculum showed coefficient of variation of 2-128%.

The objective of this subtasks is to show the impact of the inoculum and the digestion system and give a suggestion to get a lower CV. This is done by using different inocula and digestion systems with the same substrate. The different settings are investigated separately to find the reasons for the wide range of CV.

2 Comparison of Biological Efficiency Assessment Methods and Their Application to Full-Scale Biogas Plants

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2.1 Abstract

For calculation of biological efficiency of a biogas plant (BP), it is required to determine the specific methane potential (SMP) of the substrate. A study comparing available methods for determination of SMP and the comparison with data of full-scale BPs is missing but necessary according to the differences in process conditions between both. Firstly, mass and mass associated energy balances of 33 full-scale BPs were calculated and evaluated. The results show plausible data for only 55% of the investigated BPs. Furthermore, conversion and yield efficiencies were calculated according to six different methods for SMP determination. The results show a correlation between the measured on-site specific methane yield and the calculated SMP by methods based on biological degradability. However, these methods underestimate the SMP. Calculated SMPs based on calorific values are higher, but less sensitive. A combination of biochemical and energetical methods is a promising approach to evaluate the efficiency.

2.2 Keywords

anaerobic digestion, biochemical methane potential test, fermentable organic dry matter content, gross calorific value, mass and energy balance

2.3 Introduction

In Germany alone, approximately 8,700 biogas plants (BP) were in operation in the year 2020 with an installed capacity of 6,2 GWel in total [56]. However, the installation of new BPs has come to a near standstill in recent years, mainly due to the lower feed-in tariffs and premiums for electricity generation from the amendments to the Renewable Energy Sources Act (EEG) since 2012 [24]. At the same time, BPs built before 2012 will phase out from their guaranteed 20-year time period of tariffs and premiums in the coming years [57]. In order to compensate for falling tariffs, the substrate conversion rate has to be in-creased. Therefore, methods are needed to assess the biological process efficiency. The efficiency of a conversion process like anaerobic digestion can be defined by the extent of conversion of an initially available potential of the substrate in two ways (i) the, produced methane related to the methane potential of the substrate called yield efficiency (YE) in the following and (ii) the actually used potential, i.e. the differences between the methane potential of the substrate and the residual methane potential of the digestate related to the methane potential of the substrate, called conversion efficiency (CE) in the following.

While the substrate is weighed and recorded in most full-scale biogas plants, the output in the form of digestate and biogas is hardly never measured and must therefore be estimated. Schievano et al. [38] estimated the methane production of the full scale biogas plant based on the electricity generation of the combined heat and power plant (CHP). Thus, under steady state conditions the mass of digestate can be calculated from the mass balance of the input (substrate) and output (biogas and digestate).

In addition to the mass flows, the methane potential of substrates and digestates must be estimated. Various approaches to this problem can be found in the literature. Several studies are based on organic dry matter content (ODM) degradation (CE_{ODM}) [43,58,59]. Since the range of substrates typically used in practice varies greatly in terms of the proportion of anaerobically degradable organic matter, a substrate-independent comparison of BPs with this method is not possible [60]. To overcome this disadvantage, other methods based on a more precise determination of the anaerobic conversion potential of substrates have been developed. One of the most common methods is the so-called biochemical methane potential test (BMP), which is a laboratory batch test performed according to VDI 4630 [49]. Anaerobic biodegradability and microbial growth are considered by the method and the methane potential can be calculated directly for any kind of substrates and digestates. Several impact factors were reported and show which efforts are necessary for getting re-producible results [54,61]. To create a common database for specific methane yields of commonly used substrates, BMP

results of various laboratories were compiled and published by the Association for Technology and Structures in Agriculture (KTBL) [62], which are referred to as "KTBL values" in the following.

However, the KTBL values do not consider the effects of natural fluctuation in dry matter content (DM), ODM and the degradability of ODM. These parameters are considered by a method based on fermentable organic dry matter (FOM), which was developed by Weißbach [41]. The FOM represents a part of ODM, from which the non-degradable organic fraction is subtracted. Weißbach [63–65] defined fermentation coefficients based on feeding experiments with sheeps where FOM of the substrates was derived from a correlation between fiber content in substrate and fiber content in the excrements [41,63–66].

In contrast to the aforementioned specific considerations of the biological anaerobic process, in industrial energy conversion processes the energy output is simply related to the calorific value of the substrate, representing the total energy content (tE). To compare the efficiency of the biogas process with other industrial conversion processes, two methods were developed to consider the non-fermentable fraction of the substrates. Mächtig et al [42] suggested subtracting the energy of the lignin fraction from the gross energy content, as lignin is the largest non-biodegradable fraction in the feedstock, and called this the anaerobically degradable energy (adE). However, the method does not take into account that besides lignin, the encrusted parts of hemicellulose and cellulose are also inaccessible to microorganisms. Moreover, the authors reported a relative high error of prediction of the lignin content by this method. Alternatively, Fischer et al [67] proposed to correct the calorific value by the fermentation coefficient from the FOM methodology to calculate the energy content of the fermentable organic dry matter (EFOM). Herein, the non-degradable part of the substrate is assumed to be lignin.

Although biological efficiency is very important for optimizing biogas plants, there are only few scientific publications on this topic and there is no comparative study of the presented evaluation methods for calculating the yield and conversion efficiency of the biological process in large-scale BPs, nor is there a systematic analysis on their validity.

A state-supported monitoring program with 33 participating full-scale biogas plants has now provided the first opportunity for this research. The aim of this study was to compare different methods of evaluating efficiency in order to identify the most suitable method. Especially, the differences in methodology and accuracy of data collection as well as the problems in transferring laboratory data to full-scale agricultural BPs are included in the consideration.

2.4 Materials and Methods

2.4.1 Study design

In this study, 33 full-scale agricultural BPs in Germany were investigated in the years 2016-2018 for the efficiency of their digestion processes. The descriptive process data of the BPs such as temperature in the first digester, hydraulic retention time (HRT) in heated and gas tight system, the organic loading rate (OLR) and the feed ratio of manure, are listed in Table 2.1, the substrate ratio of feeding is listed in Table S1. The 33 BPs are a selection from 61 BPs from the biogas measurement program III [40], for which mass and energy balances could be calculated consistently according to the procedure described below. All examined BPs utilize the produced biogas in CHP units exclusively. The average electrical power varied from 73 kW to 1796 kW, calculated by dividing the accumulated amount of electricity generated during the year under investigation by 8760 hours. Different methods were applied to quantify the initial potential for biogas formation of the substrates as well as of the residual potential of the digestates to every BP. All methods are based on a common mass balance. Mass balances were calculated based on monthly values of the material flows. Efficiency indicators were calculated as yearly values based on the sum of the monthly values from mass balances.

Table 2.1 Average electrical power production, temperature of the first digester, stages, hydraulic retention time (HRT), organic loading rate (OLR), manure share of the 33 investigated biogas plants (BP)

BP	Average electrical power	Temperature first digester	Stages	HRT heated	HRT gas-tight	OLR	Manure Share
	kW	°C	HY/FD/SD/ST	d	d	kg_{ODM} d^{-1} m^{-3}	%mass
1	73	42	0/1/0/1	50	153	3.0	91.4
2	532	27-33	1/1/1/4	73	73	2.2	75.5
3	74	44	0/1/1/1	148	148	1.1	81.9
4	671	36-40	0/1/2/1	231	275	1.0	36.4
5	1229	45	0/1/1/2	72	213	3.3	58.0
6	77	42	0/1/0/1	73	221	1.9	82.1
7	498	44	0/1/1/2	127	346	3.4	32.9

BP	Average electrical power kW	Temperature first digester °C	Stages HY/FD/SD /ST	HRT heated d	HRT gas-tight d	OLR kg_{ODM} d^{-1} m^{-3}	Manure Share %mass
8	209	43	0/1/0/2	66	66	4.9	10.5
9	316	38-47	0/1/1/2	104	156	3.1	37.7
10	358	42	0/1/1/1	225	225	1.6	7.7
11	508	47-53	0/1/1/1	59	116	4.8	34.9
12[a]	207	45	0/2/1/0	142	142	1.8	43.6
13	512	40	0/2/1/2	61	61	2.6	67.9
14	451	44	0/1/0/1	42	168	4.9	50.9
15	942	41	0/1/1/1	81	81	3.8	0.3
16	469	40	0/1/1/1	113	113	2.3	32.5
17	1706	43-45	0/2/1/1	72	118	4.3	0.0
18	649	45	0/1/1/1	133	189	2.5	0.0
19	571	43	1/2/0/1	63	129	3.5	56.3
20	199	39-45	0/1/0/1	65	134	2.5	52.9
21	1796	43	0/2/1/2	73	156	4.1	0.0
22	635	43-49	0/1/1/1	71	168	3.2	51.5
23	459	52-59	0/1/1/5	101	101	2.9	34.6
24	381	35-43	0/1/0/1	78	78	2.2	51.6
25	560	43	0/1/1/2	89	218	1.9	55.9
26	712	42	0/1/0/1	54	104	3.1	75.6
27	739	43	0/1/1/1	124	192	2.5	0.0
28	557	44	0/2/0/6	45	45	3.6	73.0
29	371	43	0/1/1/1	87	208	2,3	42.7
30	515	42	0/1/0/1	81	226	3.6	32.0
31	511	42	1/2/1/1	120	120	1.4	62.1
32	512	44	0/1/1/1	61	96	1.6	84.9
33	975	50	0/1/2/2	59	272	4.3	51.7

[a] BP 12 is a research biogas plant with high measurement accuracy

2.4.2 Data collection and laboratory analyses

2.4.2.1 Process data

For calculation of the different efficiency indicators, process data of the examined BP were necessary. These were recorded automatically from sensors by process control systems or manually by plant operators.

The input mass of every solid substrate was weighed daily by scales. The input volume of every liquid substrate was measured daily via flowmeters or calculated based on livestock units. The concentration of methane in the produced biogas was measured mostly continuously but at least monthly. Operating hours and produced electricity from CHP units was recorded monthly, as well as the feed-in amount of electricity and the amount of internal electricity consumption of the BP. For pilot injection CHP engines, the amount of consumed ignition oil was recorded monthly.

2.4.2.2 Sampling

The input substrate and digestate material streams had to be characterized for their inherent methane and energy potentials by laboratory analysis. Therefore, sampling of these materials was necessary. The sampling method was standardized. Samples of input substrates were taken monthly. Solid substrates were sampled from silos or piles by taking subsamples at 20 cm depth from different positions and mixing them together. Liquid samples, e.g. manure, were taken after complete mixing of storage tanks. Digestate samples were taken at the last gas-tight digester in flow direction at least every three months. A minimum of 10 L of the digestate were discarded before taking samples from sampling pipes. Afterwards, the samples were cooled down to 2 ± 5 °C on field-site and stored at -20 ± 1 °C in the laboratory except for digestate samples for BMP test. These samples were cooled down to 4 ± 1 °C on field-site and stored at the same temperature in the laboratory.

2.4.2.3 Dry matter content and organic dry matter content

DM and ODM were analyzed for every sample at least in duplicate according to German standards DIN EN 15935 [68]. The DM and ODM of all silage and sugar beet samples were corrected for volatile fatty acids according to Weißbach et al. [41,63–65]. The pH values and acid concentrations were measured in duplicate for the DM/ODM correction of silages and sugar beet. More information about the measurement methods can be found in the literature [69–71].

2.4.2.4 Biochemical methane potential test

The biochemical methane potential (BMP) test was done in three different laborato-ries, two of them used the Hohenheim biogas yield test (HBT). HBT is a continuous mixed system with a 100 mL-syringe as the reactor. The determination of the methane percentage was done by an infrared-spectrometric methane-sensor Advanced Gasmitter, Pronova Analysetechnik (Berlin, Germany). Between both HBTs only the methane quality meas-urement was different. BP 5-17 and 24-32 were measured in dry gas and BP 1-4 and 20-23 were measured in wet gas and corrected afterwards. The third laboratory used a Bergedorf fermentation test [49] with a volume of 1.5 L and measured the BP 18-19 and 33. Gas was measured by a tipping cell counter (MilligasCounter, Ritter Apparatebau GmbH, Bochum, Germany). Methane percentage was measured by an infrared sensor (Awite Bioenergie GmbH, Langenbach, Germany).

The BMP test of all substrate samples was done once year for all substrates according to VDI 4630 [49]. Temperature for all tests was 37 °C and the tests stopped, for HBTs, after 35 days and for Bergedorf fermentation after reaching less than 0.5% total methane pro-duction in one day. All samples were measured at least in triplicates and with an inoculum to substrate ODM ratio of 2:1. Inocula from a 400 L laboratory reactor was used to in-vestigate samples from BP 5-17 and 24-32, inocula from a wastewater treatment plant to investigate samples from BP 1-4 and 20-23 and inocula from 2500 L reactor to investigate samples from BP 18-19 and 33. Hülsemann et al. [61] describes in detail the systems, the inocula and the measurement accuracy.

The specific methane potential of the digestate was measured according to VdLuFa [72] at 37 °C for 60 days.

2.4.2.5 Fiber content

The raw fiber content of biomass in general describes the organic, non-fat, acid- and alkali-insoluble fraction and was determined for FOM calculation. Raw fiber was determined according to the protocol published by Dittrich-Zechendorf [73]. The fat free sample material was successively treated in boiling sulphuric acid and caustic potash of a defined concentration. The remainder is separated, dried, weighed and finally incinerated at 500 °C. The loss of mass during incineration corresponds to the raw fiber content of the sample. The fiber content of each of the BP´s substrates was analyzed four times a year and in triplicates for statistical validation.

2.4.2.6 Gross calorific value

The gross calorific value (GCV) was determined according to DIN EN ISO 18125 [74]. A correction for sulfur or nitrogen content was omitted. The samples were dried at 105 °C and

milled to a particle size smaller than 1 mm prior to analysis. This way, dry matter specific GCVs were measured. The GCV was corrected for volatile fatty acids and alcohols, like done in DM determination for silage samples. For the substrate and digestate of each BP, the gross calorific value was determined four times in a year in triplicates.

2.4.3 Mass Balance

The system boundary for mass balances was chosen to enclose all gas-tight digesters (Figure 2.1) in order to describe the biological process alone and also be independent of the BP´s biogas conversion technologies [39]. For mass balances all material streams crossing the system boundary were determined.

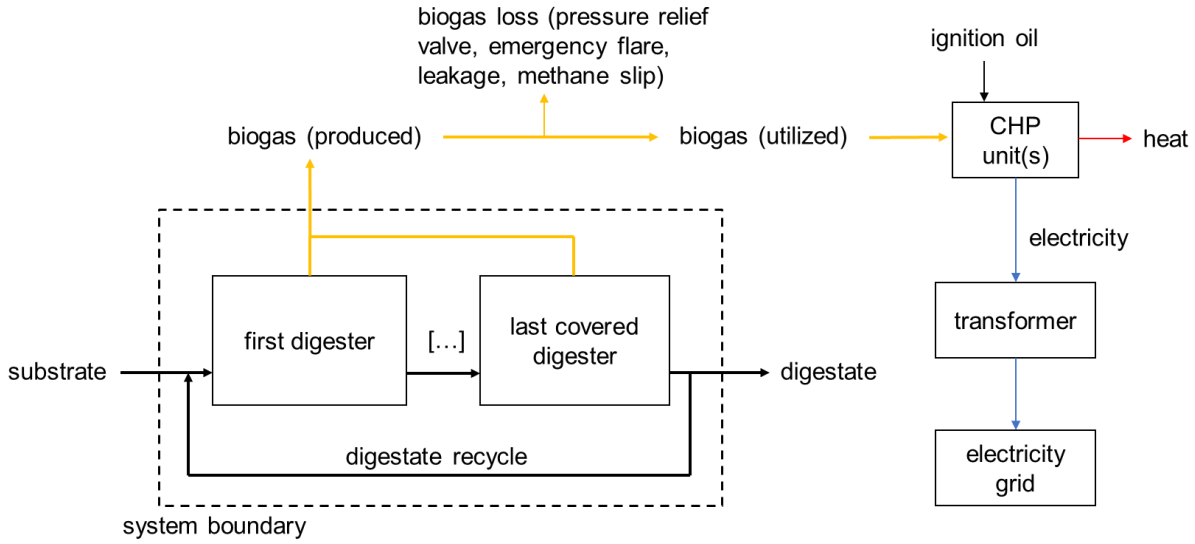

Figure 2.1 System boundary for efficiency assessment; starting with the first digester and ending with the last covered digester

All examined BPs performed a continuous digestion process. Feeding intervals were between 20 minutes and 1 hour. Fluctuating liquid filling levels in covered digestate storage tanks, due to agricultural logistics in digestate application, were handled by choosing an investigation period of 12 months. This way, seasonal variations during the observation period were reduced. Therefore, steady state conditions were assumed. Based on the defined system boundary, three material streams had to be considered in the mass balance: substrate, biogas and digestate. Recycled digestate was not considered in the balance, since it is not leaving the system boundary (Figure 2.1). In case of solid-liquid-separation prior to recycling of the liquid digestate, both fractions were considered in the mass balance.

The following equation was used for steady-state mass balancing:

$$\Delta m = 0 = m_{sub} - m_{gas} - m_{dig} \quad (2.1)$$

With m_{sub} as mass of the substrate, m_{gas} as mass of the biogas and m_{dig} as mass of digestate.

2.4.3.1 Substrate

The masses and/or flow rates of substrate input were measured at every BP. Liquid substrate intake was measured or calculated as flow rate and converted to mass assuming a density of 1000 kg m^{-3} due to the high water contents of more than 90%.

2.4.3.2 Biogas

Measurement equipment for biogas flow is rarely available at the examined agricultural biogas plants. In order to apply a common procedure, the amount of utilized biogas was assumed to be equal to the produced amount of biogas, which was based on the amount of electricity, which was fed into the grid. This value was measured and recorded by grid operators and is the only reliable value that is available for each of the BP. Losses by biogas leakages in pipes, digester roofs or pressure relief valves were not measured and could therefore not be considered.

For the calculation of produced biogas, the following assumptions were made:

- the transformation loss between the feed-in point and the CHP unit is 2% of the amount of electricity fed in, which is the average value of all examined BPs for which this transformation loss could be calculated based on alignment of electricity measurement at CHP units and at the grid access point;
- gas leakages and losses, like gas burned in the emergency flares, were not considered;
- for BPs using more than one CHP unit: The fed-in electricity from the BP was allocated to single CHP units by their rated power and operating hours in the investigated 12-month period;
- the electrical efficiency of CHP units was assumed to be equal to the published values by the manufacturers minus 3.1%, which reflects the average efficiency loss as determined by Aschmann and Effenberger [75]. Factors for efficiency loss are engine wear, site of installation above sea level, properties at different loads and engine settings. A higher accuracy in this value was not possible with the available data;
- the biogas was simplified to consist of methane and carbon dioxide only. The methane concentration was measured at every BP at least one time a month. The residual was assumed to be carbon dioxide only. Justification: Water vapor in produced biogas was

condensed by gas cooling at every BP. The condensed water was pumped into digestate storage tanks and accounts to digestate mass in the mass balance. Other trace gas components produce a negligible error.

The gross electrical energy produced by the CHP units of a BP was calculated by:

$$W_{gross} = 1.02 \cdot W_{grid} + W_{oc} \quad (2.2)$$

where W_{gross} gross electricity, W_{grid} electricity feed in grid and W_{OC} is the amount of produced electricity which is used internally by the BP. 31 of the examined biogas plants inject the total produced electricity, so that W_{OC} equals zero in these cases.

For BPs with more than one CHP unit, the ratio a_k of the electricity produced by a single CHP k was calculated by:

$$a_k = \frac{t_k \cdot P_k}{\sum_k t_k \cdot P_k} \quad (2.3)$$

The energy of utilized biogas in all CHP units of a BP was calculated by:

$$V_{gas} = \frac{E_{gas} - W_{PIO}}{NCV_{CH_4} \cdot x_{CH_4}} \quad (2.5)$$

where NCV_{CH4} the net calorific value, x_{CH4} the methane ratio and W_{PIO} the amount of energy from ignition oil, which was subtracted for BPs, which used pilot injection engines as CHP. Finally, the mass of biogas was calculated by:

$$m_{gas} = V_{gas} \cdot [x_{CH4} \cdot \rho_{CH4} + (1 - x_{CH4}) \cdot \rho_{CO2}] \quad (2.6)$$

With the densities ρ_{CH4} = 0.72 kg m^{-3} and ρ_{CO2} = 1.98 kg m^{-3} at temperature of 0°C and pressure of 101,325 kPa.

Relating the utilized volume of biogas to the amount of ODM of fed substrate in the same timespan leads to the on-site specific methane yield (SMY).

$$\text{On-site SMY} = \frac{V_{gas}}{m_{sub,ODM}} \quad (2.7)$$

2.4.3.3 Digestate

The mass and volume of digestate was not recorded at the examined BPs and there-fore for the calculation using the mass balance:

$$m_{dig} = m_{sub} - m_{gas} \quad (2.8)$$

2.4.3.4 ODM material balance

An ODM material balance was used to evaluate the plausibility of the mass balance. Mass of ODM for each substrate, gas and digestate (i) was calculated for each month j = 1…12 and summed up for the year.

Two cases were investigated. First, it was assumed, that biogas was produced from ODM only. Second, water incorporation of 10% of the mass of biogas was considered, originating from cellulose degradation during digestion.

Evaluation was done by calculating the ODM balance residual (ODMBR) in the following equation:

$$ODMBR\ (\%) = \frac{\sum_{sub\ i}\sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} - \sum_j m_{gas,j} \cdot (1 - w_{H2O}) - \sum_{dig\ g}\sum_j m_{dig,g,j} \cdot DM_{g,j} \cdot ODM_{g,j}}{\sum_{sub\ i}\sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j}} \cdot 100\% \quad (2.9)$$

with w_{H2O} = 0.1 for 10% water incorporation or w_{H2O} = 0 for neglecting water incorporation.

2.4.4 Energy Balance

The system boundary for energy and energy balances was chosen equal to the one for mass balance (Figure 2.1).

Energy flows associated with mass flows were examined to evaluate energy-based efficiency indicators as well as to prove the plausibility of the used process data for mass balancing. According to the defined system boundary the only mass associated energy intake is the substrate input. Energy outputs are biogas and digestate. The residual of the input energy leaves the process as a loss of heat and entropy as a result of the conversion process of the organic matter.

The following balance was applied to calculate the part of the substrate energy, which is lost in the digestion process as heat, entropy or leakage of biogas:

$$E_{loss} = E_{substrate} - E_{digestate} - E_{gas} \quad (2.10)$$

$E_{substrate}$ is the potential of the substrate fed in a BP as input. $E_{digestate}$ is the potential of the digestate as output, E_{gas} is the potential of produced biogas and E_{loss} is the potential lost during

the process (e.g. burned gas by emergency flare, leakage, open pressure relief valve, heat loss) (eq. 2.10).

The energy balance residual (EBR), was calculated as:

$$EBR\ (\%) = \frac{\sum_{sub\ i}\sum_j m_{sub,i,j}\cdot DM_{i,j}\cdot GCV_{i,j} - \sum_j V_{biogas,j}\cdot x_{CH4,j}\cdot GCV_{CH4} - \sum_{digestate\ g}\sum_j m_{dig,g,j}\cdot DM_{g,j}\cdot GCV_{g,j}}{\sum_{sub\ i}\sum_j m_{sub,i,j}\cdot DM_{i,j}\cdot GCV_{i,j}}\cdot 100\% \quad (2.11)$$

2.4.5 Specific methane potential of substrate mixtures

Six different methods were used to calculate the annual average ODM-specific me-thane potential (SMP) of the fed substrate mixtures of the 33 BPs. The formulas represent the ODM-weighted average of the SMP of the single substrates used. For methods based on energy quantities, the SMP was calculated by simply dividing the energy amount by the GCV of methane. By that, conversion losses are neglected.

2.4.5.1 Biochemical methane potential test (BMP)

The BMP is a batch test, with which the specific methane potential of the substrate can be measured directly. The mixture from direct BMP measurements was calculated by:

$$SMP_{BMP,SM} = \frac{\sum_{sub\ i}\sum_j m_{sub,i,j}\cdot DM_{i,j}\cdot ODM_{i,j}\cdot SMP_{BMP,i}}{\sum_{sub\ i}\sum_j m_{sub,i,j}\cdot DM_{i,j}\cdot ODM_{i,j}} \quad (2.12)$$

2.4.5.2 Values according to literature (KTBL)

The specific methane potential of the substrate mixture using KTBL values from literature was calculated by:

$$SMP_{KTBL,SM} = \frac{\sum_{sub\ i}\sum_j m_{sub,i,j}\cdot DM_{i,j}\cdot ODM_{i,j}\cdot SMP_{KTBL,i}}{\sum_{sub\ i}\sum_j m_{sub,i,j}\cdot DM_{i,j}\cdot ODM_{i,j}} \quad (2.13)$$

$SMP_{KTBL,i}$ is the SMP of a single substrate i from the KTBL- values, which are based on the results of biochemical methane potential test and are given for the most common agricultural substrates in Germany [62]. For rarely used substrates, for which KTBL values were not defined, $SMP_{BMP,i}$ values were used.

2.4.5.3 Fermentable organic dry matter (FOM)

The FOM is a part of ODM, according to equation 2.14. FOM considers that not all of the ODM can be anaerobically degraded. Calculation is done by subtracting a part of the fiber content from ODM, which is a substrate specific calculation of the so called fermentation coefficient f_i based on regression equations investigated by fermentation experiments in sheep stomach [13]. For manure, fermentation coefficients were defined based on BMP results [15-16].

$$FOM_i = f_i \cdot ODM_i \tag{2.14}$$

The specific methane potential of the substrate mixture based on FOM was calculated by:

$$SMP_{FOM,SM} = \frac{\sum_{sub\ i} \sum_j m_{sub,i,j}\ DM_{i,j} \cdot FOM_{i,j} \cdot SMP_{avFOM}}{\sum_{sub\ i} \sum_i m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j}} \tag{2.15}$$

SMP_{avFOM} is the average specific methane potential of FOM, which is used as a constant factor according to Weißbach [41] (eq. 2.16).

$$SMP_{avFOM} = 420\ \mathrm{L\ kg^{-1}} \tag{2.16}$$

For substrates without a regression equation by Weißbach [41,63–66], the fermentation coefficient f was calculated. The $SMP_{BMP,i}$ was used to determine the fermentation coefficient for FOM calculation by:

$$f_i = \frac{SMP_{BMP,i}}{SMP_{avFOM}} \tag{2.17}$$

2.4.5.4 Energy of fermentable organic dry matter (EFOM)

With EFOM, the FOM is considered energetically by measuring the gross calorific value of ODM and distinguishing degradable and non-degradable fraction using the fermentation coefficient from FOM-methodology according to Fischer et al. [67]. Herein, the non-degradable fraction is assumed to be lignin.

The specific methane potential of the substrate mixture based on the energy of FOM was calculated by:

$$SMP_{EFOM,SM} = \frac{\sum_{sub\ i} \sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} \cdot GCV_{FOM,i,j}}{\sum_{sub\ i} \sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} \cdot GCV_{CH4}} \tag{2.18}$$

$GCV_{FOM,i,j}$ is the gross calorific value of FOM, calculated according to equation 7 of Fischer et al. [67]. The gross calorific value of methane GCV_{CH4} was assumed to be 39.73 MJ m^{-3} [76].

2.4.5.5 Anaerobically degradable energy (adE)

The adE is the energy of anaerobically degradable parts of ODM, which is calculated by subtracting the energy of lignin from tE. In contradiction to EFOM methodology, the non-degradable part of ODM is not calculated using fermentation coefficients, but by estimating the lignin content of digestates from measured gross calorific values of the digestates. As lignin is assumed to be non-degradable, the energy of lignin in the substrate mixtures has to be the same amount as in the respective digestates.

The specific methane potential of the substrate mixture using the anaerobically de-gradable energy content was calculated by:

$$SMP_{adE,SM} = \frac{\sum_{sub\ i}\sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot GCV_{i,j} - \sum_{dig\ g}\sum_j m_{dig,g,j} \cdot DM_{g,j} \cdot ODM_{g,j} \cdot w_{lig,g,j} \cdot GCV_{lig}}{\sum_{sub\ i}\sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} \cdot GCV_{CH4}} \quad (2.19)$$

The lignin content w_{lig} in digestate was calculated from measured gross calorific values of the digestate according to the regression equation M1 by Mächtig et al. [42]. The authors stated a gross calorific value of lignin of 33.74 MJ kg^{-1} for this model, which was used here for GCV_{lig}.

2.4.5.6 Total Energy (tE)

The total energy content is calculated from measured gross calorific values and does not consider the different anaerobic degradability of substrates. The specific methane potential of the substrate mixture using the total energy content was calculated by:

$$SMP_{tE,SM} = \frac{\sum_{sub\ i}\sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot GCV_{i,j}}{\sum_{sub\ i}\sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} \cdot GCV_{CH4}} \quad (2.20)$$

2.4.6 Efficiency indicators

2.4.6.1 Yield efficiency

The yield efficiency (YE) is an efficiency indicator, which describes which part of the initial potential of the input was converted to the desired output of methane.

$$YE = \frac{amount\ of\ produced\ methane}{methane\ potential\ of\ input\ substrate} \quad (2.21)$$

The numerator can either be the mass of methane or the energy of methane. The denominator, which represents the initial potential, has consequently to be given in the same dimension.
YE was calculated using different methods to quantify the methane or energy potential.

2.4.6.1.1 Yield based on BMP

The YE based on biochemical methane potential tests YEBMP was calculated as follows:

$$YE_{BMP} = \frac{\sum_{month\ j} V_{gas,j} \cdot x_{CH4,j}}{\sum_{sub\ i}\sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} \cdot SMP_{BMP,i}} \quad (2.22)$$

2.4.6.1.2 Yield based on KTBL

The YE based on KTBL-values YEKTBL was calculated as follows:

$$YE_{KTBL} = \frac{\sum_{month\ j} V_{gas,j} \cdot x_{CH4,j}}{\sum_{sub\ i}\sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} \cdot SMP_{KTBL,i}} \quad (2.23)$$

$SMP_{KTBL,i}$ is the specific methane potential from the KTBL-values [62]. Where KTBL values were not defined, $SMP_{BMP,i}$ values were used.

2.4.6.1.3 Yield based on FOM

The YE based on methane potential of fermentable organic dry matter content YE_{FOM} was calculated as follows:

$$YE_{FOM} = \frac{\sum_{month\ j} V_{gas,j} \cdot x_{CH4,j}}{\sum_{sub\ i} \sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot FOM_{i,j} \cdot SMP_{FOM}} \quad (2.24)$$

2.4.6.1.4 Yield based on EFOM

The YE based on the energy of fermentable organic dry matter YE_{EFOM} was calculated as follows:

$$YE_{EFOM} = \frac{\sum_{month\ j} V_{gas,j} \cdot x_{CH4,j} \cdot GCV_{CH4}}{\sum_{sub\ i} \sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} \cdot GCV_{FOM,i,j}} \quad (2.25)$$

2.4.6.1.5 Yield based on adE

The YE based on the energy of anaerobically degradable part of the substrate YE_{adE} was calculated as follows:

$$YE_{adE} = \frac{\sum_{month\ j} V_{gas,j} \cdot x_{CH4,j} \cdot GCV_{CH4}}{\sum_{sub\ i} \sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot GCV_{i,j} - \sum_{dig\ g} \sum_j m_{dig,g,j} \cdot DM_{g,j} \cdot ODM_{g,j} \cdot w_{lig,g,j} \cdot GCV_{lig}} \quad (2.26)$$

2.4.6.1.6 Yield based on tE

The YE based on the total energy of substrate YE_{tE} was calculated as follows:

$$YE_{tE} = \frac{\sum_{month\ j} V_{gas,j} \cdot x_{CH4,j} \cdot GCV_{CH4}}{\sum_{sub\ i} \sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot GCV_{i,j}} \quad (2.27)$$

2.4.6.2 Conversion efficiency

The conversion efficiency (CE) is an efficiency indicator, which describes which part of the initial potential of the input was converted.

$$CE = \frac{potential\ of\ input\ substrate - potential\ of\ the\ digestate}{potential\ of\ input\ substrate} \quad (2.28)$$

Different methods were used for the calculation of CE.

2.4.6.2.1 Conversion based on BMP

The CE based on biochemical methane potential tests CE_{BMP} was calculated as follows:

$$CE_{BMP} = \frac{\sum_{sub\ i} \sum_j m_{sub,i,j} \cdot DM_{sub,,i,j} \cdot ODM_{sub,i,j} \cdot SMP_{BMP,i} - \sum_{dig\ g} \sum_j m_{dig,g,j} \cdot DM_{g,j} \cdot ODM_{g,j} \cdot SMP_{BMP,dig,g,j}}{\sum_{sub\ i} \sum_j m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} \cdot SMP_{BMP,i}} \quad (2.29)$$

The $SMP_{BMP,dig}$ describe how much gas can be produced out of the digestate by an additional hydraulic retention time of 60 days and 37 °C.

2.4.6.2.2 Conversion based on FOM

The CE based on fermentable organic dry matter CE_{FOM} was calculated as follows:

$$CE_{FOM} = \frac{\sum_{sub\ i}\sum_{j} m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} - \sum_{dig\ g}\sum_{j} m_{dig,g,j} \cdot DM_{g,j} \cdot ODM_{g,j}}{\sum_{sub\ i}\sum_{j} m_{sub,i,j} \cdot DM_{i,j} \cdot FOM_{i,j}} \quad (2.30)$$

Due to missing correlation equations to calculate the residual FOM in the digestate, the amount of degraded organic matter is set as numerator, as by the theory of the method degradation can only occur from FOM.

2.4.6.2.3 Conversion based on EFOM

The CE based on energy fermentable organic dry matter CE_{EFOM} was calculated as follows:

$$CE_{EFOM} = \frac{\sum_{sub\ i}\sum_{j} m_{sub,i,j} \cdot DM_{i,j} \cdot GCV_{i,j} - \sum_{dig\ g}\sum_{j=1}^{12} m_{dig,g,j} \cdot DM_{g,j} \cdot GCV_{g,j}}{\sum_{sub\ i}\sum_{j} m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j} \cdot GCV_{FOM,i,j}} \quad (2.31)$$

Due to missing correlation equations to calculate the residual FOM in the digestate and the inherent energy, the amount of converted total energy is set as numerator, as by the theory of this method the converted energy can only be released from degradation of FOM.

2.4.6.2.4 Conversion based on adE

The CE based on the energy of anaerobically degradable part of the substrate CE_{adE} was calculated as follows:

$$CE_{adE} = \frac{\sum_{sub\ i}\sum_{j} m_{sub,i,j} \cdot DM_{i,j} \cdot GCV_{i,j} - \sum_{dig\ g}\sum_{j} m_{dig,g,j} \cdot DM_{g,j} \cdot GCV_{g,j}}{\sum_{sub\ i}\sum_{j} m_{sub,i,j} \cdot DM_{i,j} \cdot GCV_{i,j} - \sum_{dig\ g}\sum_{j} m_{dig,g,j} \cdot DM_{g,j} \cdot ODM_{g,j} \cdot w_{lig,g,j} \cdot GCV_{lig}} \quad (2.32)$$

CE_{adE} describes the conversion with the assumption that lignin cannot be degraded.

2.4.6.2.5 Conversion based on tE

The CE based on total energy CE_{tE} was calculated as follows:

$$CE_{tE} = \frac{\sum_{sub\ i}\sum_{j} m_{sub,i,j} \cdot DM_{i,j} \cdot GCV_{i,j} - \sum_{dig\ g}\sum_{j} m_{dig,g,j} \cdot DM_{g,j} \cdot GCV_{g,j}}{\sum_{sub\ i}\sum_{j} m_{sub,i,j} \cdot DM_{i,j} \cdot GCV_{i,j}} \quad (2.33)$$

GCVg,j describes the energy content in the digestate without distinguishing the non-degradable part.

2.4.6.2.6 Conversion based on ODM

The CE based on the organic dry matter content of the substrate CE_{ODM} was calculated as follows:

$$CE_{ODM} = \frac{\sum_{sub\ i}\sum_{j} m_{sub,i,j} \cdot DM_{sub,,i,j} \cdot ODM_{sub,i,j} - \sum_{dig\ g}\sum_{j} m_{dig,g,j} \cdot DM_{dig,g,j} \cdot ODM_{dig,g,j}}{\sum_{sub\ i}\sum_{j} m_{sub,i,j} \cdot DM_{i,j} \cdot ODM_{i,j}} \quad (2.34)$$

2.5 Results and Discussion

2.5.1 Mass & Energy balance

The efficiency determination was based on mass and energy balances. They are fundamental for subsequent calculation of efficiency indicators. The balance residual is determined for ODM material balance and energy balance of the 33 investigated BPs (eq. 8 and 10). Based on the balance residuals the credibility of measured mass and energy flows can be evaluated [60].

The results show negative as well as positive balance residuals for ODM material and energy balances, which may be caused by several reasons (Figure 2.2). Positive values indicate lower mass and energy output than input. Negative values indicate a higher mass and energy output than input. Random residuals cannot be completely avoided based on possible non-steady state conditions and the error in sampling regarding the place and time, e.g. the DM and ODM content of substrates show daily variation [77]. The accuracy of DM and ODM measurements between the laboratories have a small deviation of less than 1% and consequently only have a minor effect on the residuals, according to the internal validation of the participating laboratories. Therefore, the calculated residuals cannot solely be based on the measurement accuracy of the laboratory methods. Hence, a more likely reason is the on-site data accuracy.

Positive ODMBRs were observed for 10 BPs. A possible reason for a positive ODMBR is a too high assumed feeding mass by errors in measurement device as well as unknown and unrecorded substrate inputs. Addition of unrecorded substrate streams like rain water or silage seeping water lead to a dilution of digestate and therefore a lower ODM con-centration, which consequently results in an underestimation of the digestate´s potential. Another reason for positive ODMBRs could be the assumption of a too high CHP unit efficiency. This results in a lower calculated biogas yield and a positive ODMBR. A leakage of biogas from pipes and pressure relief valves leads to the same error.

In contrast, negative ODMBRs can result from an assumption of a too low CHP unit efficiency. An error in substrate mass measurement devices, e. g. by omitted calibration, can also lead to a negative ODMBR, if the measured mass is smaller than the real input mass.

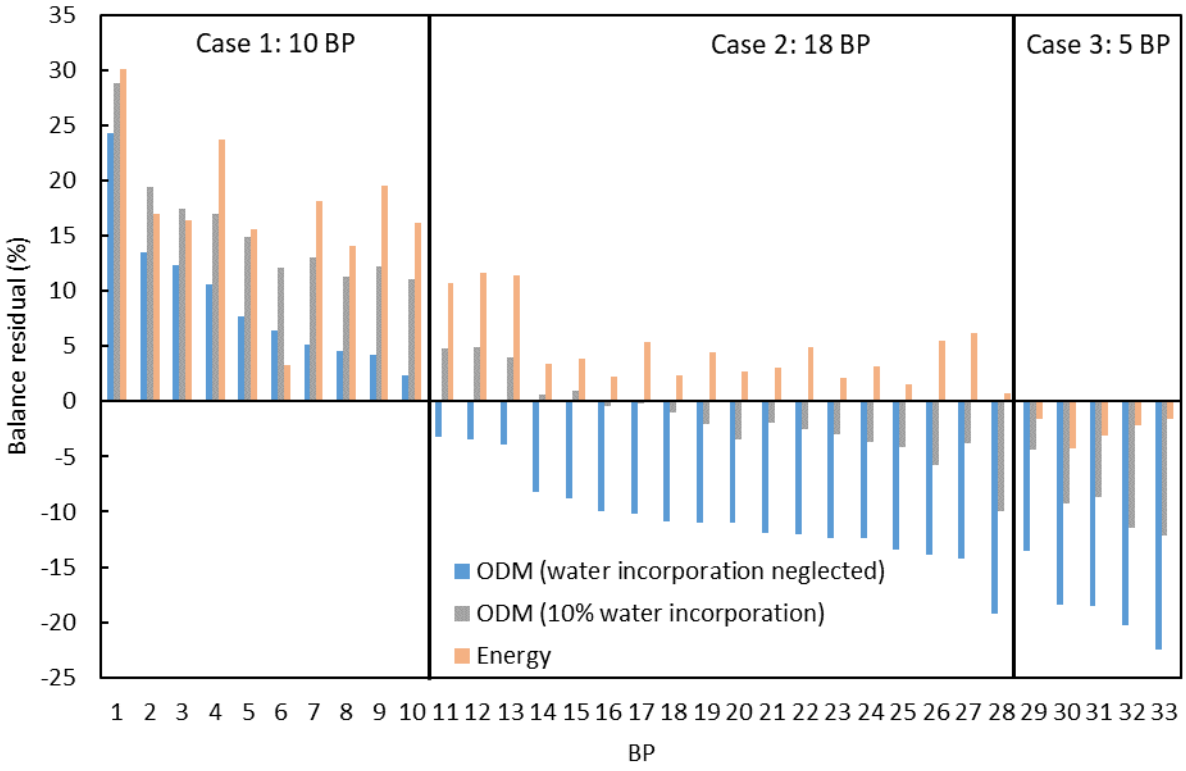

Figure 2.2 Balance residual of the organic dry matter content (ODM) material balance without and with considering a 10% water incorporation and the energy balance for 33 biogas plants (BP). A positive value means missing mass/energy in the output. BPs are grouped in three categories (Case 1: positive ODM and energy balance, Case 2: negative ODM balance and positive energy balance and Case 3: negative ODM and energy balance), sorted by the three cases at first and the ODM balance residual without consideration of water incorporation as second

However, both cases randomly occur across all plants and cannot explain that the most BPs (70%) show negative ODMBRs. A methodical error is the neglect of water in-corporation in ODM during the biogas production process. Water incorporation leads to an overestimation of ODM content via biogas output, as biogas is assumed to be built solely from ODM. Based on stoichiometric calculation for cellulose conversion the necessary water addition is 0.11 g g^{-1} Cellulose. This results in a fraction of 10% of biogas mass build from water. Pröter et al. [69] calculated a value of 11.25% of water incorporation in biogas for a maize silage. Using this factor of 11.25% water incorporation for the substrate mixtures of the BPs leads to an ODMBR of -3% instead of -7% averaged across all investigated biogas plants. However, for BPs with a positive ODMBR, the residuals increase proportionally (maximum +29% instead of +24%). The extent of water incorporation de-pends on the substrate´s constituents. The investigated BPs use diverse substrates in substrate mixtures, so that using a fixed value for respecting water incorporation for all BPs is not justifiable. Anyway, by disregarding water incorporation,

negative ODMBRs are the expected case for accurate process data. Ultimately, the water incorporation only effects the ODM balance for checking the mass balances plausibility and not the mass balance itself.

Even though EBRs are also affected by measurement errors in mass balance, there are other possible factors responsible for the distribution. A positive EBR is observed at more than 80% of the BPs, which appears to be caused by two main factors. Energy outputs without a relation to the mass flow like heat and entropy loss based on exothermal reactions cannot be detected by the chosen approach. Furthermore, the calculated biogas yield might be too low due to overestimation of CHP unit´s electrical efficiency or due to gas losses. Biogas loss can happen, amongst other reasons, through leakages and the pressure relief valves, just as Liebetrau et al. [78] determined emission factors of agricultural BPs to be in the range of 1.1 to 13.7%$_{CH4}$ of the total production. A third reason might be, like al-ready mentioned for positive ODMBR, that unrecorded substrate mass was fed to the bio-gas plant. Even if this unrecorded mass was only water without energy content, it would lead to a wrong mass balance assuming to low digestate mass and therefore would cause a lower energy output by the digestate mass flow.

Negative EBRs are smaller than 5% among all BPs and are only shown by 20% of the BPs. The negative EBRs are linked with the energy balance in which strongly negative ODMBRs also result in negative EBRs. Therefore, reasons for negative EBRs are the same as for negative ODMBRs, i.e. possibly underestimated input mass or underestimated CHP unit efficiency leading to overestimated biogas yields. A negative EBR can be reported only for BPs with a negative ODMBR of more than 14%. This reveals the large impact of the mass balance, as errors here are reproduced in the energy balance.

The reflection of either ODMBR or EBRs alone does not allow a distinct decision regarding most probable errors and the credibility of the material and energy flows. The coherence of mass and energy balance reveals more useful information. From Figure 2.2, three cases can be distinguished:

1. positive ODM balance residual and positive energy balance residual

10 BPs show a positive value of ODMBR and EBR. This positive ODMBR increases the positive EBR. For these few plants a clear positive error in feeding mass measurement device, an overestimation of CHP unit efficiency or biogas leakage is assumed. However, correction of this data is not possible in hindsight. Operators of these BPs should check the accuracy of their measurement devices and the efficiency of the CHP unit.

2. negative ODM balance residual and positive energy balance residual

18 BPs show a negative ODMBR and positive EBR. This is attributed to water incorporation and entropy loss. A high data quality for the investigated BPs can be assumed, but more detailed research into water incorporation and entropy loss are necessary to be more specific. From the presented methodology this is the expected case.

3. negative ODM balance residual and negative energy balance residual

5 BPs show negative EBRs, which is generally impossible. However, the negative residuals are comparably small. In coherence with the negative ODMBRs the most probable errors are negative deviations in feeding mass measurement or an underestimated CHP unit efficiency. In this case, the accuracy of mass measurement should also be checked by plant operators.

The residuals follow reasonable directions only in case 2. Therefore, the evaluation suggests that only the 55% of the examined biogas plants give credible results on mass and energy balances by the chosen approach.

BP 12 is a research biogas plant, where data quality is known to be accurate. This BP is one of the BPs with a negative ODM and a positive EBR. This fact strengthens the assumption that BPs with this combination are credible.

The findings can be further distinguished with regard to the diversity of the process parameters of the examined BPs. For BPs fed with 100% energy crops, in every case a negative ODMBR and a positive EBR has been found. The ODM balance of these BP are credible. Different to that all BP with a power production less than 100 kW and also 4 of 6 BP with a manure content higher than 75% show a positive balance residual for energy and ODM. The reason for the latter is, that the installation of measurement devices, e.g. for manure mass flows, is not economically feasible on small-scale BPs. The balances of these plants are less credible.

The ODM and energy balance reveals the problems in carrying out an efficiency analysis. The analysis is based on both balances. The necessary assumptions and the use of on-site process data can result in low accuracy, mainly due to missing measurement equipment or inadequate calibration. The inability to determine water incorporation, entropy loss and gas loss for full-scale biogas plants prevent the determination of a correction factor.

2.5.2 Specific methane potential

The specific methane potentials (SMP) from substrate mixtures of 33 biogas plants (BP) in Figure 2.3 were determined by literature values of Association for Technology and Structures in Agriculture (KTBL), biochemical methane potential test (BMP), fermentable organic matter (FOM), energy of fermentable organic matter (EFOM), anaerobically degradable energy (adE), total energy (tE) and the on-site measured specific methane yield (on-site SMY). $SMP_{KTBL,SM}$,

$SMP_{BMP,SM}$, $SMP_{FOM,SM}$ and $SMP_{EFOM,SM}$ show similar tendency for the specific methane potential between the BPs (Figure 2.3). The tendency is also similar to the on-site SMY, which is the specific methane yield of the fed substrate mixtures. This indicates a good sensitivity of the methods. However, $SMP_{KTBL,SM}$, $SMP_{BMP,SM}$, $SMP_{FOM,SM}$ and $SMP_{EFOM,SM}$ are mostly lower compared to the on-site SMY. The main reason is an underestimation of the potential by the methods, as discussed later. Another possible reason, like false process data, is only a possibility for 5 of 33 BPs (Case 3, Figure 2.3), by underestimation of the fed substrate mass and/or underestimation of CHP unit efficiency.

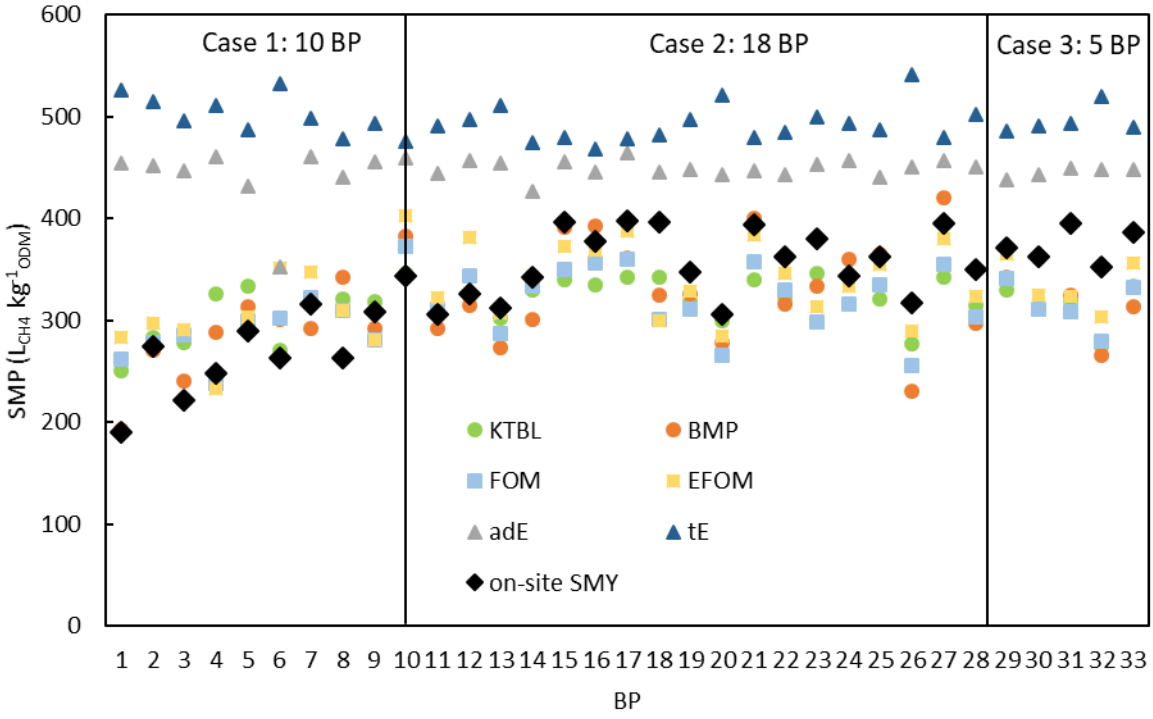

Figure 2.3 The specific methane potential (SMP) from substrate mixtures of 33 biogas plants (BP) determined by literature values of Association for Technology and Structures in Agriculture (KTBL), biochemical methane potential test (BMP), fermentable organic matter (FOM), energy of fermentable organic matter (EFOM), anaerobically degradable energy (adE), total energy (tE) and the on-site measured methane yield (on-site SMY). BPs are separated according to three cases (Case 1: positive ODM and energy balance, Case 2: negative ODM balance and positive energy balance and Case 3: negative ODM and energy balance)

$SMP_{AdE,SM}$ and $SMP_{tE,SM}$ are much higher than SMP of the other methods (Figure 2.3). As the methods for adE and tE give energy values as results, they had to be converted to methane yields for comparison. This was done by dividing the energy values by the gross calorific value of methane (eq. 2.19 and 2.20). By that, losses by chemical conversion of substrates to methane

are neglected, leading to higher SMP values. Within the other methods, these losses are methodologically included.

$SMP_{adE,SM}$ are lower than $SMP_{tE,SM}$, as anaerobically non-degradable lignin in the substrates is subtracted from the total energy potential by using adE. The sensitivity of the calculated $SMP_{tE,SM}$ and $SMP_{adE,SM}$ is lower than for the other methods. This is expected for $SMP_{tE,SM}$, as this value does not reflect the anaerobic degradability of the substrate mixture. In contrast, $SMP_{adE,SM}$ respects the composition of the substrate mixture but does not respect the accessibility of the degradable components for microbial degradation. The degradable components hemicellulose and cellulose are typically incrusted by lignin, which makes them not accessible for microbial degradation without physical pretreatment.

Figure 2.2 and Figure 2.3 indicate an effect between the SMY of a BP and the ODMBR. The SMY correlates also according to the fed manure (Table 2.1), because of less SMY of manure compared to energy crops.

Figure 2.3 also reveals the tendency that a negative ODM and energy balance follow in lower estimated SMP compared to the on-site SMY, during positive ODM and energy balance follow in a higher estimated SMP compared to the on-site SMY, according to an aforementioned probable negative/positive feeding mass error. These findings support the assumption, that the data quality is low for 45% of the BPs.

Besides the SMP of the substrate, the methane potentials of the digestate were used to determine the conversion efficiency (CE). Only the methods BMP, adE and tE determine the potential of digestate (Figure 2.4). For FOM and EFOM a required fermentation coefficient for the digestate is not determinable.

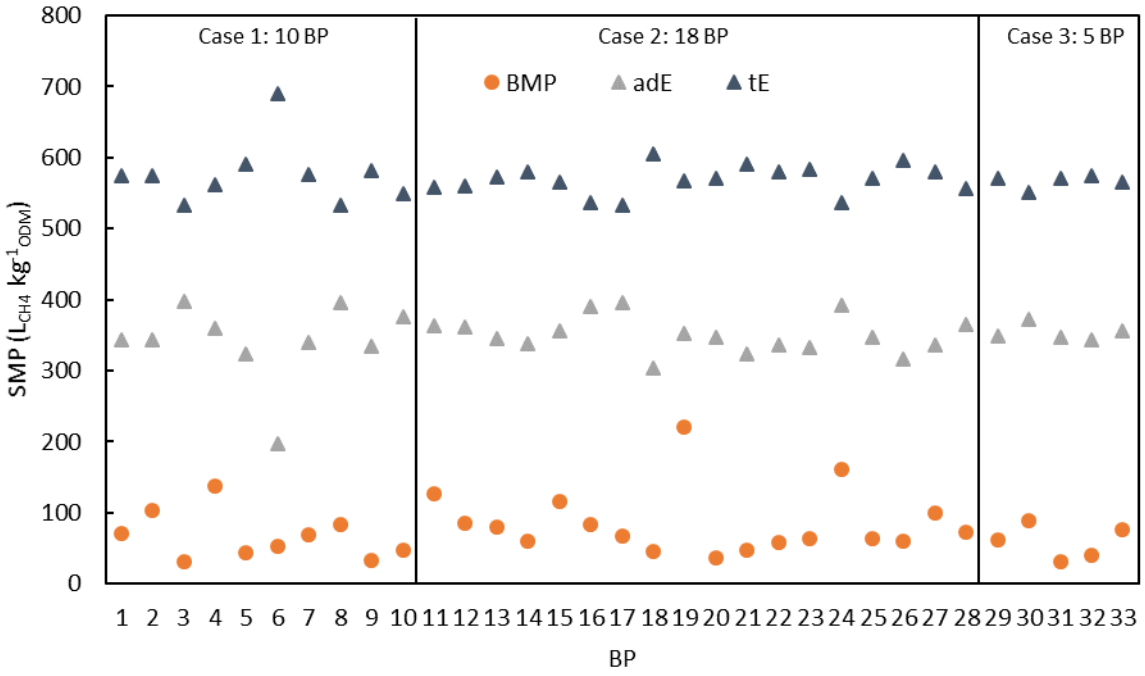

Figure 2.4 The spec. methane potential of digestate (SMP) of 33 biogas plants (BP) determined by biochemical methane potential test (BMP), anaerobically degradable energy (adE) and total energy (tE), based on the ODM in digestates.

In contrast to Figure 2.3 the SMP of digestates in Figure 2.4 were determined by biochemical methane potential test (BMP), anaerobically degradable energy (adE) and total energy (tE), based on the ODM in digestates. Again, the energy of adE and tE was converted to SMP by dividing with the gross calorific value of methane and by that neglecting losses of conversion. The potentials show major differences based on different assumptions in the three methods.

$SMP_{tE,dig}$ was the highest calculated SMP and the values are even higher, than the SMP of the substrates calculated by this method, which is caused by using ODM-specific values. In accordance with the lignin ratio in ODM, the ODM specific energy in digestate is higher than in substrate. Since low calorific components of ODM are degraded (mainly carbohydrates with around 17-18 MJ kg^{-1}), high calorific lignin (around 25-26 MJ kg^{-1} [70]) remains undigested. This is also the reason why the pattern of tE and adE of the 33 BPs is symmetrical (Figure 2.4). Higher $SMP_{tE,dig}$ means higher lignin contents, resulting in lower $SMP_{adE,dig}$.

The $SMP_{adE,dig}$ in Figure 2.4 is around 3 times higher than $SMP_{BMP,dig}$. Most probable reason for the difference is that hemicellulose and cellulose in the digestates are incrusted by lignin and not accessible for microbial degradation in BMP test. In median, based on the results of this study, 39% of the energy potential of the digestates are lignin. Additional 48% of the energy

potential of the digestates are not accessible to microbial degradation, as calculated by the difference of adE and BMP. This should be the maximum possible potential, which is achievable with further treatment. Further research on this topic could lead to a useful parameter set in future. However it has to be mention, that the temperature effects the $SMP_{BMP,dig}$ strongly [79].

2.5.3 Conversion & yield efficiency

The yield efficiencies (YE) were calculated for all BPs according to six different methods based on eq. 2.21. The results are listed in Table 2.3, grouped in the three described cases.

The calculated YEs show a similar distribution like the SMPs calculated for different methods in Figure 2.3. Table 2.3 clearly shows that the mass balance also effects the results of YE for every method. BPs with a positive ODM and energy balance residual (case 1) show low YE for every method according to a positive feeding mass error. Different to that, YE of BP with negative ODMBRs and EBRs (case 3) show a tendency for high YE according to a negative feeding mass error, but the difference to case 2 is not that obvious.

Table 2.3 yield efficiency (YE) of 33 biogas plants (BP) determined by literature values of Association for Technology and Structures in Agriculture (KTBL), biochemical methane potential test (BMP), fermentable organic matter (FOM), energy fermentable organic matter (EFOM), anaerobically degradable energy (adE) and total energy (tE). The minimum (Min), maximum (Max) and median values were calculated for each parameter. The median of BP fitting Case 2 were also calculated.

		yield efficiency [%]					
	BP	BMP	KTBL	FOM	EFOM	adE	tE
Case 1	1	98	76	73	67	42	36
	2	101	97	98	92	61	53
	3	92	79	77	76	50	45
	4	86	76	104	107	54	49
	5	92	87	96	95	67	59
	6	88	98	87	75	75	50
	7	108	99	98	91	69	63
	8	77	82	85	85	60	55
	9	106	97	110	110	68	62
	10	90	99	92	85	75	72
Case 2	11	105	97	99	95	69	62
	12[a]	104	101	95	86	71	66
	13	114	103	109	101	69	61
	14	114	104	103	100	80	72
	15	101	117	113	107	87	83
	16	96	113	106	102	85	81
	17	110	116	110	103	86	83
	18	122	116	132	132	89	82
	19	107	109	112	106	77	70
	20	110	102	115	107	69	59
	21	98	116	110	103	88	82
	22	115	113	110	105	82	75
	23	114	110	128	122	84	76
	24	96	109	109	103	75	70
	25	99	113	108	102	82	74
	26	138	115	124	109	70	59
	27	94	116	111	104	87	82
	28	118	111	115	108	78	70
Case 3	29	109	113	109	102	85	76
	30	100	116	116	111	82	74
	31	122	124	128	122	88	80
	32	132	129	126	116	79	68
	33	123	116	116	109	86	79
	Min	77	76	73	67	42	36
	Max	138	129	132	132	89	83
	Median	105	109	109	103	77	70
	Median Case 2	109	110	112	105	79	73

[a] BP 12 is a research biogas plant with high measurement accuracy

Table 2.4 conversion efficiency (CE) of 33 biogas plants (BP) determined by biochemical methane potential test (BMP), fermentable organic matter (FOM), energy fermentable organic matter (EFOM), anaerobically degradable energy (adE), total energy (tE) and organic dry matter content (ODM). The minimum (Min), maximum (Max) and median value were calculated for each pa-rameter. The median of BP fitting Case 2 were also calculated.

	conversion efficiency [%]						
	BP	BMP	FOM	EFOM	adE	tE	ODM
Case 1	1	89	101	123	77	66	69
	2	90	104	121	80	70	73
	3	95	80	104	68	61	64
	4	96	133	159	80	72	75
	5	97	123	120	84	75	79
	6	94	86	80	80	53	64
	7	96	91	117	88	82	84
	8	93	99	107	75	69	72
	9	98	121	144	89	82	85
	10	99	100	104	92	88	90
Case 2	11	97	101	111	81	73	76
	12[a]	94	91	101	84	77	80
	13	93	111	120	81	72	75
	14	96	95	105	84	76	80
	15	97	111	112	91	87	89
	16	97	106	105	87	83	85
	17	98	106	109	91	89	90
	18	98	126	136	92	85	88
	19	85	105	112	82	74	78
	20	95	106	112	72	61	65
	21	99	108	106	91	85	88
	22	97	108	112	87	80	83
	23	96	116	125	86	78	81
	24	89	106	108	79	73	75
	25	96	100	104	84	76	80
	26	91	96	120	77	64	67
	27	98	108	112	93	89	91
	28	93	106	109	78	70	73
Case 3	29	97	104	100	83	75	79
	30	93	97	105	77	69	73
	31	98	115	117	85	77	80
	32	95	104	112	76	66	69
	33	95	101	106	84	77	80
	Min	85	80	80	68	53	64
	Max	99	133	159	93	89	91
	Median	96	105	112	84	75	79
	Median Case 2	95	106	112	85	77	80

[a] BP 12 is a research biogas plant with high measurement accuracy

Similar to YE in Table 2.3, CEs of all BPs are listed in Table 2.4. The CE was determined based on the potentials of the substrate and the digestate determined by BMP, FOM, EFOM, adE, tE and ODM (Table 2.4). Dependencies between process data, e.g. process temperature, HRT or OLR, and efficiency indicators were not observed and are therefore not presented.

The KTBL values and the BMP values are based on measured values in a BMP test. Both show a YE higher than 100%. It appears that the methods underestimate the real SMP. The values of the research BP (BP 12) support these results even if the values are near to 100% (BMP 104% and KTBL 101%). Efficiency values higher than 100% was also reported for both in literature [80,81]. Underestimation of $SMP_{BMP,SM}$ and $SMP_{KTBL,SM}$ can result, due to the effects of co-digestion in a full-scale BP instead of mono-digestion in the laboratory batch test [82,83]. Pöschel et al. [28] estimated 10% higher values. Other possible reasons could be methodological differences between lab and full-scale, like the higher temperature in a full-scale biogas plant, a higher consumption for bacterial growth based on a missing steady state condition in laboratory tests as well as unacclimated inoculum or a too short HRT in laboratory tests [84].

CE_{BMP} is the state-of-the-art method to determine the CE. A CE higher than 100% is not possible for this method. The CE reveals the achievable extra potential by extending the HRT of gas-tight digesters for 60 days in a 37 °C heated digester. In Germany, the total HRT of gas-tight digesters built after 2016 and the HRT of a secondary digester built after 2011 are already higher than 150 days according to EEG 2017. This leads to a high CE_{BMP} found in this study and also to a small spread in the values, which corresponds to results by Ruile et al. [43] of 21 German biogas plants. The CE_{BMP} reveals a small potential in increasing the digestion duration nowadays compared to lower CE_{BMP} in other former studies [43,79,85], which is supported by a comparison of the SMP_{BMP} to the SMP_{BMP} of former studies [80,86]. Further optimization cannot be done for most BPs based on this. However, it is the only CE method, which can show the reachable potential by a longer HRT. This information is of interest for BPs operation in different countries today. For three outliers with a CE_{BMP} lower than 90%, clear reasons can be found, e.g. low retention time in heated system by feeding substrate with a high lignin content. CE_{FOM} and CE_{EFOM} show a higher spread for CE, but CE and YE higher than 100% can be reported for both. Values higher than 100% for YE_{EFOM} and YE_{FOM} are reasoned by underestimated SMP of the substrate. Lower residual ODM masses in the digestates than are expected by the fermentation coefficients used in these methods are responsible for CE_{EFOM} and CE_{FOM} values above 100%. Based on the results, the applied substrate specific fermentation coefficients are too low. In order to utilize FOM and EFOM for CE or YE calculations, more

research on fermentation coefficients is necessary. Especially, the variability of manure cannot be considered adequately by using a fixed fermentation coefficient, which only depends on the type of manure. For the research BP, both methods show a value lower than 100% (FOM 95% and EFOM 86%). Weißbach [87] analyzed the efficiency of three different biogas fermenters of the same biogas plant based on FOM and found CEs between 96.4 and 99.5% and YEs between 99.7 and 103.7%.

YE_{adE} and YE_{tE} are throughout lower than 100%, which is lower than that found with other methods. For the research plant BP 12 adE reach a value of 71% and tE of 66%. As YE_{adE} is applied for the first time here, comparative literature values are missing. However, it is possible to calculate expected values by stoichiometry with the so called Buswell's formula [88]. For example, for cellulose a maximum YE_{adE} of 95% can be expected based on a GCV of cellulose of 17.3 MJ kg-1. Based on the reference value for the specific methane yield of cellulose from VDI 4630 [49], a YE_{adE} of 86% is expected. For cellulose, YE_{adE} and YE_{tE} are equal, as cellulose is completely degradable under anaerobic conditions. The example shows, that the calculated YE_{adE} of the examined BPs are in a reasonable range.

CE_{adE} and CE_{tE} are lower than CE with other methods and show a higher spread compared to CE_{BMP}. The CE_{adE} is lower than CE_{BMP} in every case as expected by the different residual SMP in the digestates. Comparison of CE_{adE} and CE_{tE} shows the energy potential in lignin. The study reveals that in median 9% of the total energy of the substrate is stored in lignin. CE_{tE} and YE_{tE} can be used as a reference to compare the biogas process with other biomass conversion processes, like ethanol production, pyrolysis or biomass combustion. Moreover, CE_{tE} is revealing how much additional energy can be utilized from the digestate. 11-47% of the total energy potential is not used by the BPs according to the results of this work. Bio-economy concepts could increase the utilization of the potential. However, CE_{tE} and YE_{tE} are also strongly affected by the used substrate similar to CEODM and thereby hinder the comparison of BPs, which use substrates with different degradability.

CE_{ODM} is used several times for determining the CE and a clear divergence between the BPs can be reported. It is clearly impacted by the fed substrate. The ODM of maize is nearly completely anaerobically degradable, because of the low lignin content. Compared to that, cattle manure has a higher lignin content and a lower CE_{ODM}. Therefore, a comparison of two BPs with different feedstock like done here would not be useful. CE_{tE} and CE_{ODM} are strongly dependent to each other. Only for one BP the two parameters show 11% difference to each other. In every other case CE_{ODM} is 1-4% higher than CE_{tE} as expected, due to the linkage of ODM content and gross calorific value.

As shown, CE or YE are strongly dependent on the SMP of the substrate. KTBL, BMP, FOM and EFOM underestimate the substrate potential. AdE and tE are more coherent, but the sensitivity to the on-site methane yields of the BPs is low and the substrate´s degradability, as an interaction between biomass composition and accessibility for degradation, is not fully considered. Hence, more research is necessary to investigate and implement in-fluencing factors on SMP, especially to describe the differences between laboratory scale, where most of the determination methods were developed and commercial full-scale digestion, where the methods are to be applied. Typically, the accuracy of measurements is higher in laboratory experiments, but process conditions differ to those in full-scale biogas plants. From this point of view, it was a necessity to compare the methods with data from full-scale biogas plants, even though high measurement accuracy is difficult to achieve, as shown with presented mass and energy balances.

2.6 Conclusion

Overall, the results of the current research show that benchmarking agricultural biogas plants is challenging regardless of the method chosen. It is worthwhile to check the reliability of the recorded operating parameters by evaluating mass and energy balances, as shown by the fact that plausible results were obtained for only 55% of the investigated biogas plants. Regular calibration of the measuring instruments is therefore highly recommended for determining the biological efficiency, but is repeatedly neglected under practical conditions. However, this had no influence on the comparison of the different methods, as the statements were similar for all BPs.

A conclusive recommendation for a specific method to evaluate efficiency is not possible. YE_{KTBL}, YE_{BMP}, YE_{FOM} and YE_{EFOM} show a good relation to the field measurements, but all underestimate the methane potentials of the substrate. The probable reason for this is an underestimation of the fermentable fraction of the substrate. These conclusions are supported by the fact that CE_{FOM} and CE_{EFOM} being higher than 100%. To avoid this, further research is necessary, e. g. towards substrate characterization. The results of YE_{adE} and YE_{tE}, as well as CE_{adE} and CE_{tE}, are more coherent, but the sensitivity is low and the degradability of the substrate as an interaction between biomass composition and degradability is not fully considered. Based on the YE data, an evaluation of the BPs is not possible and not done here. A combination of CE_{BMP} and CE_{adE} is a promising approach, as it can reveal the achievable potential of further substrate pretreatments. This combination should be investigated in further research. Besides the values of CE_{BMP}, an evaluation of biogas plant operation is difficult as reference values are missing.

2.7 Supplementary Materials

Table S1. substrates ratio of feeding of the 33 investigated biogas plants (BP), MS = maize silage, GS = gras silage, WPS = whole plant silage, SB = sugar beet, CE = cereals, PO = Potato, LCM = liquid cow manure, SCM = solid cow manure, HM =horse manure, CM = chicken manure, LPM = liquid pig manure, SM = sheep manure, MSM = molasses of lactose production, BT = brewer's spent grains, FO = Fodder residuals, OT = others

	Energy Crops						Manure						Processing waste			
BP	MS	GS	WPS	SB	CE	PO	LCM	SCM	HM	CM	LPM	SM	MSM	BT	FO	OT
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
1	1	8					65	2	25							
2	14	7		1	2	2	71	5								
3		17			1			41			41					
4		36	28				36									
5	18	4	3	14			28	30								
6	5	14					72	6		10						
7	57	10			0		5			28						
8	17	73								11						
9	9	22	26		5			38								
10	54	9			14	5	8							12		
11	49	16						35								
12[a]	17	23	3		5		33	9	11							
13	20	5			1		68								6	
14	45	3			1		2		0	11	39					
15	100				0											
16	65										33					

[a] BP 12 is a research biogas plant with high measurement accuracy

	Energy Crops						Manure						Processing waste			
BP	MS	GS	WPS	SB	CE	PO	LCM	SCM	HM	CM	LPM	SM	MSM	BT	FO	OT
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
17	83	12			5											
18	47	29	23		2			4								
19	41				2		53	4								
20		47					46	7								
21	70	7	9	14												
22	54	3					52	2				8				
23	30	7	5	6			30	5								
24	22	9	17				51									
25	33	6	4				56									
26		19					55	20					5			
27	82		9	6	3											
28	22	0				5	73									
29	42	9	2		2		43									3
30	65		3					22		10						
31	28	4		2			58	5								
32	13	2	0		0		85									
33	43				6		33	12		7						

3 Food waste co-digestion in Germany and the United States: From lab to full-scale systems

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3.1 Abstract

Using food waste (FW) as a co-substrate in anaerobic digestion (AD) results in increased energy production, decreases in greenhouse gas emissions, and recycles the FW nutrients back to the land for producing crops. This research investigated food waste AD systems in the United States (US) and Germany (DE) that co-digested FW with dairy manure at the lab and full-scale. In DE, the post-consumer FW had 32–49% more CH_4 potential (477–499 mL_{CH4} g^{-1}_{VS}) than maize and grass silage (368 and 331 mL_{CH4} g^{-1}_{VS}) and solid and liquid manure (243 and 91 mL_{CH4} g^{-1}_{VS}). Methane production in the full-scale DE system with 66% FW (by volume) was 882 m^3_{CH4} d^{-1}, which was 37% higher than the laboratory results due to the 86-day retention and 42 °C AD conditions in the field. The pre-consumer FW in the US had a similar CH_4 potential (264–553 mL_{CH4} g^{-1}_{VS}), but due to the lack of heating in the full-scale system, 62% less CH_4 was produced than the lab-based potential. While DE requires pasteurization of FW for AD and bans FW bans to landfills, the US does not have specific requirements for FW treatment in AD or federal FW landfill policies, with a few forthcoming FW bans in some municipalities and states. As FW diversion and utilization in AD systems is expected to grow, it is important to understand the effect of FW in biogas production and nutrient content, comparisons between lab and field-scale results, and the effect of policy on FW utilization.

3.2 Keywords

Biogas, methane, anaerobic, policy, biochemical, manure

3.3 Introduction

Food waste (FW) is increasingly being investigated as a co-substrate in anaerobic digesters (AD) to increase biogas production and receive tipping fees. Levis and Barlaz [89] found that AD was the most environmentally beneficial FW treatment option, compared to composting and landfilling, reducing 395 kg CO_{2e} (per functional unit) due to avoided electricity generation and soil carbon storage from digestate utilization. In the United States (US), FW co-digestion is slowly increasing due to forthcoming FW landfill bans for the food industry in several US states, with most taking effect by 2020 [26]. In the US, FW is the 2nd most abundant input, after paper, in municipal landfills (60 million MT/yr), representing 31% of the US food supply [90]. Largely due to this FW input, US municipal landfills emit 108 MT_{CO2e} a^{-1}. While 600 landfills use biogas for energy, most US landfills only flare the biogas. Landfill conditions are not optimal and produce only a fraction of the biogas that could be produced in AD systems. Currently, there are not adequate FW digestion facilities to divert this waste due to the nascent nature of the FW diversion industry in the US [91].

Food waste diversion is standard practice in most European cities. The European Union (EU) has strict regulations for separation of household biowaste and reducing biowaste [92,93]. Yet, it is estimated that the EU could reduce an additional 10 - 50 MT_{CO2e} a^{-1} through better prevention and biological treatment of FW [35]. The German (DE) government has an additional regulation for FW separation [94] to increase the availability of FW as a substrate for AD and reduce associated costs [95]. The potential of biowaste for AD in DE was estimated to be 8.3 - 30.5 MT a^{-1}, which would result in 2.8 - 172 PJ of renewable energy if processed through AD [96]. While there is high energy potential and regulatory support for using FW in the EU and DE, there are additional requirements for using this waste as feedstock in AD. German regulations [97], which are based on EU regulations [35], require that the AD operate at > 50°C, or pasteurize the FW at > 70 °C for at least one hour prior to AD, to protect against epidemiological and phytohygienic concerns.

As FW use in AD increases, it is important to understand process stability during AD when using FW, the differences between lab and field-based performance, and the economic and regulatory implications of FW use. In the US, where co-digestion with maize silage (MS) is not utilized and manure-based digesters are the majority of the farm-based AD systems [98], co-digestion with FW was found to make AD a net positive investment for farmers with less than 250 dairy cows due to the associated tipping fees [99]. Banks et al. [77] found FW to be the most effective means of making dairy manure-based AD economically viable. El-Mashad and

Zhang's [100] model showed that adding FW up to 60% of the initial volatile solids (VS) in a manure-based AD would significantly increase methane (CH_4) yield, and Li et al. [101] concluded that a mixing ratio of 3:1 (by volume) was optimal for co-digesting cattle manure and kitchen waste, with a resulting CH_4 potential of 233 mL_{CH4} g^{-1}_{VS}. Additional studies have shown that biogas production can be enhanced 0.8 – 5.5 times when co-digesting FW with dairy manure compared to digesting dairy manure-only [102,103], but there is a lack of research comparing the effect of co-digesting FW, MS, grass silage (GS), even though it has been shown that substrate selection is vital in preventing adverse conditions within the AD environment, such as low pH, increased volatile fatty acids (VFA) concentrations, and accumulation of toxic substances [104].

Only a few previous studies have investigated FW digestion at the full-scale, with most previous studies operated at the batch-field or pilot-scale and without testing of the co-digestion ratios used at the farm-scale. Scano et al. [105] did conduct a six-month pilot-scale study and found a CH_4 potential of 430 mL_{CH4} g^{-1}_{VS} for fruit and vegetable waste from an Italian market. Lisboa and Lansing [106] showed the importance of buffering with FW additions, and Zhang and Jahng [107] focused on the role of trace elements in FW and piggery waste co-digestion in the lab and bench-scale (150 mL).

Despite previous studies on CH_4 production from FW utilizing biochemical methane potential (BMP) testing of individual FW sources [108,109], previous studies have not compared these BMP results to field conditions. Additionally, there has not been a comparative study between the dairy manure and food waste co-digestion systems utilized in the US to the mixed silage, FW, and manure digesters utilized in DE. The objectives of this study were to: 1) evaluate the contribution of FW in co-digestion systems in DE and the US through the use of BMP tests, 2) evaluate full-scale AD systems for CH_4 production and changes in pH, VS, nutrients, and VFAs during AD, 3) compare the lab-based BMP results to the respective full-scale AD systems to better understand effects of design, operational conditions, and substrate characteristics on full-scale operations, and 4) understand how differences in the US and DE polices affect FW utilization in AD. The results will provide better understanding of how rigorous lab-based testing relates to field conditions, which are often more dynamic. In addition, the differences in lab and field-based results in DE and the US are situated within the policy frameworks that exist in these countries, which heavily influences what AD substrates utilized and how the AD facilities are operated.

3.4 Material and Methods

3.4.1 Substrates and full-scale digester characteristics in Germany (DE)

Kitchen scraps (post-consumer waste) were collected daily or weekly using 120 L waste receptacles from 53 households and restaurants in Stuttgart, Germany. First, plastic and other impurities were sorted out manually. Then, the receptacle was emptied, the FW was chopped (<10 mm), and residuals in the receptacle were rinsed out with water. The chopped FW and the wash-water were pumped to a heating vessel and heated to 70 °C for at least one hour, as required by German law, before being added to the AD twice daily. Two months prior to this study, the FW (4.73 ± 0.11 m^3 d^{-1}) content in the digester was increased from ~50% to 66% of the total input volume. For the BMP analysis detailed below, both fresh (non-pasteurized) and pasteurized FW contents were tested for CH_4 potential.

Maize silage (MS) consisted of the entire corn stalk, including the corn cob, harvested at maturity (approximately 170 growing days) in October and stored after ensilage until the study commenced in June 2018. Grass silage (GS) consisted of high quality grass clippings harvested with a dry matter (DM) content of 35%. The daily inputs of MS (0.91 ± 0.01 t d^{-1}) and GS (0.68 ± 0.01 t d^{-1}) were 13 and 9% of the total volumetric input, respectively (Figure 3.1a). Composite silage samples were taken from five locations at least 15 cm within the silage pile and mixed.

Two types of dairy manure were added to the digester bi-weekly: 1) fresh dairy manure from the packed bedding dairy stalls, and 2) liquid manure that had been stored from the year prior. The liquid and solid manure (0.75 ± 0.23 t d^{-1}) were mixed to ease pumping to the AD and constituted 10% of the weekly AD input. There was an additional 2% of 'other' AD additions (0.13 ± 0.02 t d^{-1}) that mainly consisted of pre-consumer crop waste added directly to the digester.

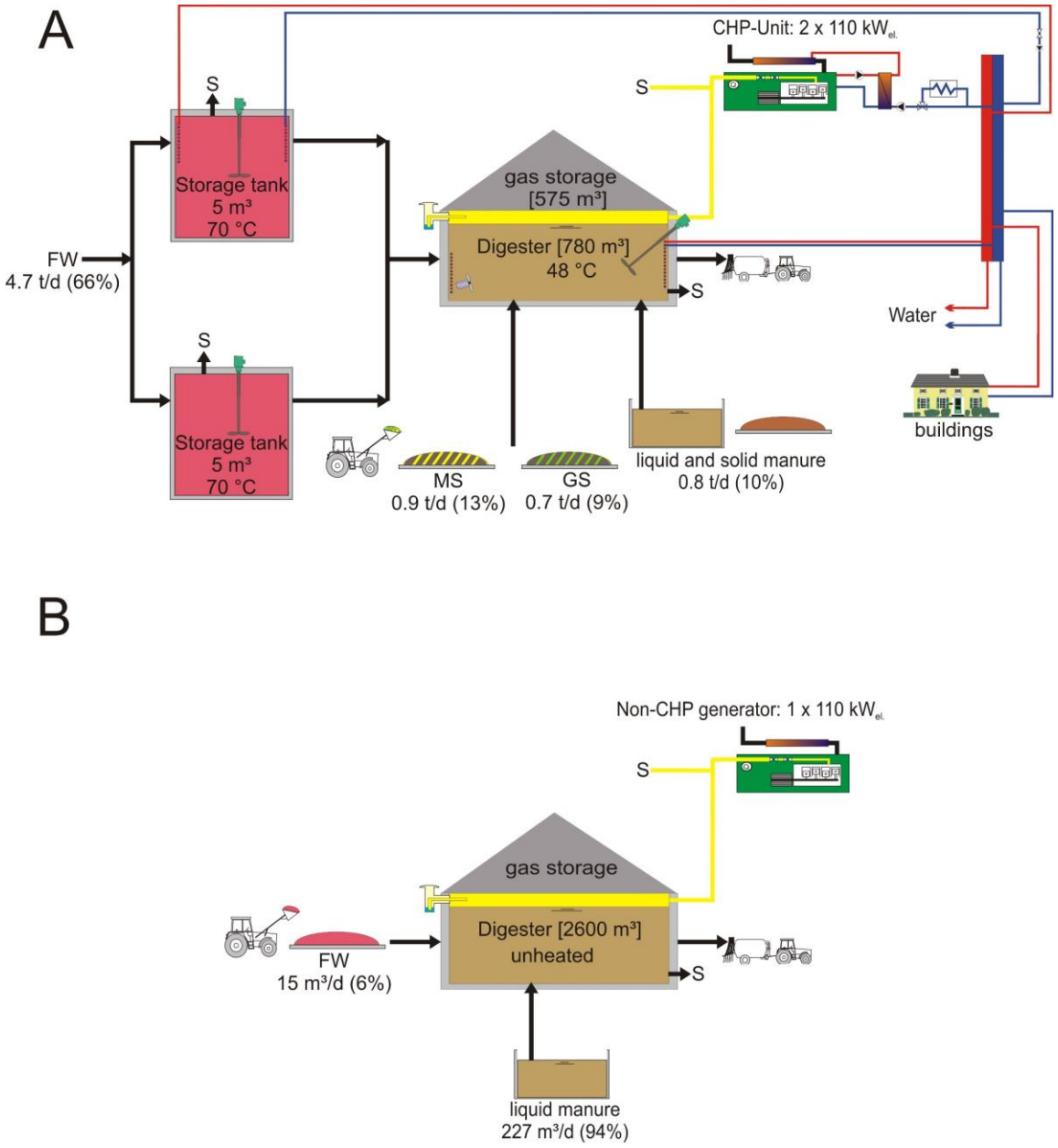

Figure 3.1 Diagram of the German (A) and US (B) farm anaerobic digestion systems, including the quantity of food waste (FW), maize silage (MS), grass silage (GS), and solid and liquid manure, with the percentage of each substrate to the total substrate inputs. The sampling (S) location as well as the generator and digester information for each system are shown.

The biogas plant consisted of a 780 m^3 complete mixed AD heated to 48 ± 0.4 °C and a 780 m^3 unheated post-AD storage (Figure 3.1a). To remove hydrogen sulfide (H_2S) from the biogas, $FeCl_2$ was added to the AD influent and air was injected to the AD headspace. The biogas was used by two 110 kW combined heat and power (CHP) generators (Model: Man-Motoren Typ 0836 LE; AVS BHKW GmbH, Ehningen-Stetten, Germany), with an electric efficiency of 38.6% and heat efficiency of 53.7%. Power was sold to the power grid, and heat was used for heating FW, the AD, water, and buildings on-site.

3.4.2 Substrates and full-scale digester characteristics in the United States (US)

Dairy manure and FW from manufacturing facilities (pre-consumer FW) was added into a covered lagoon digester in Rising Sun, Maryland, USA. The pre-consumer FW was delivered from three off-site manufacturing facilities for cranberry sauce, chicken fat for marinades, and meatball fat from frozen food processing, respectively, and one on-site ice-cream processing plant. The chicken processing FW was added once a week, the cranberry and meatball wastes were added twice a week, and the ice-cream waste was added daily. Combined, the FW (15 m^3 d^{-1}) was 6% by volume. The FW was co-digested with flushed dairy manure (227 m^3 d^{-1}), with the manure solids separated and storage in a short-term open storage lagoon (< 1 d) prior to entering the AD.

The covered lagoon digester (2,600 m^3) was unheated and unmixed, with a temperature ranging from 15-30°C (Figure 3.1b). The effluent from the digester was diluted with parlor wash water and used as barn flushing water. The biogas powered a 110 kW natural gas engine generator (Model MWM, Caterpillar Energy Solutions GmbH, Mannheim, Germany), which was used for on-site power. For H_2S removal, the biogas passed through a 210 L plastic drum filled with rusted iron and steel scrapings. A regenerative blower (Model - R5325R-50; Gast Regenair, MI, USA) was installed at the outlet of the scrubber and used to maintain a constant flow rate of biogas to the generator.

3.4.3 Laboratory-based biochemical methane potential (BMP) tests in DE and the US

A patented modification of the BMP process called the Hohenheim biogas yield test (HBT) was conducted at the State Institute for Agricultural and Bioenergy in Stuttgart, Germany. The procedure is detailed in Helffrich and Oechsner [110] and is based on the German guideline VDI 4630 [49] for BMP testing. Briefly, substrate and inoculum samples were collected and placed in 100 mL syringes without headspace and sealed with a plunger and silicone. Produced biogas was collected in the syringe, and the CH_4 content of the biogas was measured using an infrared-spectrometric methane-sensor (Pronova Anlaysetechnik, Berlin, Germany), with calibration before and after every measurement using a gas mixture of 40:60 CO_2:CH_4 [111]. Biogas measurements were taken when more than 20 ml of biogas had collected inside the syringe tubes.

For the BMP, the inoculum and individual substrates (FW, manure, MS and GS) collected from the German AD system were placed analyzed using triplicate treatments based on 2:1 inoculum to substrate ratio (ISR) on a VS basis and incubated at 37 ± 1 °C for 30 days [49]. Biogas production was corrected to standard conditions (273 K, 1013 hPA), and biogas production from the inoculum was subtracted from the substrate results [44]. Standard substrates were used

for testing confirmation, including concentrated feed (Raiffeisen Kraftfutterwerke Süd GmbH, Würzburg, Germany) and hay (Wiesen-Cobs, Marstall GmbH, Oberstaufen, Gerrmany). Prior to the BMP analysis, the MS and GS were frozen to avoid loss of acids and chopped using a Thermomix (Vorwerk & Co. KG, Wuppertal, Germany).

In DE, residual CH_4 potential tests of the digestate from the full-scale AD were conducted for 60 days at 37 °C and 48 °C without inoculum addition to quantify the residual CH_4 potential of the digestate in the field. The two temperatures were tested to understand differences in CH_4 residual potential, as the AD operator stated that his operational conditions were 48 °C and standard mesophilic AD temperature is 37 °C.

In the US, the BMP consisted of: 1) each FW substrate co-digested with flushed dairy manure and inoculum, 2) a mixture of the four FW co-digested with flushed dairy manure and inoculum, 3) flushed dairy manure and inoculum, and 4) inoculum only (control). The substrates were added in triplicate 300 ml bottles, as detailed in Lisboa and Lansing [37]. Briefly, the headspace in each bottle was purged with 30:70 CO_2:N_2, sealed with a rubber septum, placed on a shaker, and incubated at 35°C for 69 days. All assays, including the inoculum control, were performed in triplicate. Biogas production was measured via volume displacement using a 50-mL wetted glass gas tight graduated syringe, with daily, tri-weekly, bi-weekly, and then weekly biogas quantification based on reduced biogas production over time. The CH_4 content of the biogas was determined using an FID gas chromatography (GC) (Agilent 5900 GC) with an injection temperature of 200 °C, a detector temperature of 250 °C, and helium as the carrier gas at a flow rate of 300 mL min^{-1}, and normalized to standard conditions.

3.4.4 Analytic methods

Dry matter (DM) and volatile solid (VS) concentrations were determined following Standard Methods [91] and DIN 15935 [68] in DE for liquids and methods by Weißbach [41] for silage (MS and GS). In DE, a Vapodest® 50s (Gerhard Analytic System, Königswinter, Germany) was used for total kjeldahl nitrogen (TKN) and total phosphorus (TP) determination. The VFA concentrations were determined by GC (CP-3800, Varian), with a capillary column (WCOT fused silica), a flame ionization detector (FID) (280 °C), and helium as the carrier gas, as detailed in Haag et al. (2015). FOS-TAC was analyzed according to Method FAL (Buchauer 1998), with centrifuging at 5000 rpm (Model Z323, Fa. Hermle, Wehingen, Germany) and analyzing using the 785 DMP Titrion (Metrohm, Filderstadt, Germany), which determines the acid volume needed to titrate to pH 5 and 4.4.

In the US, samples were acidified to pH of 1.5 - 2 using 5.25 N sulfuric acid. Acidified samples were filtered through a 0.45-micrometer filter prior to ammonium (NH_3-N) analysis, and a

0.22-micrometer filter prior to VFA analysis. The NH_3-N, TKN, and TP samples were analyzed on a Lachat autoanalyzer device using QuikChem methods 10-107-06-2-O for NH_3-N analysis, 13-107-06-2-D for TKN, and 13-115-01-1-B for TKP. VFA analyses were conducted a GC (Agilent Technologies, Inc.; Shanghai China; model 7890 A) with a FID, operated at 300 °C, a DB-FFAP capillary column (Agilent J&W; USA), and He as the carrier gas at 1.80 ml/min. The injection temperature was held at 250 °C and the oven operated at 100 °C for 2 min and subsequently ramped at 10°C/min for a total run time of 10 min.

3.4.5 Field Methods

In DE, there were eight weekly sample collection events of the FW input and the AD effluent from May 29 to July 16th, 2018. Food waste was collected from heating vessels after mixing for several minutes. Samples from the AD were collected from a sample tap after the reactors were mixed for several minutes. During sample collection, two 10 L buckets were filled, with the first bucket discarded as a system flush, and the second bucket used for sample analysis. All BMP and field samples were transported on ice and stored at -20 °C before analysis. The samples for the residual CH_4 potential test were only cooled to 4 °C prior to incubation to reduce potential inhibition of the methanogenic bacteria. In DE, concentration of H_2S, CO_2 and CH_4 in biogas were determined using a GC (Shimadzu GC-2010-plus, Japan), with FID, a SGE 25m x 0.32 mm column with a Polyethylene Glycol BP21 0.25 µm film, and helium as carrier gas, as detailed in Lemmer und Krümpel (2017).

In the US, samples were collected from the digester effluent approximately every six weeks from June 2016 to August 2017. Composite samples were collected in a sterile 19 L bucket from a continuously flowing pipe over a period of ten minutes. Samples were homogenized using a drill-operated mixer before being transferred to bottles for analysis. Biogas was analyzed using a continuous biogas monitoring system for percent CH_4, CO_2, and O_2, and parts per million (ppm) H_2S (Model # 7MB2337-3CR13-5DR1, Siemens, Berlin, Germany), combined with a data logger (CR 1000, Campbell Scientific, UT, USA) and biogas flow meter (Model # 9500, Thermal Instrument Company, PA, USA). Pre- and post-H_2S scrubbed biogas samples were analyzed every two minutes over the course of 176 days (August 2016 to January 2017), with periodic breaks for calibration and maintenance. Biogas flow rates were monitored continuously over a one-year period (June 2016 to May 2017).

3.4.6 Calculations and Statistics

The results for the BMP in the US consisted of pre-consumer FW co-digested with flushed dairy manure. The cumulative CH_4 production from these food waste and dairy manure

mixtures were detailed in Lisboa and Lansing [37]. For this study, the CH_4 production attributed to only the FW portion was calculated by subtracting the CH_4 production from the manure-only treatment by the proportion of manure in the co-digestion reactors. These calculated FW-only results were not previously reported. The calculations were used to compare the BMP results to the US-based full-scale AD results collected for this project.

The projected CH_4 production values for the two full-scale sites (US and DE) were calculated based on the BMP results for each individual substrate multiplied by the average of daily substrate input data reported by the AD operators. All substrates volumes were reported in m3, except for silage, which was converted to m3 using a density of 1.25 kg m^{-3}.

In DE, Eq. 3.1 (below) was used to calculate biogas production based on the output from electric power (P) and heat (H) meters, using a 38.6% nominal electric generator efficiency (η_{el}).

$$Methane\ Production\left[\frac{m^3_{CH4}}{d}\right] = \frac{P\left[\frac{kW}{d}\right]}{H\left[\frac{kWh}{m^3}\right]} * \ \eta_{el}[\%_{el}] \qquad (3.1)$$

Analysis of variance (ANOVA) was conducted on cumulative CH_4 production from the triplicates to determine if there was statistical significance, with post-hoc Fishers least significant difference (LSD) test. P-values < 0.05 were considered significant. All values are reported as averages ± standard error (SE).

3.5 Results and Discussion

3.5.1 Biochemical Methane Potential (BMP) of substrates tested in Germany

Maize silage (MS) had a CH_4 yield of 368 ± 5 mL_{CH4} g_{VS} (Table 3.1, Figure 3.2a). Mukengele and Oechsner [112] and Mast et al. [113] reported 5% lower yields (351 and 349 mL_{CH4} g^{-1}_{VS}, respectively), likely due to differences in the maize silage composition [114]. Grass silage (GS) had a CH_4 yield of 331 ± 3 mL_{CH4} g^{-1}_{VS}, which was 3% higher than KTBL [62] of 320 mL_{CH4} g^{-1}_{VS}. Raposo et al. [115] found that the range for whole plant maize (282-419 mL_{CH4} g^{-1}_{VS}) overlapped with the range GS (270 - 388 mL_{CH4} g^{-1}_{VS}), which was within the range of our silage substrates, which were not significantly different (p-value = 0.822).

Table 3.1 Initial dry matter (DM), volatile solids (VS), total kjeldahl nitrogen (TKN), total phosphorus (TP), and pH of the substrates used in the biochemical methane potential (BMP) reactors. The cumulative methane (CH_4) production is based on 37°C for 69 days for the US substrates, 37°C for 30 days for the DE substrates, and 37 and 48°C for 65 days for the digestate residual CH_4 potential. Results are averages ± SE.

	DM	VS	pH	TKN	TP	Cumulative CH_4
	g kg^{-1}	g kg^{-1}		g kg^{-1}	g kg^{-1}	mL_{CH4} g^{-1}_{VS}
BMP Substrates for the analysis in the United States (US)						
FW: Cranberry	224 ± 6	225 ± 6	2.85	2.25	0.03	264 ± 38
FW: Chicken	289 ± 5	275 ± 4	5.79	0.03	0.01	521 ± 17
FW: Meatball	144 ± 24	135 ± 23	4.42	0.06	0.23	553 ± 35
FW: Ice-cream	9.10 ± 0.36	9.27 ± 0.53	4.39	-	-	554 ± 82
FW Mixture	166 ± 9	161 ± 8	4.94	-	-	520 ± 20
Dairy Manure	3.97 ± 0.09	1.73 ± 0.09	7.24	0.46	0.07	91 ± 42
BMP Substrates for the analysis in Germany (DE)						
FW (Heated)	198 ± 3	183 ± 1	4.42	6.36	1.19	499 ± 18
FW (Unheated)	218 ± 7	202 ± 7	4.65	6.30	-	494 ± 11
Maize Silage	316 ± 16	303 ± 16	3.80	3.71	1.71	368 ± 5
Grass Silage	303 ± 3	259 ± 5	4.75	7.15	3.57	331 ± 4
Manure: Solids	112 ± 3	88 ± 2	6.80	3.31	0.61	243 ± 1
Manure: Liquid	29.4 ± 0.1	19.5 ± 0.1	7.65	1.93	0.19	91.4 ± 2.0
Digestate	63.0 ± 1.1	43.2 ± 0.7	8.12	-	1.32	84.3 ± 0.5* 68.1 ± 3.5+

*Digested at 37°C; +Digested at 48°C

The fresh solid manure (SM) had a CH_4 yield of 243 ± 3 mL_{CH4} g^{-1}_{VS}, which is near to the standard value of KTBL [62] at 250 mL_{CH4}/g^{-1}_{VS}. The liquid manure (LM) that had been stored for more than one year produced only 91 ± 2 mL_{CH4} g^{-1}_{VS}, which was 62% lower than the SM (p-value = <0.001). Acids concentration was also 98% lower than the SM (total VFAs of 0.07 and 6.73 g kg^{-1}, respectively), likely due to storage time and the inclusion of wash water in the liquid manure.

The CH_4 yield of the post-consumer FW taken on two different dates (one week apart) were 477 ± 12 and 499 ± 18 mL_{CH4}/g^{-1}_{VS}, respectively; a difference of only 5%, which was not statistically significant (p-value = 0.8686). The FW CH_4 yield was 39 - 45% higher than MS (p-value = <0.001), and 96% higher than the LM (p-value = <0.001). While the collected FW

will change, depending on the meals of 53 private households and business where the post-consumer FW was collected, the CH_4 potential was quite similar for the two separate collection dates. Our results were similar to Heo et al. [116] investigation of traditional Korean food (Bibimbab), with a maximum CH_4 yield of 489 mL_{CH4} g^{-1}_{VS}. Cho et al. [117] found the maximum CH_4 yield of a mixture of boiled rice, cooked meat, fried egg, fresh cabbage, bean sprouts, and spinach to be 472 mL_{CH4} g^{-1}_{VS}. Banks et al. [77] investigated FW collected at different restaurants, food markets, and commercial sources and found a slightly lower CH_4 yield of 465.4 mL_{CH4} g^{-1}_{VS}, with 73% CH_4 in the biogas, which was higher than the 61% CH_4 in the biogas of our study.

In DE, the FW is required to be pasteurized before AD addition. The fresh FW (not pasteurized) had a CH_4 potential of 494 ± 9 mL_{CH4} g^{-1}_{VS}. The pasteurized FW was collected on same day, but from a separate container, and showed no significant difference in CH_4 potential (499 ± 18 mL_{CH4} g^{-1}_{VS}; p-value = <0.001) or VFAs between the pasteurized and non-pasteurized FW material (2.53 and 2.49 g kg^{-1}, respectively), with only a slight difference (8%) in the VS of the pasteurized (20.1%) and non-pasteurized FW materials (21.8%).

Both the FW and the silage had a high degradation rate, with 85-89% of the cumulative CH_4 produced in the first 14 days compared to the two manures sources; LM (75%) and SM (53%) (Figure 3.2a). Banks et al. [77] reported a lower degradation rate for FW on Days 0-5 compared to Days 5-11. This lag phase was also observed in our results, but to a lesser extent. The TKN concentrations of the FW and GS (6.4 and 7.1 g kg^{-1}, respectively) were higher than the SM and MS (3.31 and 3.71 g kg^{-1}, respectively) (Table 3.1).

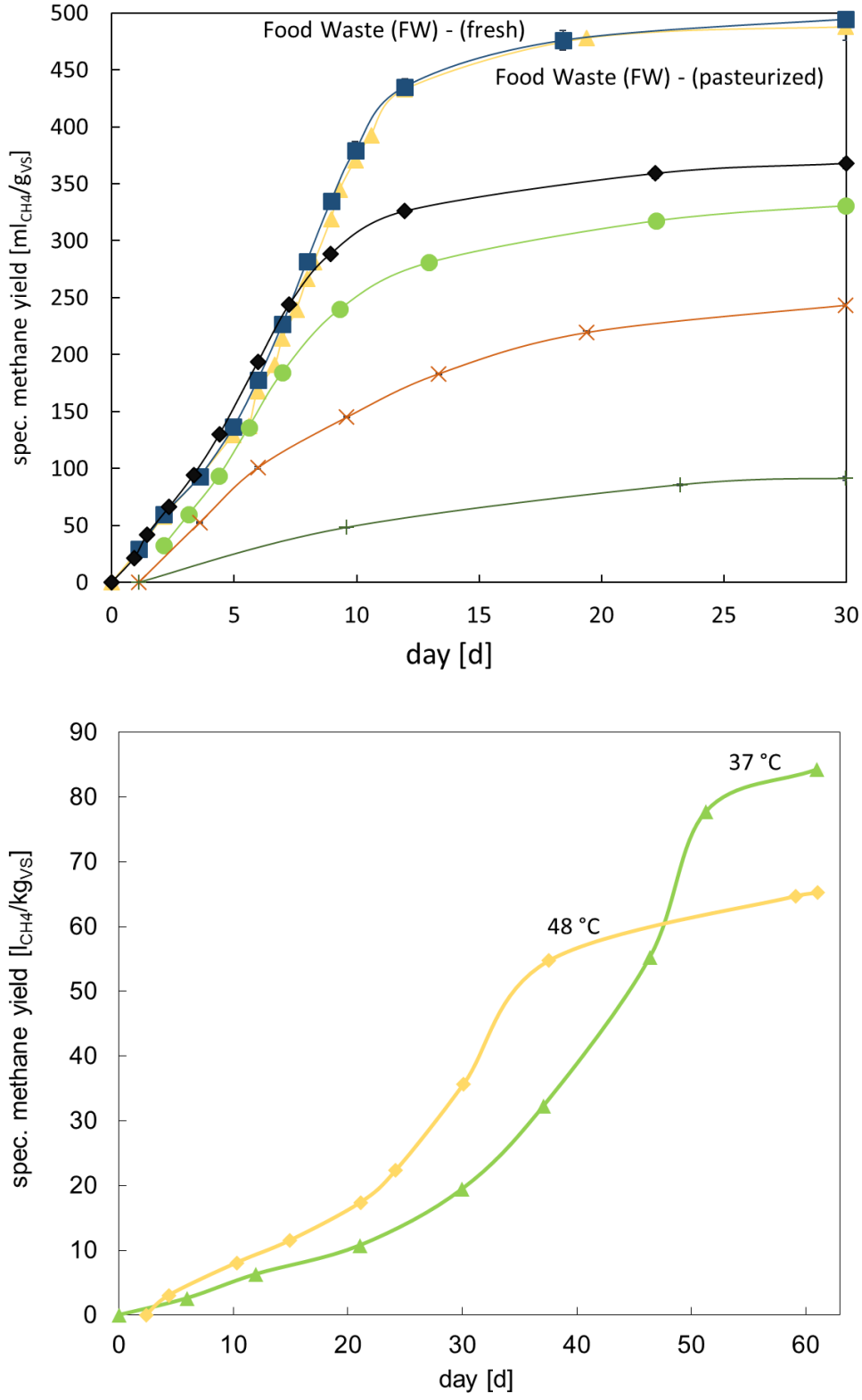

Figure 3.2 Cumulative methane (CH_4) production for the substrates in the German biochemical methane potential (BMP) tests operated at 37°C for 30 days for the food waste (FW), silage and manure substrates, shown in (A), and a residual CH_4 potential test at 37 and 48°C for 65 days for the digestate, shown in (B). Error bars are SE of the triplicate. All cumulative CH_4 values were statistically different (p-values <0.001), except the fresh and pasteurized FW (p-value = 0.686), and the maize and grass silages (p-value = 0.822).

3.5.2 Digester process stability with post-consumer food waste, manure, and silage in DE

Based on the BMP data and AD loading rates, the FW accounted for 71% of the daily CH_4 production at 66% of the volumetric input, with 16 and 10% of the CH_4 production to due to MS and GS, respectively, comprising 13 and 9% of the total loading, respectively. The two manure sources combined accounted for 12% of the volumetric input and only 3% of the CH_4 production.

The influent FW weekly testing showed a stable DM and VS (211 ± 2 and 195 ± 2 g kg^{-1}, respectively) each week over the 8-week testing period, with a stable total VFAs (2.89 g kg^{-1}) and low SE (± 0.07). The influent VFAs from the FW were mainly comprised of acetic acids (2.77 ± 0.07 g kg^{-1}), with low concentrations of propionic and butyric acids (0.02 ± 0.008 and 0.14 ± 0.04 g kg^{-1}, respectively). This FW input to the AD system was quite stable even with daily changes in the mixtures of post-consumer food waste collected sites. While the daily addition of the FW was stable, the input of LM was more variable, but did not lead to high fluctuations in biogas production during the study.

Within the AD vessel, the VFAs were utilized, with 75% less VFAs in the AD effluent (0.73 ± 0.57) compared to the FW influent, which only accounted for 66% of the total loading (Table 3.2). This concentration was less than the 1.2 g kg^{-1} approximate VFA inhibition level seen by Labatut and Gooch [118]. In addition, butyric and valeric acids concentrations were not detected in the AD effluent. This indicates a stable biogas process in fermenter. The DM and VS concentrations in the AD effluent (93.7 ± 3.9 and 64.6 ± 0.4 g kg^{-1}, respectively) were 66% lower than the FW inputs and 69 - 70% lower than the silage input, with low variability in the effluent solids concentration during the 8-week study.

Table 3.2 Methane (CH_4) production from the AD systems in the United State (US) and Germany (DE), including the CH_4 production and $\%_{CH4}$ at the full-scale systems and CH_4 potential calculated from the biochemical methane potential (BMP) results, and the efficiency. The AD effluent concentrations for pH, dry matter (DM), volatile solids (VS), total kjeldahl nitrogen (TKN), total phosphorus (TP), total volatile fatty acids (VFAs) and individual VFAs are given as averages and SE.

	Digester Biogas Production Data			
	CH_4 content	CH_4 production	CH_4 potential	efficiency
	%	$m^3\ d^{-1}$	$m^3\ d^{-1}$	%
DE	55.2 ± 0.3	882	644	137
US	65.1 ± 0.3	434 ± 124	1291	36

	AD Effluent Characteristics				
	pH	DM	VS	TKN	TP
		$g\ kg^{-1}$	$g\ kg^{-1}$	$g\ kg^{-1}$	$g\ kg^{-1}$
DE	8.1 ± 0.03	93.7 ± 3.9	64.6 ± 0.4	9.50	1.32
US	7.0 ± 0.2	6.4 ± 0.2	3.7 ± 0.6	0.477	0.06

	VFAs in the AD Effluent				
	Total VFAs	Acetic Acid	Propionic Acid	Butyric Acid	Valeric Acid
	$g\ kg^{-1}$	$g\ kg^{-1}$	$g\ kg^{-1}$	$g\ kg^{-1}$	$g\ kg^{-1}$
DE	0.73 ± 0.57	0.57 ± 0.05	0.19 ± 0.01	N.D.	N.D.
US	0.31 ± 0.14	0.13 ± 0.07	0.12 ± 0.06	0.04 ± 0.01	0.03 ± 0.01

N.D. = Non-detect

The hydraulic retention time (HRT) in the AD system was calculated to be 86 days based on the recorded AD inputs and AD size. This HRT is less than the current German law requiring 150 days HRT for new AD systems to reduce residual CH_4 potential in uncovered storages [119], but this regulation does not apply to existing systems. The organic loading rate (OLR) of the AD was 2.1 $kg_{VS}\ m^3\ d^{-1}$. This OLR on the lower end of other biogas plant fed by energy crops and manure, which range in other research from 0.9 to 7.0 $kg_{VS}\ m^{-3}\ d^{-1}$ [43,85]. Food waste is normally highly degradable material, and problems were not expected or encountered with an OLR of 2.1 $kg_{VS}\ m^{-3}\ d^{-1}$.

The residual CH_4 potential test of AD effluent was conducted at 37 °C (standard BMP temperature) and 48°C (reported AD operational temperature). Our field study revealed that the AD operating temperature was closer to the average of these two temperatures (42.0 ± 1.3 °C). The results showed 19% higher residual CH_4 potential at 37 °C (84.3 ± 0.5 $mL_{CH4}\ g^{-1}{}_{VS}$)

compared to 48°C (71.4 ± 1.0 mL_{CH4} g^{-1}_{VS}) with 60 days of digestion (Figure 3.2b; Table 3.1; p-value = <0.001). By Day 37, the majority of the CH_4 potential (84%) had been reached when the AD effluent was digested at 48 °C, compared to only 38% at 37°C (Figure 3.2b). The residual CH_4 potential based on the daily substrate loading was 41.0 and 33.1 m^3_{CH4} d^{-1} at 37 °C and 48 °C, respectively, with an average of 37.1 m^3_{CH4} d^{-1} for the two temperatures tested, which could be close to the value expected with the 42°C on-site temperature. At least about 3.5 to 3.0% of the total CH_4 yield of the AD system could be captured if the digestate was fermented for an additional 60 day (145 days total), which is advisable in order to reduce residual CH_4 production into the atmosphere. Ruile et al. [43] reported that five different biogas plant fed by manure, MS, and/or additional energy crops had HRTs of 71-86 days, with residual CH_4 potentials of 1.2 – 5.7% (86 - 149 mL_{CH4} g^{-1}_{VS}), which is within this range of our system. In addition to silage and manure, our study also included 66% FW, by volume. The FW had a high VFA reduction from the influent to effluent and high degradation rates in the BMP within the first 20 days, with little to no additional CH_4 production from days 20 - 30 (Figure 3.2). The Ruile et al. [43] study of > 25 different biogas plants showed an average AD effluent VFA concentration (0.52 ± 0.49 g l^{-1}) that was approximately 29% lower than our study (reported in g/kg). However, it should be noted that there is not a direct relationship between residual VFAs and CH_4 potential, as the degradation will vary based on the specific feedstock utilized, in addition to residual VFA and VS values [43,120].

3.5.3 Digester CH_4 production with post-consumer food waste, manure and silage in DE

Power production for the German AD system was stable during the measured period of November 13th, 2016 to August 27th, 2018, with 3519 ± 4 kWh d^{-1} of electric power produced and 1768 ± 6 kW d^{-1} of heat from the CHP system using 882 m^3_{CH4} d^{-1} (Figure 3.3). The on-site production was 37% higher than expected from the BMP results (644 m^3_{CH4} d^{-1}). One possible explanation is the longer HRT in the AD (86 days) compared to the BMP (30 days), the higher temperature in the AD (42 °C) compared to the BMP (37 °C), as well as documented benefits from co-digestion mixtures [100]. Methane quality was stable at 55.2 ± 0.3%, with H_2S values less 16 ppm each week, which is likely due to the iron additions to the digester by the farmer (25 kg FeOH every other day) and biological desulfurization within the AD vessel through continuous air injection (blower) at a rate of approximately 3% of the biogas volume.

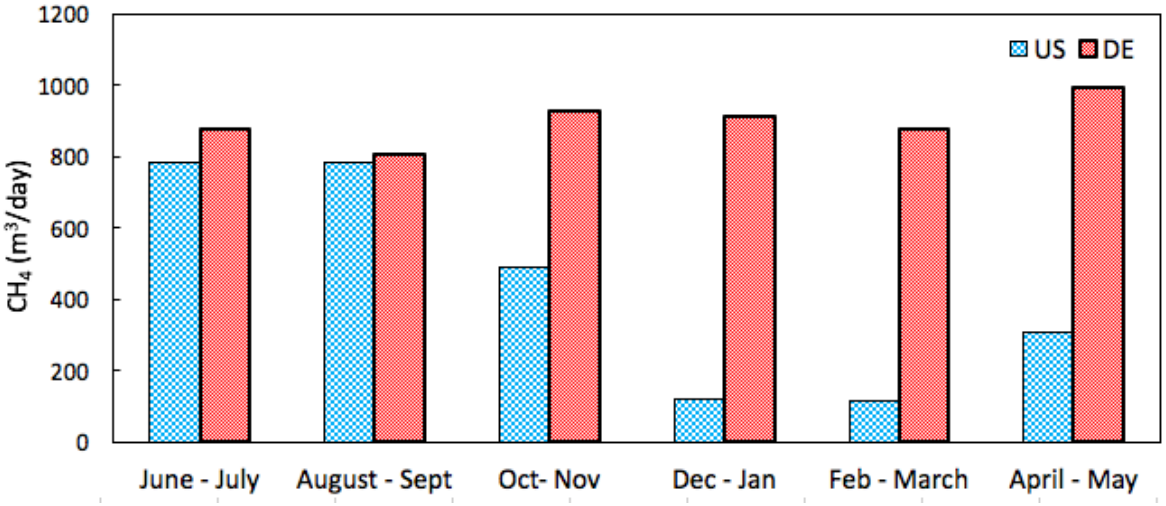

Figure 3.3 Average daily methane (CH4) production over 12 months in the German (DE) and United States (US) full-scale food waste co-digestion systems. The US system was an unheated and unmixed covered lagoon. The DE system was a complete mixed digester operated at 42°C.

While the field conditions were quite higher than the BMP results, it should be noted that measuring quantities of feedstock on-farm can have inherent assumptions and miscalculations in the flow rate. For example, the ratio of fresh cow manure solids to the stored liquid manure was estimated by the farmer. Additionally, the simplified nominal efficiency rate used in the CH_4 production calculation also effects the final daily CH_4 production rate.

The added benefit of the CHP unit is shown through this analysis, with 43.7% of CH_4 consumed was captured as heat and used for pasteurization, heating water, and heating nearby houses. The exact amount of heat used by AD for heating was not metered, but Pöschl et al. [28] calculated the typical heating consumption of an AD system as 20 - 25% of heating captured by the CHP unit.

3.5.4 Biochemical Methane Potential (BMP) of substrates tested in the US

Compared to the flushed dairy manure used in the US system, the pre-consumer FW increased CH_4 production from 192% (cranberry FW at 231 $mL_{CH4}\ g^{-1}_{VS}$) to 510% (meatball FW at 554 $mL_{CH4}\ g^{-1}_{VS}$) (Table 3.1). The FW had 58 to 85% of the cumulative CH_4 in the first 12 days, while manure only had 39% of it cumulative CH_4 during this time [37]. The CH_4 production from the mixture of the four food waste substrates (482 $mL_{CH4}\ g^{-1}_{VS}$) was 7% higher than the average of the individual substrates, likely due to increased buffering capacity for the cranberry substrate when combined, as this substrate had the lowest pH and CH_4 potential of the pre-consumer FW tested (Table 3.1). The FW substrates were within or slightly higher than the expected CH_4 production range (241 – 538 $mL_{CH4}\ g^{-1}_{VS}$) of FW reported by Moody et al. [109], Heo et al. [116], and Cho et al. [117] and similar to the cumulative CH_4 production from the

post-consumer FW in our DE study (477 - 499 mL_{CH4} g^{-1}_{VS}). The slightly higher CH_4 production from the US substrates could be due to extra buffering capacity from co-digesting the FW with the manure source in the BMP vessels; an effect that would not be captured when calculating the FW portion of the cumulative CH_4 production.

The dilute (0.4% DM) flushed dairy manure had low CH_4 production (90.8 mL_{CH4} g^{-1}_{VS}), as the solids were removed prior to AD, and the AD effluent was used to flush the barn and circulated within the manure system, which likely increased the quantity of recalcitrant material entering the digester with the manure and resulted in a value much lower than the standard value of KTBL (2013) at 210 mL_{CH4} g^{-1}_{VS}, and close to the LM (91 mL_{CH4} g^{-1}_{VS}) value in the DE system that was stored for more than one year (Table 3.1).

3.5.5 Digester process stability and CH_4 production with pre-consumer food waste in the US

The US farm produced a total of 47,158 kWh of energy from the biogas from August 10th, 2016 – December 12th, 2016, resulting in a daily average rate of 380 kWh d^{-1}. It is important to note that the generator was only used during farm operational hours. The substrate inputs included the pre-consumer FW (15 m^3 d^{-1}; 2700 kg_{VS} d^{-1}), which was 6% by volume, and large quantities of flushed dairy manure (227 m^3 d^{-1}; 392 kg_{VS} d^{-1}). Although the volumetric input of the FW was low, 87% of the VS in the AD was attributed to the pre-consumer FW. In the unheated lagoon AD, the percent CH_4 (66.2%) in the biogas was stable, but the H_2S concentration in the biogas prior to scrubbing varied from 3 to 1722 ppm (Figure 3.4a), likely due to changes in temperature resulting in changes in microbial activity from sulfate reducers in the digester. The biogas and CH_4 production fluctuated from 796 to 33.5 m^3_{CH4} d^{-1} due to these temperature changes, averaging 434 ± 124 m^3_{CH4} d^{-1} (Figure 3.3). The temperature fluctuations and settling of solids within the unmixed lagoon led to higher than expected CH_4 production in the summer and much lower production in the winter.

Based on the BMP, there should have been 1156 m^3_{CH4} d^{-1}, with 95% of the daily CH_4 attributed to FW, but the average value was 62% less than the expected value due to the temperature fluctuations, with the summer-time production at 31% less than expected. The HRT was only 11 days, which likely means the residual CH_4 potential was much higher than the DE system, but this was not specifically tested for this system. Although, as the AD effluent circulated through the system, there was less open air storage of this waste. The OLR of the AD system in the US (1.2 kg_{VS} m^{-3} d^{-1}) was about half of the OLR in the DE system at 2.1 kg_{VS} m^{-3} d^{-1}.

The effect of temperature on the microbial processes could also been observed through higher VFAs and VS values in the AD effluent in the winter (more than double) when CH_4 production

and AD temperature were low. When digestion slowed (winter), the NH_4-N values also decreased by 42%, with less organic N mineralized to NH_4 (Figure 3.4b). The total VFAs in the unheated lagoon AD effluent were 57% lower than the DE effluent, with similar acetic acid and propionic acid concentrations in the lagoon AD effluent, which were both lower than the DE system, possibly due to lower hydrolysis rates in the un-heated system (Table 3.2).

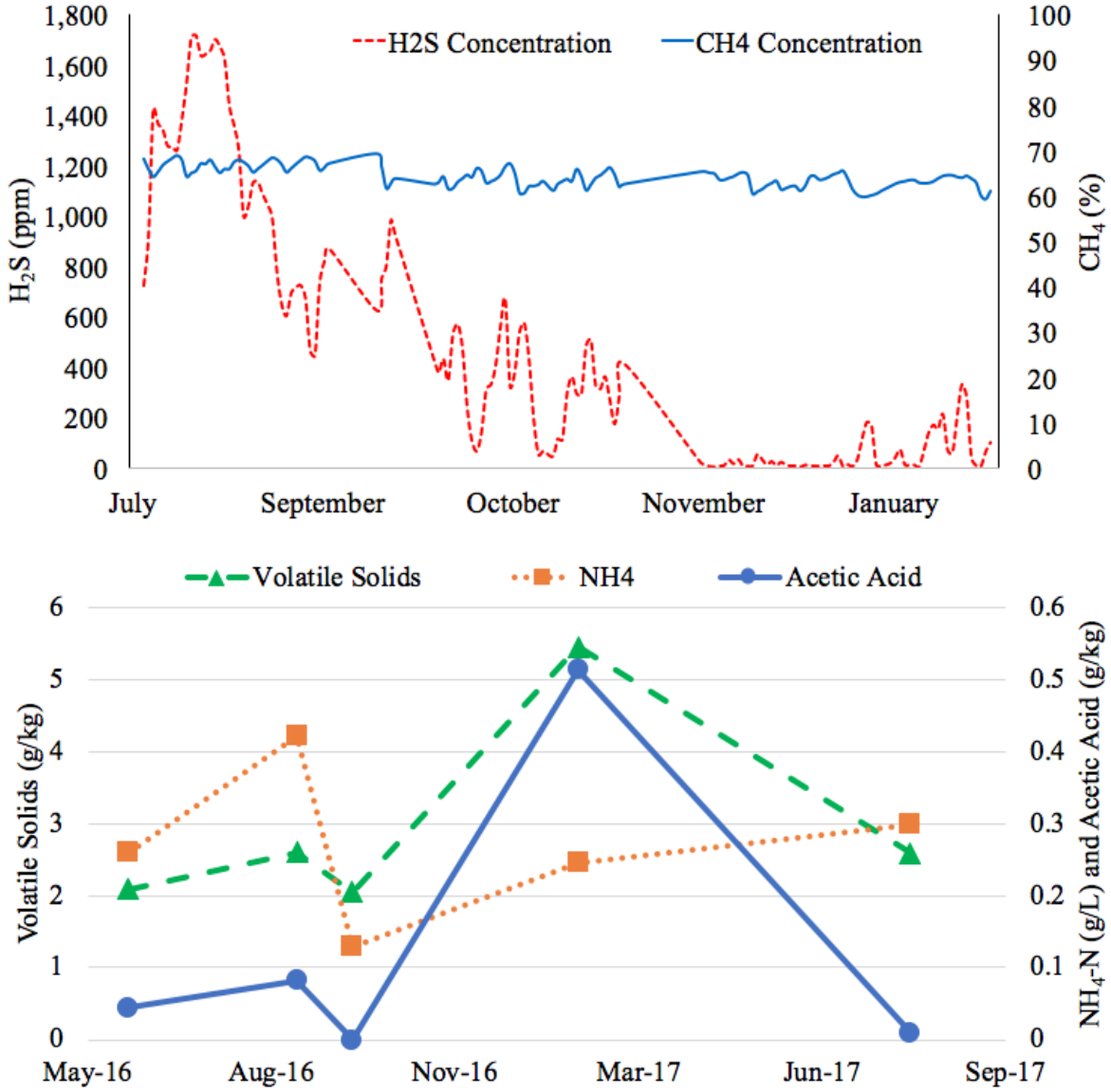

Figure 3.4 The methane (CH_4) (%) and hydrogen sulfide (H_2S) (ppm) over 12 months in (A), and the acetic acid, ammonium (NH4-N), and volatile solids concentrations over 16 months in (B) in the United States (US) unheated anaerobic digestion (AD) full-scale system.

3.5.6 Comparison of the Effect of US and German Policies and Regulations on AD

While this study investigated two FW co-digestion systems, the German AD system utilized energy crops and a higher share of FW compared to the US system. The influence of AD and FW diversion policies has had a large effect in AD adoption rates in the two countries.

Historically, German digesters in the 1990s, used manure and crop residues, but by 2009, 98% of on-farm digesters in Germany utilized energy crops as a substrate [121]. There were 600-800 digesters built in both 2005 and 2006, with a further increase in 2009, due to revisions in the German Renewable Energy law that had a specific strategy for increasing energy from digestion [31]. By 2017 in Germany, there are operated approximately 9,000 agricultural biogas plants with an installed electric power of 4,500 MW. Energy crops comprised the majority of the AD substrate inputs (≈ 53%), with 1,374 Mha of arable land (11.6% of total DE arable land) used for producing these energy crops [122].

The new 2017 German law resulted in decreases in the number of plants built, with less maize silage allowed (50% by 2018; 44% by 2022) for preferred electricity rates. These regulations are less strict than Denmark's 2016 law of <25% energy crops, reduced to 12% by 2020, and 0% for renewable natural gas (RNG), but the Danish government does provide a 30% construction grant for all digesters and \$19 GWh^{-1} and \$17-19 GJ^{-1} for RNG [123]. In Germany, bonus payment for biogas plants have been reduced. In the 2017 German regulations [119], 2017), preferred electricity rates were based on generator size (13.32 ¢ up to 150 kW; 11.49 ¢ up to 500 kW; 10.29 ¢ up to 5 MW; 5.71¢ up to 20 MW) and for FW 14.88 ¢ up to 500 kW and 13.05 ¢ up to 20 MW. These new lower electricity prices have forced AD systems to be more efficient, use cheaper feedstock, and to utilize the excess heat captured by the CHP unit to continue operating the biogas plant economically. The use of CHP produced heat was already supported in EEG 2009 [31] and does provide an extra incentive (0.03 ¢ kWh^{-1} bonus payment). Additionally, the AD operator will receive tipping fees to use FW, but the pre-heating at least 70 °C for 1 hour, or higher digestion temperatures (> 50 °C), are required for these plants, because of pathogenic concerns, and an HRT of > 150 days are now required for new biogas plant to avoid residual CH_4 emission from the digestate [97]. Most food waste-based AD plants utilizing the excess heat from the CHP system for this pre-processing heat. In the US, pasteurization is not required prior to AD.

In the US, the lack of access to credit and required large capital investment for digesters has constrained US adoption of an otherwise profitable technology. Due to the large capital intensive and long-term commitment required for digestion operations, the US adoption response to policy-based financial incentives has been lower than expectations [124]. Digesters in the US can receive partial funding from the Rural Energy for America Program (REAP) in the form of grants and loans to agricultural producers and rural businesses to purchase and construct renewable energy systems, such as AD. REAP grants are limited to 25% of proposed

project cost, and loan guarantees may not exceed $25 million. When grants and loan guarantees are combined together, they may not exceed 75% of total project cost.

There is no US federal-based policy on electricity prices for AD projects. The price of electricity for AD is based on state code, with some states, such as Maryland, allowing net metering up to 200% of the electric use up to 2 MW (averaging $0.06 - $0.10 kWh^{-1}) and Rhode Island set at $0.24 kWh^{-1}, but other states having no regulations and AD operators receiving value as low as $0.02 kWh^{-1} for their generated electricity [23].

There is a US federal law for renewable natural gas (RNG) from AD, with manure-based digesters and cellulosic-based feedstocks receiving a higher value (2.3 times more) than the fraction of non-cellulosic FW feedstock. With FW added to digesters that produce RNG, the resulting RNG can be deemed 10% ineligible for the higher value, but most systems can receive the percentage of the FW feedstock that is above the cellulose limit at the higher value, with the remaining fraction at the lower non-cellulosic value [23].

By 2011 in US, following the implementation of the Energy Independence and Security Act of 2007, which set these cellulosic feedstock standards for bioenergy, there were 16 million ha of corn used to ethanol processing (40.5% of corn grain harvested). The corn-based ethanol production is calculated to 25% of US corn acreage processed to ethanol when accounting for feed co-product utilization going back to agriculture after ethanol processing. No US-based digesters use corn silage.

In the US, there are no federal policies on food waste diversion, but individual states and cities in the US have begun efforts to increase FW diversion over the past few years, with focus on commercial, institutional, and agricultural sectors, but these policies are not as rigorous as the EU. There was US federal legislation for reducing FW and promoting FW recovery proposed in 2015, the Food Recovery Act (HR484), but the legislation has not been brought up for a vote at this time. If passed, the legislation would promote donation of excess food for use and encourage AD programs through education programs and supporting technical advances in the food industry. Meanwhile, five US states (CA, CT, MA, RI, VT) and seven localities have implemented organic waste bans or waste recycling laws that restrict the amount of food waste an entity can send to a landfill. Specifically, California instituted a Waste Recycling Law that requires commercial generators of organic waste (> 3 m^3) to either compost or anaerobically digest this waste. The specifics of individual state and local organic waste bans and waste recycling laws vary in the types of entities covered, including how much organic waste an entity must produce to be required to landfill divert under the ban and the various exemptions for each

legislation. Currently, only Vermont has a plan to increase their FW ban to include any entity that generates any amount of FW, including residents, by 2020.

Overall, the different regulations in the two countries, and specifically, the promotion of using CHP units in DE has led to different operating conditions in the systems analyzed in the US and DE. The lack of CHP unit is the US-based AD system led to much lower biogas production in the winter and higher production in the summer, with more constant biogas production throughout the year in DE due to the higher operating temperature, longer HRT and consistent OLR. The DE system is required to pre-process the FW prior to AD introduction, which was not shown to change the CH_4 potential of the FW substrate, but does utilize the heat captured from the CHP unit, resulting in less heat for other heating purposes. The extra credit for using this captured heat has incentivized CHP installation and more utilization of the produced heat in DE. Addition national-based incentives in the US, similar to those in DE, could result in larger AD adoption rates, with the US currently having only fraction (265) of the DE farm-based AD system (9,000) [122,125].

3.6 Conclusion

The BMP predictions were 62% higher than actual CH_4 production in US full-scale system and 37% lower in the German system. The Germany system had a higher temperature and HRT than the lab-scale. In the US, there were biogas fluctuations with temperature changes. The pre-consumer (DE) and post-consumer (US) FW substrates had similar CH_4 production potential, and both field-scale systems had stable percent CH_4 in the biogas, but the VFAs varied with temperature in the US system. The AD and FW policies and incentives had a large effect on FW pre-treatment and AD adoption rates in the two countries.

4 Biomethane Potential Test: Influence of Inoculum and the Digestion System

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4.1 Abstract

High precision of measurement of methane potential is important for the economic operation of biogas plants in the future. The biochemical methane potential (BMP) test based on the VDI 4630 protocol is the state-of-the-art method to determine the methane potential in Germany. The coefficient of variation (CV) of methane yield was >10% in several previous inter-laboratory tests. The aim of this work was to investigate the effects of inoculum and the digestion system on the measurement variability. Methane yield and methane percentage of five substrates were investigated in a Hohenheim biogas yield test (D-HBT) by using five inocula, which were used several times in inter- laboratory tests. The same substrates and inocula were also tested in other digestion systems. To control the quality of the inocula, the effect of adding trace elements (TE) and the microbial community was investigated. Adding TE had no influence for the selected, well-supplied inocula and the community composition depended on the source of the inocula. The CV of the SMP was <4.8% by using different inocula in one D-HBT (D-HBT1) and <12.8% by using different digestion systems compared to the D-HBT1. Incubation time between 7 and 14 days resulted in a deviation in CV of <4.8%

4.2 Keywords

biochemical methane potential test; inoculum; methane; biogas; anaerobic digestion; inter-laboratory test

4.3 Introduction

Biogas plants in Germany receive a bonus payment for power generation, which is guaranteed by the German Renewable Energy Source Act (EEG) for a period of 20 years after installation [31]. Many biogas plants will run out of this bonus payment during the next ten years. Thus, biogas plants have to work more efficiently for economic reasons. The biochemical methane potential (BMP) test is a common method to determine the maximum theoretical methane yield of a substrate. It has already been used for several years for dimensioning biogas plants [45]. High accuracy of the BMP test will be necessary to precisely predict economic viability in the future.

Various protocols are available, all with the aim of achieving a high reproducibility of the BMP test. Besides the European standards (Angelidaki et al. [51] and Holliger et al. [52]), the VDI Standard 4630 [49] is the most commonly used protocol. These protocols show the same basic structure: (i) performing three technical repetitions, (ii) applying prescribed inoculum/substrate ratio (ISR), (iii) measuring methane yield of pure inoculum as a blank, and (iv) measuring methane yield of standard substrates as positive control. In each of the protocols it is pointed out, how important the inoculum, the digestion system, and the working precision are to achieve a high reproducibility.

Various inter-laboratory tests were conducted to check the accuracy of the BMP by using different digestion systems, inocula, and protocols. Raposo et al. [45] conducted an inter-laboratory test with 17 laboratories using starch, cellulose, and gelatin as substrates. The results showed a coefficient of variation (CV) of around 8–11%. Similar results were reported by a German inter- laboratory test of KTBL/VDLUFA based on VDI Standard 4630. This test was done with different substrates and around 30 laboratories over several years. The CV excluding outliers was 8–12% [126]. The impact of repeating BMP tests over several years was small, it only helped to reduce the number of outliers [54]. The École Polytechnique Fèdèrale de Lausanne carried out inter- laboratory-tests with stricter specifications and a repetition after a few months [52]. The results without eliminating the outliners revealed a CV of 15–17% [48]. Cresson et al. [127] investigated differences in the CV when using different BMP measuring protocols. Free choice of the used protocol was compared to the fix protocol for each laboratory, using a mineral substrate, NaHCO3 as pH buffer and an ISR > 2. The results showed a deviation of about 20% between the free and the fixed protocol. The measurement variability was not affected by different measuring protocols. Pham et al. [128] reported similar differences by comparing protocols of VDI 4630 [49] and Sommer et al. [129].

Several studies were carried out to find reasons for deviations in measurement results (Table 4.1). Special focus was laid on the effect of the used inoculum. One of the main categorization criteria was the origin of the inoculum. Vrieze et al. [130] and Regueiro et al. [131] reported differing microbial community composition for different inocula from full scale biogas plants. Thus, inocula from different origins might affect the methane yield depending on their microbial community composition. Li et al. [132] tested sludge from chicken manure and municipal wastewater treatment plants as inocula using similar substrates. The inoculum from wastewater treatment led to a higher biodegradability of the inoculum/substrate mixture. Pozdniakova et al. [133] revealed converse behavior, they detected a higher methane yield for inocula from a municipal solid waste landfill plant compared to inocula from wastewater treatment and other origins, when using animal by-products as substrate. Elbeshbishy et al. [134] investigated the methane yields of two different inocula. Higher methane yields were also achieved with inocula taken from anaerobic digesters. Dechrugsa et al. [55] reported a significant difference in methane yields by using inocula from two different full-scale biogas plants. Another impact was reported by Chamy and Ramos [135], where a well-adapted inoculum from digested turkey manure produced a higher methane yield when using turkey manure as a substrate. Vrieze et al. [130] measured the methane yield of four substrates using four inocula from different origins. The effects of inocula on the results depended strongly on the substrates. Koch et al. [136] reported similar results. A comparison of three inocula from different origins revealed repeatedly no significant effects in methane yield for three substrates. Only for cellulose—a common substrate standard—significant effects were observed, leading to the conclusion that the methane production rate was affected by the used inoculum.

Table 4.1 Overview on studies on the effect of different inoculum/substrate combinations on the methane yield compared by the coefficient of variation (CV) of measurement results.

Inoculum	Substrate	CV %	Reference
Brewery wastewater, animal manure, biological waste, upflow anaerobic sludge blanket	Molasses, bio-refinery waste, manure, A-sludge	3–33*	Vrieze et al. [12]
Wastewater treatment plant, sludge chicken manure	Chicken manure, Corn stover	10–19	Li et al. [14]
Wastewater treatment plant, slaughterhouse lagoon, municipal solid waste, upflow anaerobic sludge blanket	Animal by products	17	Pozdniakova et al. [15]
Wastewater treatment plant, biogas plant	Food waste, wastewater	12–74	Elbeshbishy et al. [16]
Biogas plants	Pig manure, para grass	2–128	Dechrugsaet et al. [17]
Digestate one adapted to turkey manure, one without adaption	Turkey manure	1–8	Chamy and Ramos [18]
Wastewater treatment plant, biogas plant, biowaste plant	Cellulose, food waste, maize, sewage sludge	1–5*	Koch et al. [19]

* According to Weinrich [7].

Beside the source of the inoculum, there are more possibilities influencing the methane yield, such as the incubation time and the trace elements (TE). VDI 4630 [49] prescribes the incubation of the inoculum to limit the methane production of the blanks. Other studies report no effect of incubation on their results [130,132]. Angelidaki et al. [51] recommend adding TE and vitamins.

Further effects on BMP were investigated by Strömberg et al. [137]. They examined the influence of experimental conditions and their correction to standard conditions. The biggest effect was found for samples with low methane yield, because of the high impact of the size of headspace, which determines the volume relation between produced biogas and flushing gas. The use of standard temperature showed a deviation of about 10% compared to results without correction. Also, the ambient pressure shows an impact on the biogas yield potential. It is shown that the ambient pressure can differ between 63.1 kPa (La Paz) and 103.6 kPa (sea level) [137,138].

The aim of this study was to investigate the effects of different inocula and digestion systems on the specific methane yield and methane percentage of different substrates using VDI 4630 [49] as a protocol. Unlike other publications, all investigated inocula were cultivated for several years and have been used in a national inter-laboratory test in Germany. Five long-term

cultivated inocula and five substrates were tested using equipment and procedure of the standardized Hohenheim biogas yield test (D-HBT1) in comparison to four other digestion systems. To the best of our knowledge, such an extensive comparison of inocula and digestion systems has not been performed before.

4.4 Materials and Methods

4.4.1 Digestion Systems

Four different digestion systems for performing the standardized BMP test according to VDI4630 [49] were compared (Table 4.2 and Figure 4.1): Hohenheim biogas yield test (D-HBT), Bergedorf fermentation test (D-BFT), Eudiometer (D-EUD) and an Automatic methane potential test system (D- AMP).

Table 4.2 Digestion systems used for biochemical methane potential test: digestion volume, frequency of agitation and method for determining the gas quality.

Code	System	Volume L	Agitation	Gas quality
D-HBT	Hohenheim biogas yield test	0.1	Continuous	Infrared
D-BFT	Bergedorf fermentation test	1.5	Frequently	Infrared
D-EUD	Eudiometer	1.5	Continuous	Infrared
D-AMP	Automatic methane potential test	0.5	Continuous	None

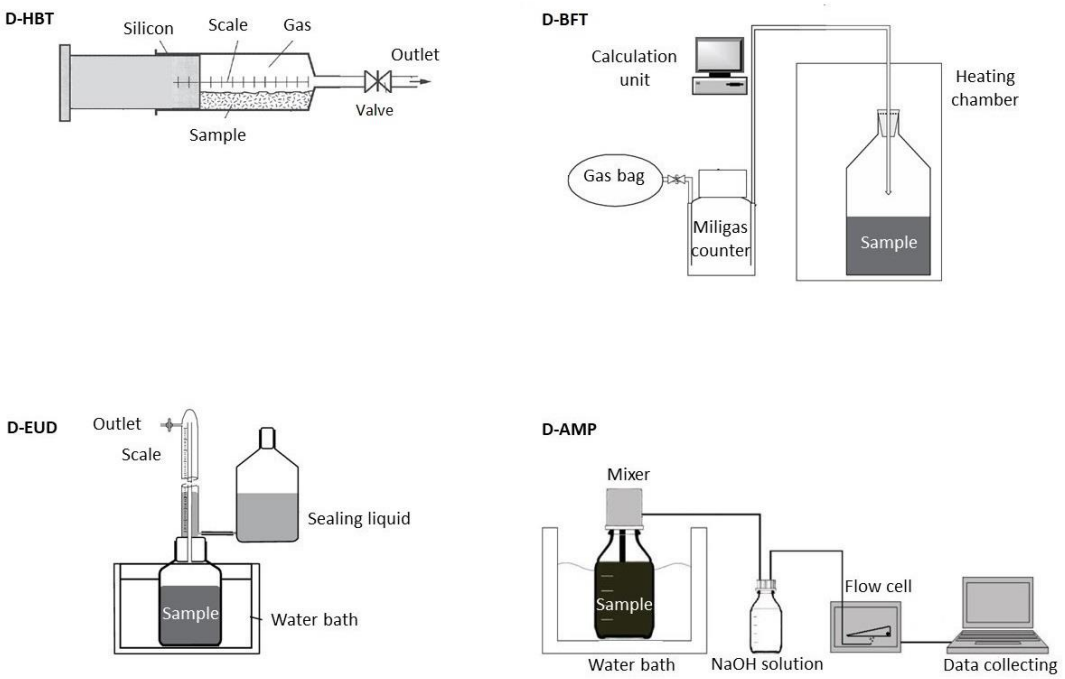

Figure 4.1 Scheme of Hohenheim biogas yield test (D-HBT), Bergedorf fermentation test (D-BFT), Eudiometer (D-EUD), and Automatic methane potential test (D-AMP). According to VDI 4630 [49].

4.4.1.1 Hohenheim Biogas Yield Test (D-HBT)

D-HBT consisted of 100 mL syringes, which are placed in a continuously rotating drum with 129 places for syringes placed in an incubator [110]. The substrates in the syringes are agitated by the rotation of the drum at a speed of 1.2 rpm. The volume was measured manually by reading from a scale on the syringes. The methane percentage was measured by an infrared-spectrometric methane- sensor ("Advanced Gasmitter", Pronova Analysetechnik, Berlin, Germany) [111]. The sensor was calibrated directly before and after each measurement with a calibration gas mixture of 40% CO_2 and 60% CH_4 (G325792, Westfalen AG, Münster, Germany). The tests were performed in two variants: in dry gas (D-HBT1) and in wet gas (D-HBT2). For dry gas measurements in D-HBT1 the gas was dried with an absorbent (SICAPENT®, Merck, Darmstadt, Germany). For the wet gas measurement, the water content of the gas was considered—by a correction of the gas volume V_0 (mL) according VDI 4360 [49] Equation (4.1).

$$V_0 = \frac{V \cdot (p - p_W)\, T_0}{p_0 \cdot T} \tag{4.1}$$

where V (mL) and p (hPa) are the measured volume and pressure, p_W (hPa) is the water vapor pressure at operation temperature T (K), and p_0 (hPa) and T_0 (K) the standard pressure and temperature (1013.3 hPa, 273.15 K).

4.4.1.2 Bergedorf Fermentation Test (D-BFT)

The D-BFT reactor had a volume of 1.5 L and was frequently agitated manually. The gas volume was measured by a tipping cell counter (MilligasCounter, Ritter Apparatebau GmbH, Bochum, Germany). Gas was collected in a gasbag and gas quality was measured in a combined sample as soon as 1.5 L of gas was produced. The methane percentage was measured by an infrared sensor (Awite Bioenergie GmbH, Langenbach, Germany) [139].

4.4.1.3 Eudiometer (D-EUD)

D-EUD (Neubert Glas GbR, Geschwenda, Germany) had a volume of 1.5 L. The headspace was flushed with nitrogen gas once a day and agitated continuously by a magnetic stirrer. The gas was collected in a tube, which was surrounded by a sealing fluid. In this tube the volume could be read by a scale bar. The gas composition was determined once at the end of the experiment with a land fill gas monitor (GA2000, Ansyco, Karlsruhe, Germany) [140].

4.4.1.4 Automatic Methane Potential Test System (D-AMP)

D-AMP (AMPTS II, Bioprocess Control AB, Lund, Sweden) had a volume of 0.5 L and was agitated by a mechanical stirrer. The CO_2 and H_2S was stripped by using 3 M NaOH solution and then the volume of methane was measured by a flow cell. The gas lifted the flow cell, which lowered back down afterwards. The digital impulse was registered by a computer. Since the volume of biogas in this digestion system was not measured, the percentage of methane could not be determined either.

4.4.2 Inocula

Five different inocula were used in this study (Table 4.3). All inocula were cooled down to 3-4 °C before being sent to avoid bias due to shipping. The dilutions and degassing were done after shipping.

Table 4.3 Characterization of inocula from different sources in terms of feedstock, fermentation temperature (T), hydraulic retention time (HRT), organic loading rate (OLR), and processing.

Code	Source	Feedstock	T °C	HRT d	OLR $kg_{oDM}\ m^{-3}\ d^{-1}$	Processing
I-LRS	400 L reactor	Maize silage, shredded wheat, soybean meal, rapeseed oil, digestate	37	200	0.3	Sieving <5 mm
I-LRD	2500 L reactor	Cattle manure, maize silage	38	19	3.0	Diluting i/w 2:1
I-BGP	Biogas plant	Cattle manure, maize silage	37	103	2.7	Sieving <5 mm
I-WWP7	Wastewater treatment plant	Waste-water	37	na	na	Sieving <1 mm Degassing (7 d)
I-WWP14	Wastewater treatment plant	Waste-water	37	na	na	Sieving <1 mm Degassing (14 d)

4.4.2.1 Inoculum from Laboratory Reactor (I-LRS)

I-LRS was taken from a 400 L laboratory reactor, where bacteria were cultivated continuously. The inoculum was fed with maize silage, shredded wheat, soybean meal, rapeseed oil, and digestate from biogas plants in Baden-Württemberg, Germany. The organic loading rate (OLR) in terms of organic dry matter (oDM) was 0.3 kg_{oDM} m^{-3} d^{-1} and temperature was 37 °C [111]. The hydraulic retention time (HRT) was 200 ± 25 d. Before using the inoculum, it was sieved using a mesh size of 0.5 mm.

4.4.2.2 Inoculum Diluted from Laboratory Reactor (I-LRD)

I-LRD was taken from a 2500 L laboratory reactor, which was fed by 80% cattle manure and 20% of a maize and grass silage mixture. OLR was 3.0 kg_{oDM} m^{-3} d^{-1}, temperature was 38 ± 1 °C and HRT was 19 d [139]. Before using, the inoculum was diluted with water in an inoculum/water ratio of 2:1 and stored at 37 °C for 7 d for degassing.

4.4.2.3 Inoculum from a Biogas Plant (I-BGP)

I-BGP was from a 942 m3 biogas plant, fed with maize silage and cattle manure. HRT was 103 d, the operating temperature was 37 °C and OLR was 2.7 kg_{oDM} m^{-3} d^{-1}. Prior to use, the inoculum was sieved using a mesh size of 5 mm and degassed for 5 d [141].

4.4.2.4 Inoculum from Wastewater Treatment Plant (I-WWP)

I-WWP was taken from a wastewater treatment plant in northern Germany and sieved at <1 mm [142]. I-WWP7 was stored afterwards for 7 days and I-WWP14 for 14 d, both at 37 °C for degassing.

Chemical characteristics and TE contents of the tested inocula are shown in Table 4.4 and Table 4.5, respectively.

Table 4.4 Dry matter (DM), organic dry matter (oDM), ash, pH, nitrogen, ammonium (NH_4+-N), volatile fatty acid (VFA) and alkalinity with standard deviation for inoculum from a 400 L laboratory reactor (I-LRS), a 2.5 m^3 laboratory reactor (I-LRD), a biogas plant (I-BGP) and a wastewater treatment plant 7 d degassing and 14 d degassing (I-WWP7, I-WWP14).

Code	DM	oDM	Ash	pH	Nitrogen	NH_4+–N	VFA	Alka-linity
	%	%	$\%_{FM}$		mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
I-LRS	4.4 ± 0.0	61.7 ± 0.1	1.7 ± 0.0	8.28	4280 ± 30	3747 ± 22	30 ± 2	15.8
I-BGP	6.8 ± 0.0	68.0 ± 0.2	2.2 ± 0.0	7.78	4620 ± 0	2811 ± 60	23 ± 2	13.5
I-LRD	2.9 ± 0.1	71.9 ± 0.3	0.8 ± 0.0	8.23	2115 ± 5	1472 ± 10	31 ± 2	7.1
I-WWP7	2.6 ± 0.0	57.5 ± 0.6	1.1 ± 0.0	8.27	3040 ± 40	1659 ± 19	103 ± 23	5.0
I-WWP14	2.3 ± 0.3	58.7 ± 0.9	1.0 ± 0.1	8.27	3155 ± 65	1961 ± 18	321 ± 2	5.0

Table 4.5 Trace element (TE) concentration (dry matter base) of inoculum from a 400 L laboratory reactor (I-LRS), a 2.5 m^3 diluted from laboratory reactor (I-LRD), a biogas plant (I-BGP) and a wastewater treatment plant (I-WWP) together with the recommend range according to [143].

Code	Trace Element Concentration, mg $kg^{-1}{}_{DM}$								
	Fe	Ni	Co	Mo	W	Mn	Cu	Se	Zn
I-LRS	3244	5	3	7	2	316	91	1	378
I-BGP	2710	22	3	6	2	386	418	2	362
I-LRD	1131	5	1	10	1	177	98	1	284
I-WWP	92,096	18	5	6	20	220	797	0	643
Recom-mended[141]	750–5000	4–30	0.4–10	0.05–16	0.1-30	100–1500	10–80	0.05–4	30–400

4.4.3 Substrates

Five substrates with different nutrient compositions were chosen, where hay (S-HAY) and dried maize silage (S-DMS) represent widely used substrates and triglyceride fodder (S-TGF), concentrated fodder (S-CON) and microcrystalline cellulose (S-MCC) represent model feedstock with high content of fat, protein and fiber, respectively (Table 4.6).

Table 4.6 Characterization of the substrates in percentage of dry matter content (DM), ash, fat, protein, and fiber in percentage of fresh matter.

Code	Name of Substrate	DM	Ash	Fat	Protein	Fiber
		%	%	%	%	%
S-HAY	Hay	94.2	5.4	1.0	9.2	31.8
S-DMS	Dried maize silage	92.8	4.3	2.3	7.4	18.7
S-TGF	Triglyceride fodder	93.0	10.4	24.4	19.8	8.5
S-CON	Concentrated fodder	92.8	7.1	2.6	18.4	7.4
S-MCC	Microcrystalline cellulose	96.8	<0.3	<0.6	<0.5	59.4

Hay (S-HAY) (marstall Wiesen-Cobs, marstall GmbH, Oberstaufen, Germany) is a mixture of more than 50 different grass and herb species from the first cut from Allgäu (South Germany) in the year 2012. S HAY was dried by hot air, chopped to 16 mm, milled with a laboratory mill (Pulverisette 19, Fritsch GmbH, Markt Einersheim, Germany) and stored at −20 °C.

Maize silage (S-DMS) was taken from Unterer Lindenhof (Eningen unter Achalm, Germany). S- S-DMS was dried and milled with the laboratory mill.

Triyglyceride fodder (S-TGF) was provided as a homogenous standard material with well-known molecular structure ($C_{18}H_{32}O_8N$) and a known theoretical biogas yield of 609 L kg_{oDM}^{-1} [8]. S-TGF was stored at 4 °C.

Concentrated fodder (S-CON) (Raiffeisen Kraftfutterwerke Süd GmbH, Würzburg, Germany) was milled with the laboratory mill and stored at −20 °C.

Microcrystalline cellulose (S-MCC) (CAS: 9004-34-6, Acros Organics, Pittsburgh, USA) was used as standard substrate with known biogas yield of 745 L kg_{oDM}^{-1} with a methane percentage of 50% [49]. S-MCC had an average particle size of 50 µm and was stored at room temperature.

4.4.4 Measurement Procedure

All BMP tests were performed according to VDI 4630 [49] at ISR > 2 and a temperature of 38 ± 0.5 °C. In all digestion systems, beside D-HBT1 and D-HBT2, tests were performed in three replicates and digestion was terminated according to the 0.5% criteria, i.e., when the increase in gas production was less than 0.5% d^{-1} for three days. In both D-HBT, tests were performed in six replicates. Digestion time was terminated after 35 d, whereby the 0.5% criterion was met in each test run. Specific methane yield was calculated for biogas yield and methane percentage that were measured for each test run. Gas volume was corrected to standard conditions of 101.33 kPa and 0 °C.

Investigated combinations of digestion systems, substrates and inocula are listed in Table 7. All substrates were tested in all digestion systems. However, the full range of inocula was only tested in D-HBT1, which was chosen because of the low sample volume (30 mL) required and its high repeatability. With the other digestion systems only one or two inocula could be tested due to the limited number of reactors for parallel tests (Table 4.7). Additionally, trials with supplementation of TE for all inocula in D-HBT1 on substrate S-DMS were performed by adding a TE solution as described by Angelidaki et al. [51]. In this test series, blanks for all inocula were also tested.

Table 4.5 Investigated digestion system/Inoculum/Substrate-combination.

		Digestion Systems				
		D-HBT1	D-HBT2	D-BFT	D-EUD	D-AMP
Substrate	S-Hay	X	X	X	X	X
	S-CON	X	X	X	X	X
	S-TGF	X	X	X	X	X
	S-MCC	X	X	X	X	X
	S-DMS	X	X	X	X	X
	S-DMS +TE	X				
Inoculum	I-LRS	X	X			
	I-BGP	X			X	X
	I-LRD	X		X		
	I-WWP7	X				
	I-WWP14	X	X			

4.4.5 Taxonomic Profiling and Statistical Analysis

Taxonomic profiles of the microbial community within the analyzed inocula were determined by 16S RNA amplicon-sequencing. Microbial DNA was extracted with the FastDNA ® SPIN Kit for Soil (MP Biomedicals, Illkirch-Graffenstaden, France) and cleaned with Genomic DNA Clean & Concentrator TM Kit (Zymo Research, Irvine, USA). The 16S RDNA gene amplicon-library was constructed by using the "16S Metagenomic Sequencing Library Preparation" protocol (Illumina, San Diego, USA) and the primer pairs Pro341F and Pro805R [144]. The sequencing was done on the Illumina MISeq platform applying the 300x bp paired-end protocol. Afterwards bioinformatics preprocessing of the sequencing data was done. Forward and reverse reads were merged with FLASH [145], primer were removed with cutadapt [146], while quality trimming of reads was done with sickle [147]. Taxonomic classification was done by using the QIIME platform [148] in combination with the SILVA 16S rDNA reference database (Release 132, 10.04.2018). Taxonomic profiles were presented as a bar chart for each inoculum. More detailed information is given in Hassa et al. [149].

The statistical analysis of specific methane yield was performed by ANOVA post-hoc Tukey test at $\alpha = 0.05$ using Microsoft Excel 2016.

4.5 Results and Discussion

4.5.1 Microbial Community Composition

In Figure 4.2 the composition of the microbial communities of all analyzed inocula before starting the BMP test are shown. Differences in the microbial composition between the inoculum from wastewater sludge and the inocula from other origins were observed. The microbiome can be categorized into bacteria and archaeal populations.

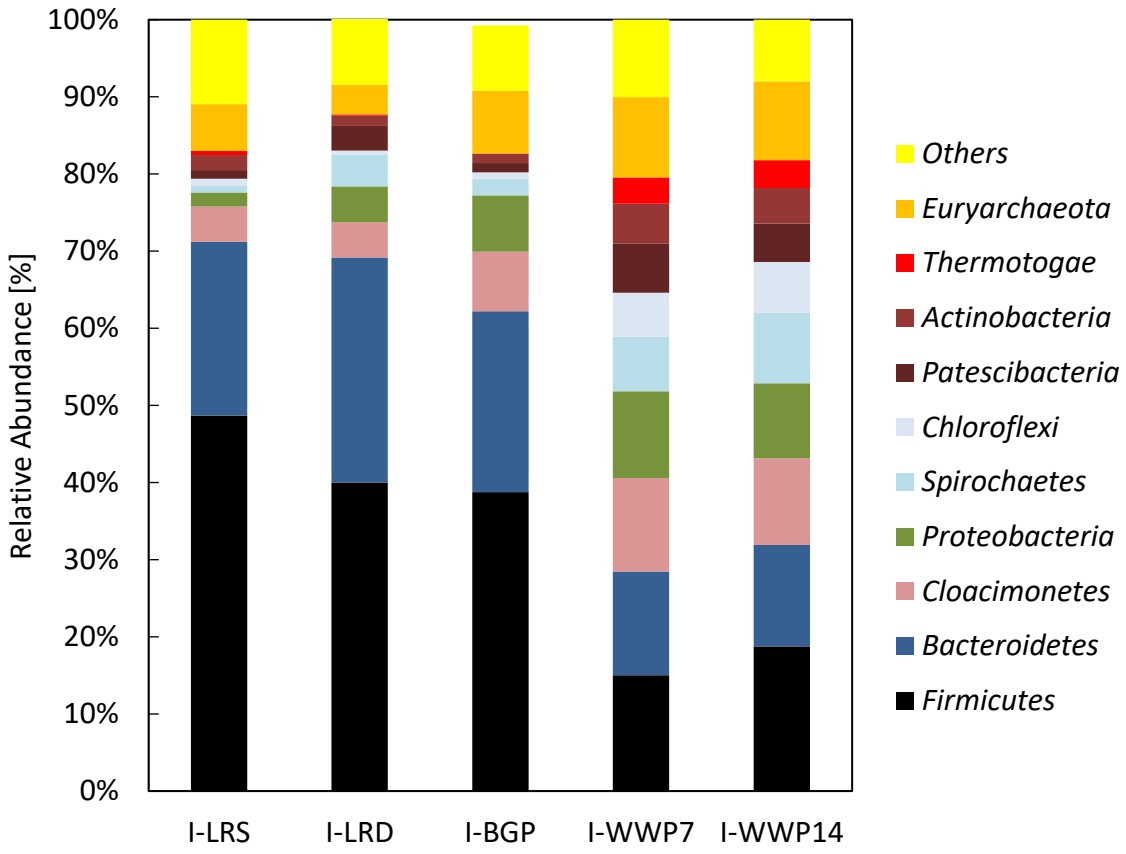

Figure 4.2 Microbial community of inoculum from laboratory reactor (I-LRS), laboratory reactor, diluted (I-LRD), biogas plant (I-BGP), and wastewater treatment plant 7 d and 14 d degassed (I- WWP7, I-WWP14).

4.5.1.1 Bacteria

The inocula I-LRS, I-BGP, and I-LRD showed a high abundance of Firmicutes within the bacterial population. I-LRS had the highest ratio with 49%, followed by I-LRD with 40% and I-BGP with 39%. Desvaux et al. [150] described the capability of Firmicutes to degrade complex materials like cellulose. It was also shown, that Firmicutes grow when fed with maize silage [151,152]. Additionally, all inocula contained a high number of Clostridia. As much as 40.5% of all bacteria in I-LRS were classified as Clostridia, as well as 33% in I-BGP and I-LRD.

The classes Clostridia and Bacilli (phylum Firmicutes) are able to decompose protein, cellulose, fat, and carbohydrates to acetic, propionic, and butyric acids [153,154].
However, members of the class Clostridiales are also reported to replace bacteria of the phylum Bacteroidetes. Most Bacteroidetes are acid producers and are capable of performing acidogenic-, acetogenic-, and syntrophic acetate oxidation breakdown [155]. A reduction of activity caused by self- inhibition of produced acid can occur. The high ratio of Bacteroidetes for I-LRS, I-BGP, and I-LRD (22.5–29.2%) could reveal a condition without high volatile fatty acid (VFA) as reported from Alsouleman et al. [155] for increasing the amount of poultry manure on feeding.
Inocula WWP showed a different bacteria composition and a higher diversity. Members of the phylum Firmicutes (15–19%) and Bacteroidetes (13%) were less abundant and additionally the phyla Cloacimonetes (11–12%), Patescibacteria (5–6%), Spirochaetes (7–9%), Proteobacteria (10–11%), Actinobacteria (5%), Chloroflexi (6–7%) and Thermotogae (3–4%) were identified. Members of the phylum Cloacimonetes are responsible for acetogenesis, and the degradation of amino acids, sugars, and alcohol. A lower abundance of this phylum could result in fewer educts of acetogenesis. The abilities of the phyla Atescibacteriam and Spirochaetes have not yet been described in the literature [156,157]. Campanaro et al. [158] showed that some members of the phylum Patescibacteria are more abundant in wastewater sludge compared to the digestate of agricultural feedstock. Proteobacteria are described as secondary degraders of polysaccharides [159]. The availability of more complex substrates should increase their population, which are common in wastewater sludge. The phyla Actinobacteria and Chloroflexi were previously described as highly abundant in wastewater sludge [156]. Thermotogae are found in several habitats. They can resist high temperatures and degrade a large diversity of organic sources [160].

4.5.1.2 Archaea

Large differences were observed in the ratios of the archaeal part of the microbial community microbiota. The archaea ratio was 10.4% for I-WWP7 and 10.2% for I-WTT14, which was almost 2.5 times higher than the ratio of I-LRD (4.1%) as well as higher than that of I-LRS (6.3%) and I-BGP (8.3%). De Vierze et al. [130] recommend a high abundance of methanogens for a good performance of the inocula.
The majority of archaea (93%) were members of the phylum Euryarchaeota. The I-BGP and I-LRD were dominated by members of the genus Methanosaeta (I-BGP 88% and I-LRD 73%). This reveals that within both inocula the acetoclastic methanogenesis pathway is favored and that both inocula seem to have a low VFA and ammonium (NH_4+–N) concentration. It was

shown, that the genus Methanosaeta decreases with high VFA and NH_4+–N concentration [136,157]. In contrast, the archaeal community of I-LRS consisted of the genera Methanoculleus (43%) and Methanosarcina (8%). Both species could also be found in smaller ratios (1–11%) in all of the other inocula. The high abundance in I-LRS is probably due to the high NH_4+–N concentration within this inoculum (Table 4.6). Members of the genera Methanoculleus and Methanosarcina can replace those of to the genus Methanosaeta in habitats with higher VFA and NH_4+–N concentrations. Kougias et al. [161] described the occurrence of Methanoculleus sp. in many biogas plants with different feedstocks and that this genus uses the hydrogenotrophic methanogensis pathway. Member of the genus Methanosarcina are described as stress resistant, hydrogentrophic archaea [153].

In I-WWP7 and I-WWP14, the archaeal community composition was similar. Both communities consisted of 80% Methanomicrobia. The genus of this archaeal class could not be detected.

4.5.1.3 Effects of Pre-Incubation

Based on the data of inocula I-WWP7 and I-WWP14, it is possible to determine the influence of pre-incubation on the microbial community composition. The ratio of the phylum Firmicutes was enhanced after 14 days of pre-incubation. Compared to only 7 days of incubation, the ratio was 3.7 ± 0.5% higher. One possible explanation for this is the higher degradation of complex material. However, the Proteobacteria ratio decreased by 1.4 ± 0.3% after 14 days compared to 7 days of pre- incubation. It was expected, that the higher amount of complex material would increase the Proteobacteria population. Luo et al. [162] found a similar behavior for the batch test. Additionally, there was no effect regarding the ratio of the phylum Bacteroidetes, which was expected to be lower when more complex material was used.

The phyla Cloacimonetes, Patescibacteria, Verrucomicrobia, and Tenericutes showed an increased ratio when the pre-incubation time was longer. The lower abundance of Cloacimonetes may be a result of fewer educts of acetogenesis. The functions of Patescibacteriam, Tenericutes, and Verrucomicrobia are not yet described in the literature [156]. The increase of the phylum Spirochaetes of 2.1% cannot be explained as its function is not yet known.

The different incubation times did not show any effect on the population of the phylum Actinobacteria. During incubation, the ratio of the phylum Chloroflexi showed a slow increase (0.9%).

4.5.2 Impact on Specific Methane Yield and Methane Percentage

4.5.2.1 Trace Element Addition

The results of TE supplementation are presented in Table 4.8. There were no significant differences in the specific methane yield of blanks and the substrate S-DMS with and without adding TE (CV between 0–3%) according to the results of ANOVA post-hoc Tukey test. Values for S-DMS are also in the range of dried maize silage of Mukengele et al. [112]. In contrast to a recommendation of Angelidaki et al. [51], the addition of TE was not necessary for the tested inocula. The TE concentration without adding additionally TE shows already, that inocula I-BGP, I-LRS, and I-LRD were in the optimal range for biogas plants reported by Oechsner et al. [143] (Table 4.5). The exception was Cu where the concentration was higher for all inocula. The inoculum I-WWP had higher concentrations of Fe and Zn whereas the concentration of Se was lower. To achieve optimal TE concentrations, the use of digestate is recommended. However, other publications also show a good performance for inoculum from wastewater treatment plants [131,132]. The values of I-WWP7 and I-WWP14 for S-DMS did not show any inhibition in methane production compared to the other inocula (Table 4.8).

Table 4.8 Specific methane yield and methane percentage tested with and without adding trace elements (TE) to blanks and dry maize silage (S-DMS) using inoculum from laboratory reactor (I-LRS), diluted from laboratory reactor (I-LRD), biogas plant (I-BGP), wastewater treatment plant 7 d and 14 d degassed (I-WWP7, I-WWP14). ANOVA post-hoc Tukey test was done for each pair with and without TE.

	I-LRS	I-BGP	I-LRD	I-WWP7	I-WWP14
Specific methane yield, L kg^{-1}					
Blank	22 ± 1^{a}	48 ± 1^{a}	77 ± 3^{a}	66 ± 1^{a}	60 ± 3^{a}
Blank + TE	20 ± 1^{a}	49 ± 1^{a}	81 ± 4^{a}	65 ± 2^{a}	58 ± 4^{a}
S-DMS	361 ± 4^{a}	342 ± 8^{a}	346 ± 4^{a}	354 ± 7^{a}	354 ± 10^{a}
S-DMS + TE	357 ± 10^{a}	343 ± 10^{a}	341 ± 9^{a}	371 ± 11^{a}	349 ± 11^{a}
Methane percentage, %					
Blank	64 ± 2^{a}	56 ± 1^{a}	58 ± 0^{a}	73 ± 1^{a}	78 ± 1^{a}
Blank + TE	68 ± 2^{a}	56 ± 1^{a}	59 ± 1^{a}	72 ± 0^{a}	79 ± 1^{a}
S-DMS	52 ± 1^{a}	50 ± 1^{a}	52 ± 1^{a}	54 ± 1^{a}	54 ± 0^{a}
S-DMS + TE	52 ± 1^{a}	51 ± 1^{a}	51 ± 1^{a}	53 ± 0^{a}	53 ± 0^{a}

4.5.2.2 Effect of the Inoculum

Figure 4.3A shows the specific methane yield for all inoculum/substrate combinations tested in digestion system D-HBT1. In Figure 4.3B, inoculum I-LRS is used as a reference and the specific methane yield of all the other inocula is related to the mean value of I-LRS.

The deviation of the specific methane yield when using different inocula differed for each substrate as also shown in other publications [55,135]. The CV differed between 1.9% and 4.8%.

Substrate S-HAY is the only substrate that showed no statistical differences for different inocula in the results.

Substrates S-HAY and S-CON had the lowest CV, both with 2.3% and 1.9%. Both substrates were homogenous standard substrates, which could be the reason for the small CV.

Substrates S-DMS has two well adapted inocula, namely I-BGP and I-LRD, characterized by a higher percentage of Firmicutes. However, both produced a significantly lower yield than I-WWP7. Other studies report that inocula, which have already adapted to the feedstock, produce a higher methane yield [134,135]. This cannot be confirmed by our data and more research will be needed to clarify the reasons.

Results of S-MCC showed statistical differences between I-WWP and all other inocula, which is also reflected in the highest CV (4.8%). Koch et al. [136] also reveals the biggest CV for S-MCC (around 5%). Yields achieved with I-LRS and I-BGP were around 370 L_{CH4} kg^{-1}_{oDM}. This value is expected as it falls within the range of average values between 363 and 371 L_{CH4} kg^{-1}_{oDM} determined by calculation and inter-laboratory tests [54]. It is also 99% of the theoretical value [49]. Inocula I-WWP7 and I-WWP14 produced more methane, reaching 384 and 393 L_{CH4} kg^{-1}_{oDM}, respectively, which is 103–105% of the theoretical value. However, Czepuck et al. [163] also report such a high spec. methane yield (392 L_{CH4} kg^{-1}_{oDM}) for substrate S-MCC. One possible reason could be the lack of carbon in inocula I-WWP7 and I-WWP14. Adding S-MCC as a source of carbon might improve the C/N-ratio and lead to a higher degradation of the inoculum.

Values of CV up to 4.8% can be explained by various influences. All the inocula had different microbial community compositions. This can result in a variance of substrate consumption for microbial growth [55]. Additionally, a stimulation of inocula by adding a carbon-rich substrate can result in a higher methane potential of the inoculum than measured in the blanks. An overestimation of the methane yield is a possible consequence [135].

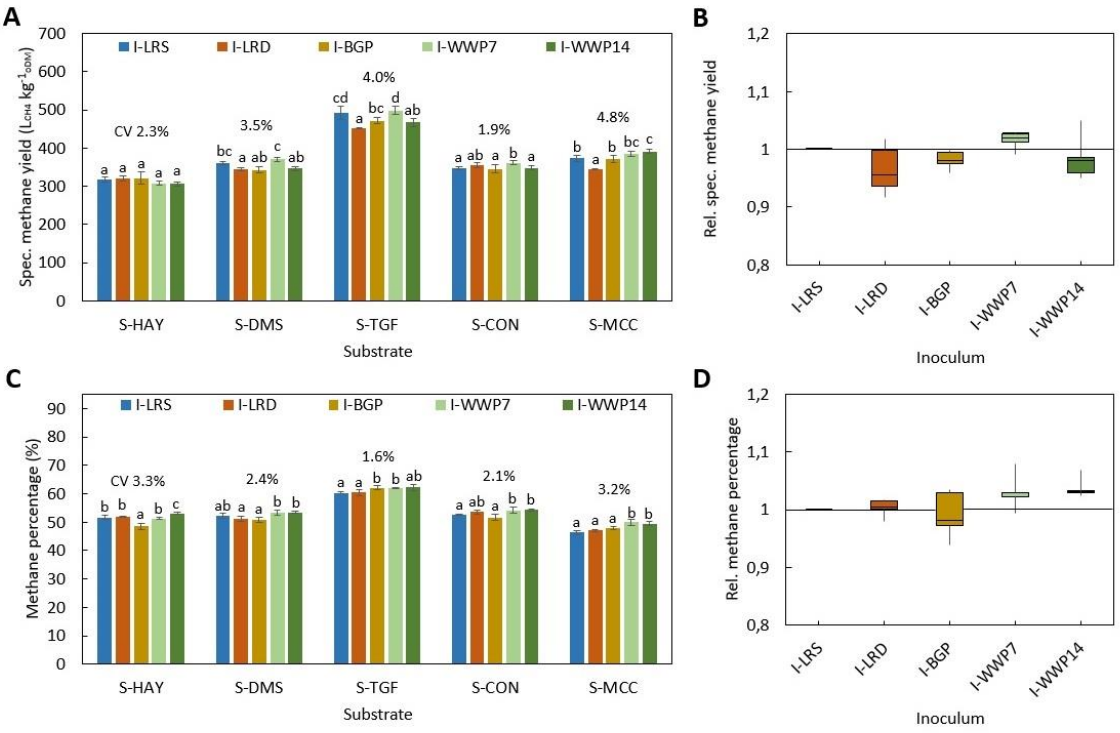

Figure 4.3 Specific methane yield (A) and methane percentage (C) of various substrates digested with different inocula in the digestion system D-HBT1 (error bars indicate standard deviation, different letters indicate significant differences within substrates at $p \leq 0.05$); rel. specific methane yield (B) and rel. methane percentage (D) of the different inocula compared to inoculum I-LRS (boxplots show divergence of the average values of the inoculum/substrate-combination); for code of digestion systems, inocula, and substrates see Tables 4.2, 4.3 and 4.6 respectively.

The methane percentage of the different inocula is presented in Figure 3C. The CV between the inocula was less than 3.3%. The methane percentage showed an almost similar behavior for all substrates.

Inocula I-LRS and I-LRD did not show statistically significant differences to each other.

I-BGP was only significantly higher than I-LRS and I-LRD for substrate S-TGF (1.2%$_{CH4}$ below average) and S-HAY (0.6%$_{CH4}$ above average), but in every case lower than for I-WWP7 and I-WWP14.

Inocula I-WWP7 and I-WWP14 had the highest methane percentage, as shown in Figure 3D. A statistically significant difference between I-WWP7 and I-WWP14 was only reported for S-HAY. For all other substrates I-WWP7 and I-WWP14 performed similarly. Thus, in case of I-WWP7 and I-WWP14, a dependency of the methane percentage on inoculum was shown. One possible reason for this can be the larger diversity of bacteria and a higher abundance of

archaea, which results in a shorter hydrolysis time with a low methane percentage at the beginning.

4.5.2.3 Effect of the Degassing

The effect of degassing on specific methane yield and methane percentage can be seen by the differences between inocula I-WWP7 and I-WWP14 (Figure 4.3). I-WWP7 and I-WWP14 were statistically significantly different for all substrates except S-MCC. I-WWP7 had a 7 to 15 L_{CH4} $kg^{-1}{}_{oDM}$ higher methane yield (CV 0.3–4.8%) compare to I-WWP14. These results differ from literature, where no effect of the degassing time was shown [130,132]. One reason might be that within I-WWP7 a smaller amount of substrate was used for the growth of the microorganisms, because of higher activity of microbiological populations by shorter degassing time. A longer degassing time resulted in a higher abundance of members of the phylum Firmicutes, which degrade complex material. This resulted in a higher methane yield of substrates with high fiber content like S-MCC and S-HAY. The German protocol VDI 4630 [49] recommends pre-incubation for at least seven days. Based on our results a longer pre-incubation time should be recommended.

4.5.2.4 Effects of the Digestion System

The inoculum I-LRD was tested in digestion system D-HBT1 and D-BFT (Figure 4.4). The CV for the digestion systems differed for the specific methane yield between 1.3% and 6.6% and for the methane percentage between 0.0% and 2.9%.

However, differences between D-HBT1 and D-BFT were only significant for substrates S-TGF and S-MCC. By using I-LRD in D-BFT, the methane yield of S-MCC is 101% of the theoretical methane yield.

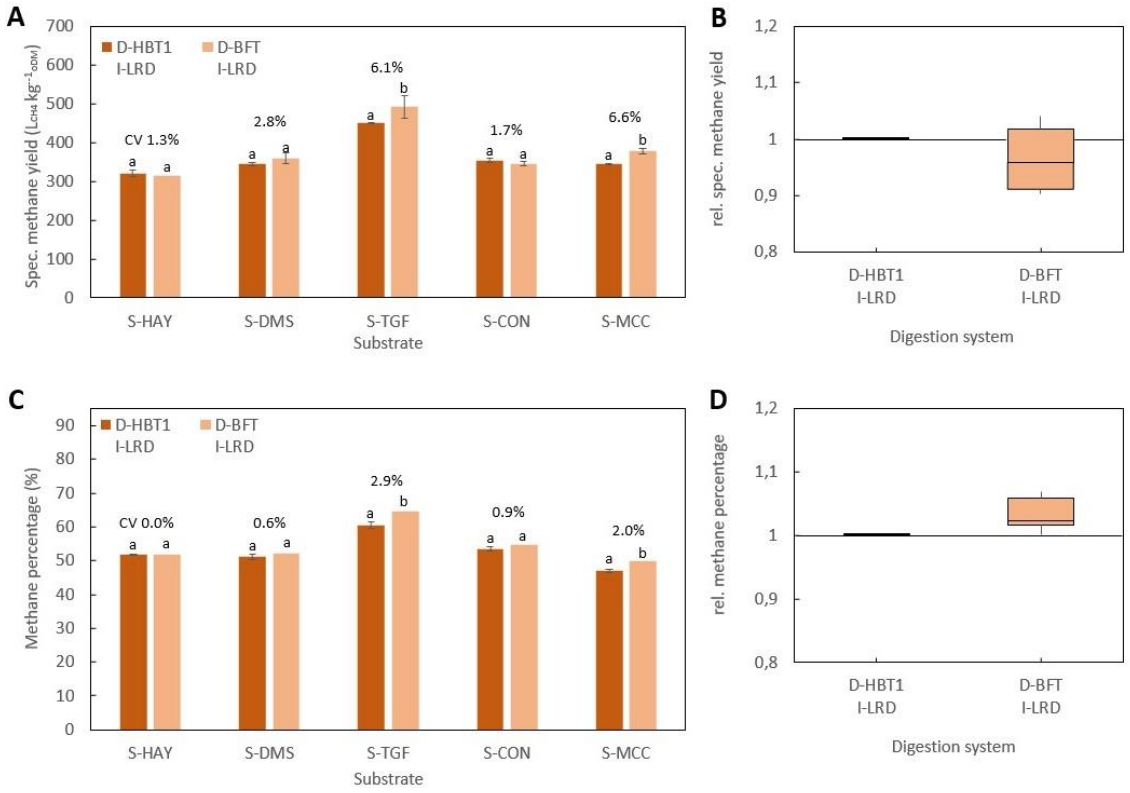

Figure 4.4 Specific methane yield (A) and methane percentage (C) of various substrates digested with inoculum I-LRD in the digestion systems D-HBT1 and D-BFT (error bars indicate standard deviation, different letters indicate significant differences within substrates at $p \leq 0.05$); rel. specific methane yield (B) and rel. methane percentage (D) of the different inocula compared to digestion system D- HBT1 (boxplots show divergence of the average values of the digestion system/substrate- combination); for code of digestion systems, inocula and substrates see Tables 4.2, 4.3 and 4.6 respectively.

The inocula I-BGP was used in three different digestion systems (D-HBT1, D-AMP, and D-EUD) (Figure 4.5). The CV for the specific methane yield was between 2.4% and 12.8% and for the methane percentage between 1.7% and 7.3%.

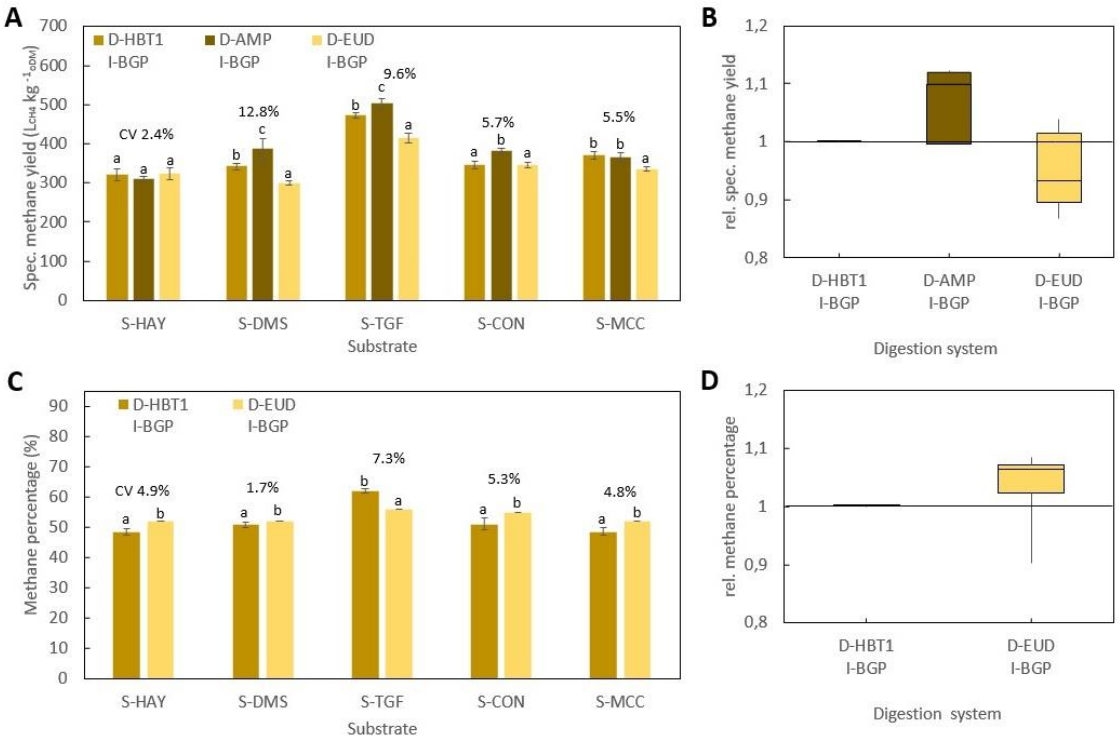

Figure 4.5 Specific methane yield (A) and methane percentage (C) of various substrates digested with inoculum I-BGP in the digestion systems D-HBT1, D-AMP, and D-EUD (A) respectively D-HBT1 and D-EUD (B) (error bars indicate standard deviation, different letters indicate significant differences within substrates at $p \leq 0.05$); rel. specific methane yield (B) and rel. methane percentage (D) of the different inocula compared to digestion system D-HBT1 (boxplots show divergence of the average values of the digestion system/substrate-combination); for code of digestion systems, inocula, and substrates see Tables 4.2, 4.3 and 4.6 respectively.

The specific methane yields of the digestion systems were significantly different for all substrates beside S-HAY Figure 4.5A.

The digestion system D-EUD showed in most cases the lowest methane yield (e.g., for S-MCC only 90% of the theoretical value). This could be explained by the fact that D-EUD has long pipes and could therefore be vulnerable to gas leaks.

D-AMP showed a higher methane yield than D-HBT1 and D-EUD for most substrates. The D-AMP measures automatically and consequently avoids manual mistakes. Another reason for random differences could be, that the D-EUD and D-AMP have a headspace, which can result in a deviation of up to 15% to 25% as described in Strömberg et al. [137].

The methane percentage could only be presented for D-HBT1 and D-EUD because it is not possible to measure the methane percentage in D-AMP Figure 4.5C.

D-HBT1 and D-EUD showed statistically significant differences for all substrates, even when the difference was small.

4.5.2.5 Effects of the Way in Which Water Vapor is taken into account

Although the digestion system is the same, D-HBT1 showed for most of the substrates a lower methane yield and also a lower methane percentage Figure 4.6. The differences are because of the way in which water vapor was taken into account by the two laboratories. In D-HBT1 the methane content was measured in dried gas and in D-HBT2 it was measured in wet gas and mathematically corrected according to VDI 4630 [49]. It seems that these differences in the measurement procedure and calculation affect the results. A cooling down of the syringes and condensation of water before gas analysis might lead to an overestimation of the methane percentage. Strömberg et al. [137] also reported measurement errors in this respect of up to 10%. Therefore, the drying of the gas is preferable to a mathematical correction.

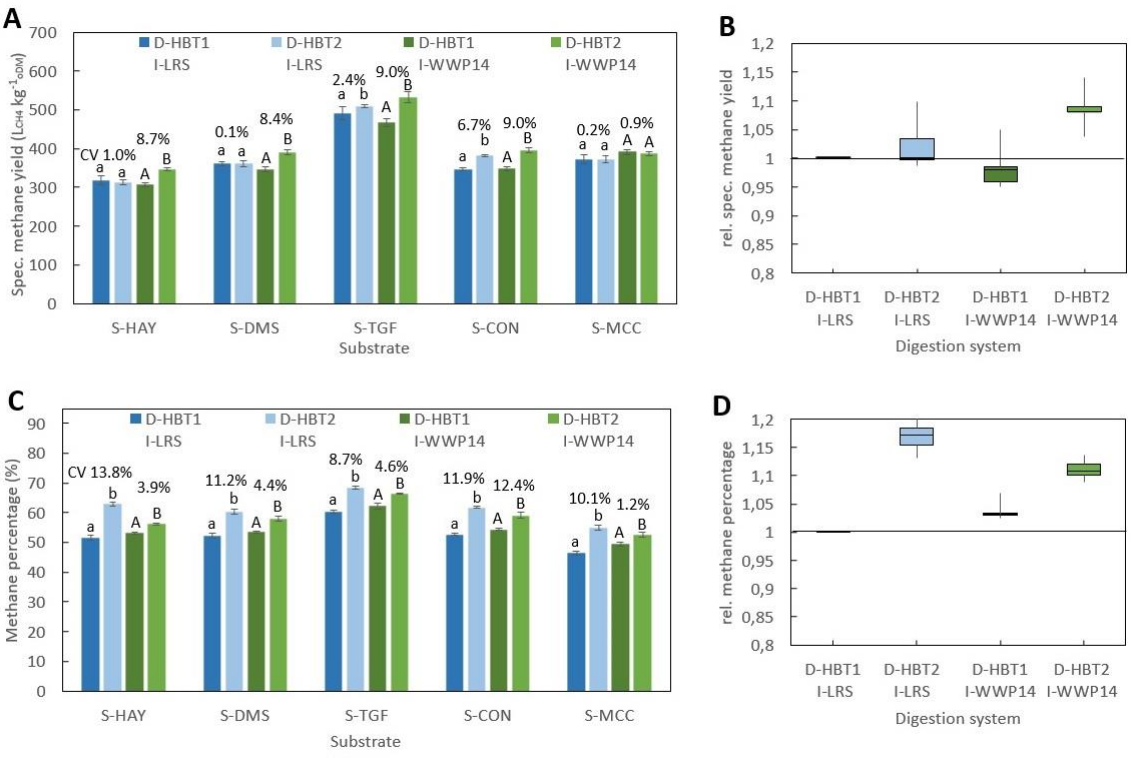

Figure 4.6 Specific methane yield (A) and methane percentage (C) of various substrates digested with inocula I-LRS and I-WWP14 in the digestion system D-HBT1 and D-HBT2 (error bars indicate standard deviation, different letters indicate significant differences within substrates and same used inocula at $p \leq 0.05$, lower case letters for I-LRS and capital letters for I-WWP14); rel. specific methane yield (B) and rel. methane percentage (D) of the different inocula compared to inoculum I-LRS (boxplots show divergence of the average values of the digestion system/substrate/inoculum- combination); for code of digestion system, inocula and substrates see Tables 4.2, 4.3 and 4.6 respectively.

4.6 Conclusions

Several bio-chemical parameters determine the performance of the used inocula in biomethane potential tests. The microbial community composition strongly depends on the origin of the inoculum. The inoculum from a wastewater treatment plant showed a high diversity of the microbial community, which was completely different to the community composition of inocula from biogas plants and laboratory reactors. The adding of trace elements to well supplied inocula did not affect the results. An impact of different incubation times (7 and 14 d) to a coefficient of variation of up of 4.8% was measured. The coefficient of variation for the specific methane yield was up to 4.8% for different inocula using the same digestion system. The coefficient of variation for the impact of the used digestion systems was maximum 12.8%. The digestion systems showed a higher effect, but the deviation strongly depends on the substrate. A clear effect of the digestion system cannot be identified due to missing data of one inocula in all the digestion systems. This point needs further research. The way in which water vapor is taken into account seems to be important and the drying of the gas is preferable compared to a mathematical correction.

5 General discussion

A high efficiency and the optimization of the biogas production are important for BPs to be economically viable. In Germany, the topic is receiving increased attention as the EEG subsidy for BPs older than 20 years expire. In most other countries, there are no incentives for the biogas sector, such as subsidies. Therefore, higher efficiency and consequently higher revenues is an important issue for the biogas sector worldwide. In order to develop further potential, the possible losses have to be identified and eliminated. The methods to do this have been developed in this thesis.

In this chapter, the results of the biological efficiency determination of 34 German and one US BP are discussed and the accuracy of the developed efficiency method is evaluated. Then, the reasons of the measurement inaccuracy on both the field-site (mass balance) and the laboratory-side (methane potential of input) are analyzed in more detail. Finally, the laboratory-side is discussed in-depth based on the biochemical methane potential test.

5.1 Biological efficiency of investigated Biogas plants

The biological efficiency of 34 BPs was investigated in Germany. The results showed a biological yield efficiency of above 100% for more than 60% of the biogas plants by determining the SMP of the substrates with the methods biochemical methane potential, fermentable organic dry matter (FOM) and energy of fermentable dry matter (EFOM). This is not physically possible. It reveals that the accuracy of the mentioned methods seems to be lower than required for a detailed efficiency analysis based on this parameter. However, the reason for these high values is, among others, a high efficiency of the German BPs due to the hydraulic retention time of 12 to 231 days in heated systems and 61 to 346 days in covered systems, which has been extended in recent years due to the EEG [30]. This assumption is supported by the results of the conversion efficiency (CE) and by the comparison with biological yield efficiency (YE) of the US BP.

Based on the CE using the BMP (CE_{BMP}) as a method, it is possible to evaluate the investigated BPs. Weiland et al. [85] and Ruile et al. [43] determined the CE_{BMP} of 61 BPs in 2009 and of 21 BPs in 2014, and their values can be used as a references to demonstrate the development of the CE_{BMP}. Only 33% of the BPs studied in this work have a CE based on the biochemical methane potential test (CE_{BMP}) lower than 95%. In Addition, three BPs (12%) have a CE_{BMP} of less than 90%. The CE_{BMP} is slightly higher than the CE_{BMP} in Weiland et al. [85] and Ruile et al. [43]. A CE_{BMP} higher than 95% means that only a 5% increase in methane production can

be obtained by adding 60 days retention time in the heated system, which seems to be an uneconomical way to increase the efficiency.
For the other investigated methods, such a statement is not possible because references are lacking. According to the results of the investigation, 9% of the energy potential of the substrates is stored in the lignin and 25-30% of the energy potential cannot be used in the anaerobic process because the anaerobic degradation is limited. In conclusion, 16-21% of the substrate potential is not stored in the lignin, but is also not currently degraded in German BPs (e.g. due lignin-encrusted components). This shows further potential of a BP by a pretreating the substrate or using the anaerobic non-degradable lignin in other processes to develop a bio-economic concept. Developing bioeconomic models to unlock this potential before or after the digestion process is an option to increase the economics of the biogas process. However, the results of the potential are only based on a rough estimation [42].

The investigation of the BPs in the US and Germany provides further interesting information. The YE based on the BMP of the US BP shows that a BP with a low efficiency can be easily detected by the biological efficiency method. The lack of heating system in the digester of the US BP leads to a low gas production in winter time and consequently to a low average efficiency for the whole year (36%). This fact can also be verified by analyzing the gas production. During winter, methane production decreases to 33.5 m^3/d compared to 796.0 m^3/d in summer. The methane production during summer time is even higher than the calculated potential. The low overall efficiency of the US BP can be explained by different legalities in Germany compared to the US. Since the heat use is not promoted in the US, the US BP lacks CHP plants and heating systems. The same situation can be reported about other countries [86,164]. For example, in China, CHP unit are absent and the biogas plant is heated with other renewable energies, resulting in a low heat supply in winter, as reported in another study by the author [86].
Even if the heat exchangers and thermal insulation are expensive, the heat supply of the biogas plant is indispensable, even in winter, to achieve high efficiency with high environmental benefits. In particular, due to the fact, that the heat generated during the operation of a CHP unit with biogas is higher than the heat required for the digester, there is an possibility to sell heat as an additional product [40,165]. For biogas plant using food waste as substrate, it is also important to sanitize the food waste by a digestion temperature above 50 °C or a pasteurization at 70 °C before applying it on the field [35].
Unlike the US BP, the investigated German BP with food waste as feedstock has an efficiency of 137%. This is higher than the highest efficiency reported for the 33 German agricultural BPs

– even if the conversion losses at the transformer are not considered and the nominal CHP unit efficiency is used for the determination. In addition to poor data quality and irregular samplings, the inhomogeneity of the input material also leads to an underestimation of the SMP of the substrate.

Nevertheless, the results of our study clearly show that the German EEG laws follow a reasonable strategy by paying a bonus for power generation by using special substrates and for external heat use.

It should be noted that the US samples were determined using a different BMP guideline than the German samples, which differ in parameters such as retention time and digestion system. In addition, there are many impacts on the results based on the field-site data quality in both countries. For example, the gas volume of the US BP was measured instead of calculated. These impacts are discussed in more detail in the following chapters. However, the large discrepancy in the results between the two BPs cannot be explained by these impacts alone.

In summary, an installed heating system at the BP as well as a bonus payment corresponding to the BP's electricity and heat production are worthwhile to achieving a high efficiency.

5.2 Measurement accuracy of the produced biogas estimation by the efficiency method

The efficiency method is developed to be able to calculate the biological efficiency of all German BPs that generate power. Only measured values by each BP are taken into account. The produced electric power is favored as output value for calculating the produced biogas amount, because the electricity meters are frequently calibrated and have a high precision compared to gas meters, which are only installed at few BPs in Germany. Determining the biogas produced from the power generated requires several assumptions that may affect the accuracy. For the gas yield, a conversion loss at the transformer of 2.0% and a CHP unit efficiency of 3.1% below the manufacturer's efficiency are assumed. Both of these assumptions are weak because they cannot be proven. However, if the CHP unit efficiency and conversion loss at the transformer are the main reasons for an overestimation of the field-site data, the CHP unit efficiency will be underestimated while the transformation loss will be overestimated. The trouble is that the methane potential of the substrate is also underestimated if the calculation is based on the nominal CHP unit efficiency and the conversion losses at the transformer are not taken into account, as shown for the German BP with food waste as substrate.

The efficiency method must be adapted for those BPs which do not feed into an electricity grid, as shown for the US BP. In this case, the gas flow meter must be considered instead of the

power generation. This has the advantage that the efficiency of the CHP unit and the conversion losses at the transformer can be omitted. Nevertheless, it also has its limitations, as the measurement on the full-scale BP can be distorted if the gas volume is measured while the gas is not fully dried or the correction of gas temperature and pressure is done only with help of a standard value instead of a measurment.

The results of German biomethane BPs, which were investigated for one year as part of the Biogas Measurement Program III [29] and the measurements during the summer months for the US BP reveal an efficiency of more than 100% for the biological yield efficiency determined by the BMP. This shows that the suppositions for calculation of the produced biogas are not the main reason for values above 100% even though an influence is possible.

Anyway, most of the BPs do not spend a lot of money metering equipment. Usually, the operators are farmers who have a low starting capital and measurement equipment is not mandatory for the operation. However, these facts limit the accuracy of determining the biological efficiency. To increasing the accuracy, the development of low-cost measurement equipment is essential.

Apart from this, the results of the present study are influenced by several other factors.

5.3 Measurement accuracy of the mass balance of full-scale plants

The accuracy of the efficiency analysis is highly dependent on the field-site data and the sampling. Resulting measurement errors lead to a low accuracy of the efficiency analysis.

The combination of ODM mass balance residual and energy balance residual reveals that 45% of the BPs have non-credible results. An ODM residual of up to 25% was calculated, while an ODM residual of about 11% was expected due to water incorporation [69]. This demonstrates that an error of about 14% seems to be possible when measuring the feedstock mass. Again, the problem is due to the fact that most BPs are operated by farmers or small companies. Unlike large chemical companies, BP operators do not spend a lot of money on measurement equipment and calibrate it on a regular basis. For example, most BPs calculate the mass of manure by the number of animals or by the time of pumping. Some BPs were also reported to measure only the total mass of feed. In practice, most types of silages are mixed in layers in the same silo. In this case, their individual mass cannot be accurately determined. Therefore, the operator only measures the mass of the mixture and then estimates the amount of the individual substrate. Likewise, the amount of silage leachate is not measured for most BPs.

For those BPs which install less than 100 kW power a lack of data can be reported. These BPs also usually have a higher proportion of manure in their feeding ratio compared to others. This

results from the bonus payment in the EEG 2017 and EEG 2021 for the use of more than 80% manure in the feeding [30]. The correlation of the manure ratio to the installed power seems to be the main reason for the reported correlation between the manure ratio and the measurement accuracy.

Based on these findings, an efficiency analysis of a small BP supported by the EEG 2017 or EEG 2021 (75-150 kW installed capacity and 80% manure content in the feed) is not reasonable, but even for other BPs, the efficiency determination of full-scale BP will not have satisfactory accuracy without financial support from the federal government through another EEG to equip them with measurement devices.

Another impact not yet discussed is the sampling. Sampling frequency and sampling method affects the results. The sampling method is the same throughout this work, and the sampling frequency is 12 times within one year for each BP. The DM and ODM show large variations depending on the charge and environmental conditions during the measurement year, such as weather (Figure 5.1). This shows a large impact of the measurement frequency.

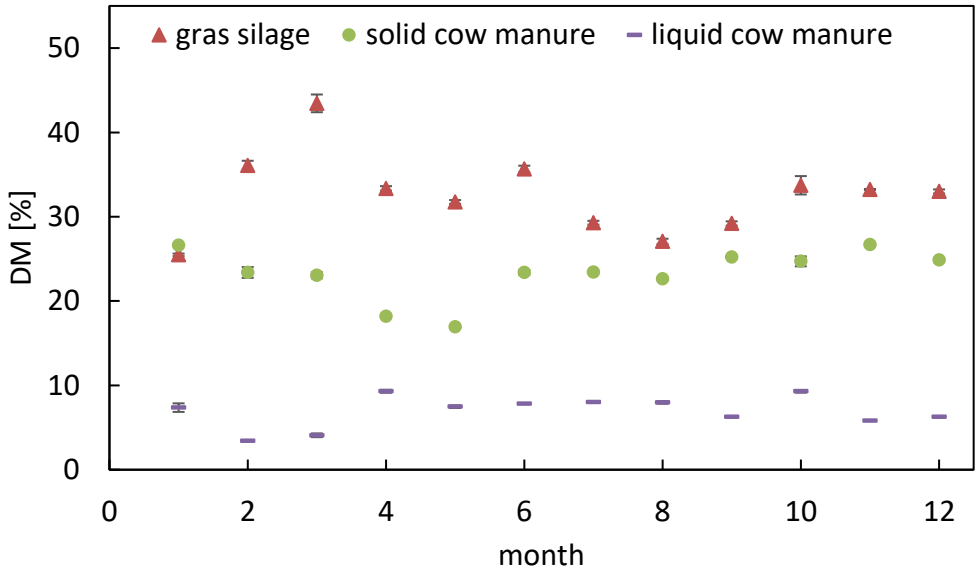

Figure 5.1 Dry matter (DM) of grass silage as well as solid and the liquid cow manure, taken from a biogas plant during one year of sampling (n=3, error bars indicate standard deviation)

Comparing a German BP that feeds food waste with a US BP shows the problems one faces when investigating a BP in countries other than Germany. The laws in most other countries are less stringent. This results in an inexpensive measuring equipment. The BP under investigation in the US, for example, only measures the volume of the feedstock. This means that the mass must be calculated using an assumed density. Lower measurement accuracy may be the

consequence. In contrast, the law in Germany requires a measurement of the substrate mass, which seems to maintain more reliable data [33]. Only small BPs are excluded from this law. However, DM/ODM data of the digestate for US BPs are lacking for a more detailed analysis of the plausibility of the feeding masses. In addition, the frequency of sampling (only one-time sampling of the biogas plant in the US could have a very large influence.

5.4 Accuracy of methods for methane potential determination

The efficiency analysis shows an underestimation of the input potential of the BP by the biochemical methane potential test, the fermentable organic dry matter (FOM), the energy of fermentable organic dry matter (EFOM) and literature values of the Association for Technology and Structures in Agriculture (KTBL). These methods result in a biological yield efficiency of more than 100% for more than 50% of the BPs. However, even if the potential is underestimated, all these methods show a large sensitivity to the measured methane yield (Figure 5.2).

The values of the KTBL are based on data determined by the BMP. Reasons for the underestimation of the BMP compared to data from full-scale BP could be a lower temperature, a higher consumption for bacterial growth or a lower hydraulic retention time in the batch-test as well as an effect of co-digestion in the full-scale biogas plant, which leads to a higher degradation rate. The impact of these parameters could not be quantified until today [82–84].

The biological CE determined by the BMP (CE_{BMP}) is also based on the underestimated SMP of the substrates. This results in an underestimation of CE_{BMP}, but the total measurement error on the CE_{BMP} is unknown because the measurement error of the BMP test for the SMP of digestate is also unknown and cannot determined. The determination of the SMP of digestate differs from that of the SMP of substrate. No Inoculum is added and other effects, such as co-digestion, can be neglected due to the use of original digestate. Anyway, it must be mentioned that the definition of the CE_{BMP} is clearly set to the temperature of 37 °C and the hydraulic retention time of 60 days according to the guideline of VDI 4630. Both parameters strongly influence the results.

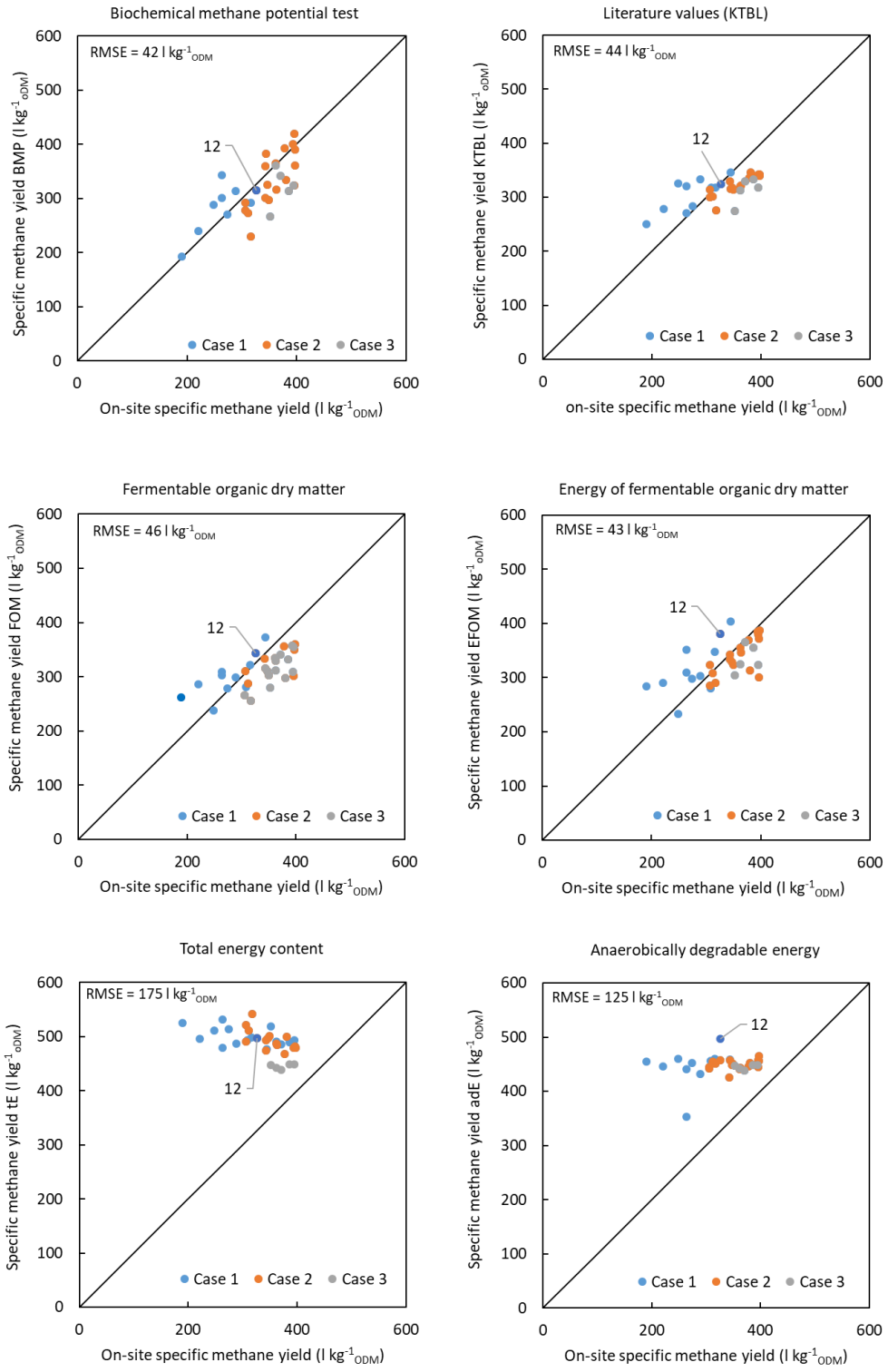

Figure 5.2 Comparing of measured and calculated specific methane yield based on the method and on on-site data; methods investigated are biochemical methane potential test (BMP), the fermentable organic dry matter (FOM), the energy of fermentable organic dry matter (EFOM), literature values of the Association for Technology and Structures in Agriculture (KTBL), the total energy (tE) and the anaerobic digestate energy (adE); labeled biogas plant 12 is a research BP with expected higher accuracy of measured data; Case 1,2,3 are according to Hülsemann et al. defined [166]

The FOM and EFOM methods are both based on the same fermentation coefficient, which in turn is based on a batch tests in sheep stomachs. The results appear to be similar to those of the BMP. It can be seen that the fermentation coefficient underestimates the fermentable fraction of the substrate. This is supported by the fact that the CE_{FOM} and the CE_{EFOM} show values higher than 100%. These high values are possible because the ODM in the digestate is lower than the estimated value. The estimation is based on the expected degradation according to the fermentation coefficient. However, it is not possible to adjust the fermentation coefficient based on this work because the effects of several parameters overlap each other. Further research is needed to isolate the effects of the fermentation coefficient.

In this work, a research BP is also investigated. At this BP, the meters are calibrated frequently, resulting in a high data quality (Figure 5.2). The results of this BP are close to 100% for yield efficiencies (BMP 104%, KTBL 101%, FOM 95% and EFOM 86%). This suggests that the quality of other full-scale BPs is responsible for the low measurement accuracy. Still, it is impossible to confirm such a conclusion using data based on measurements at only one BP.

The anaerobically degradable energy (adE) and the total energy (tE) do not have a yield efficiency higher than 100%. The sensitivity of these two methods is lower than that of the other methods because the potential used for microbial growth and the potential of the non-degradable parts are not fully subtracted (Figure 5.2). In tE, the degradability of the material is not considered, resulting in a high estimated input potential. This is because the non-degradable part, such as lignin, has a higher gross calorific value (33.74 MJ/kg) than the other parts. The lignin potential is not included in the adE because the lignin content is subtracted according to Mächtig et al. [42]. Other inaccessible parts are not subtracted anyway because of incrustation by lignin. The main conclusion of the adE and the tE differs from other methods. The CE based on the tE shows the energy potential maximum that can be reached when the material is burned and by comparing the CE_{adE} and the CE_{tE}, the energy fraction of the substrate stored in lignin can be determined. According to these results, the additional potential to be expected from the pretreatment can be estimated. Anyhow, it should be noted that the estimation of the lignin fraction in the CE_{adE} is based only on a rough estimation [42].

Overall, there is no method for determining the yield efficiency that can be used to obtain reasonable results for BPs without additional research. The inaccuracy seems to be high, as the values for biological efficiency are up to more than 130% for all methods based on the batch tests. In contrast, CE determined using the BMP, the tE or the adE shows reasonable results. However, they are limited by the fact that they only indicate the efficiency for a special case. A reliable measurement method to determine the SMP of a substrate is still missing today.

5.5 Measurement accuracy in the laboratory in the case of the BMP

As shown above, there is still a lack of a method to accurately estimated the SMP of a substrate. For this reason, a detailed analysis of the measurement accuracy of laboratory methods is necessary. In this work, the BMP is analyzed in detail. It can be influenced by the used inoculum, the digestion system or the experimental procedure.

The impact of the experimental procedure has already been discussed by many scientists. The temperature, the hydraulic retention time, the inoculum-to-substrate ratio and several other parameters affect the measurements. Therefore, the procedure is specified in different guidelines. In this work, the German guideline VDI 4630 [49] is used. The effects of the used guideline show strong deviations as already shown in several scientific studies [55,137,138]. Further research in this field seems to be necessary.

The research in this thesis focused on the other two impacts: the impact of the inoculum and of the digestion system. Six different inocula were used in a Hohenheim biogas yield test (HBT). All inocula had been proofed several times in an interlaboratory test of the KTBL. In this way, outliers were excluded. The investigation resulted in a coefficient of variation (CV) of 4.8% when using different inocula. This variation is lower than those previously reported by several researchers [54,130,133,167]. The conclusion from this data is that the usage of a well-known inoculum is preferable. However, when different inocula are used, the SMP varies greatly depending on the substrates. Even if there is a tendency between two inocula, this tendency cannot be found for every substrate. Therefore, the implementation of a correction factor is impossible. The CV of up to 4.8% when using different inocula in the batch test must be considered. This variation can only be prevented by using the same inoculum in each laboratory, but this is of limited practicality. Even if each laboratory orders its inoculum from the same place, a large quantity of inoculum would often have to be shipped. Most of the setups requires more than two liters of inoculum for each batch test. This quantity can be reduced by drying the inoculum, but the drying process degrades the quality of the inoculum. Heerenklage et al. [168] developed a method to produce standardized and storable inocula that can be shipped to multiple laboratories, but several problems, such a lag phase of 7 to 10 days, have been reported to date.

The second influencing factor investigated is the digestion system used for BMP. The SMP of five substrates were compared with the following digestion systems: 1) HBT and Bergedorf fermentation test, 2) HBT, eudiometer and automatic methane potential test and 3) two HBT. The SMP between the digestion systems showed a CV of up to 12.8%. A weak trend can be

observed between the systems, but the CV and trend are different for each substrate. A CV of 12.8% may be a reason for the low measurement accuracy of the efficiency analysis. For example, the biological yield efficiency of 21 of the 35 investigated BPs is in the range of 100% +/- 12.8%. Hafner et al. [169] also reported an impact of the digestion system in a study of 37 laboratories from 14 countries, but the variation also appears to be random. In any case, the results highlight the need for more precise and stringent instructions for the digestion system in the guidelines. Without reducing this influence, detailed efficiency analysis based on the BMP does not seems feasible. The results of interlaboratory tests such as the annual interlaboratory test of the KTBL [54] (8-12%) or the results of Fruteau de Laclos et al. [48] (15-17%) support this assumption.

The examination of the two HBT shows the great importance of small details in the experimental procedure. For the first, the gas was dried by Sicapent® before measurement. For the second HBT in another laboratory, the amount of dried gas was calculated using a formula according to VDI 4630, and the measurement took place when the gas was not yet dried [46]. The results show a measurement deviation between the two HBT. Nonetheless, a specific error cannot be found.

However, even if the used digestion system has a strong impact, the underestimation of the SMP cannot be explained by this alone. As for the efficiency of the BPs studied in different laboratories, no clear impact of the laboratories can be found. Future research should investigate the differences between BMP results and field-site data. However, for such an investigation, the field-site data must be measured with a high accuracy as indicated for the research BP and the sampling must be representative.

Even though the CV is quite high, the standard deviation of a test in one laboratory is only 1-7%, which suggests that a much higher accuracy is obtained in the laboratory when using one digestion system and one inoculum. On this bais, a comparison between BPs could be possible with a higher accuracy by comparing the data.

5.6 Conclusion and Outlook

The transferability of laboratory data like the biochemical methane potential test to full-scale BP seems to be low on account of certain factors which reduce the measurement accuracy. The evaluated method requires the assumption of a CHP unit efficiency and a conversion loss at the transformer. There is little or no data in the literature for either. Further measurements of both parameters are needed to determine their possible range. In the case of the US BP, the gas volume was measured rather than the power generated. Thus, it is not necessary to determine

both parameters. Unfortunately, the gas volume is measured only at some German BPs. The installation of frequently calibrated gas volume meters could be a solution to achieve a higher measurement accuracy.

The efficiency analysis also requires parameters form the full-scale BP like the feeding mass, the produced power, the methane ratio or the methane yield. The quality of these data is limited due to various factors such as the lack of accurate measuring equipment or the storage of a mixture of substrates in the silos. These parameters have a great impact on the results. For example, a measurement error of up to 25% has been reported based on the ODM mass balance. In addition, the ODM balance is influenced by parameters like the water incorporation or the sampling. The impact of the field-site data cannot be isolated. Therefore, it is impossible to determine the measurement accuracy for the individual parameters. The results of a research BP that has an accurate equipment and is calibrated frequently are closer to 100% for the batch-based efficiency and even less than 100% for the FOM and the EFOM. This may indicate that field-site data has a large impact on the measurement accuracy. However, based on only one BP, it is not possible to draw a general conclusion. Further research on well-equipped BP may help to isolate the factors of the field-site data and their influence on the accuracy of the measurements.

Besides the field-site data, sampling has also a great influence. The sampling procedure was not changed during the measurements in this work and an attempt was made to take representative samples. Nonetheless, a systematic impact cannot be excluded. The results of the DM/ODM values of samples taken monthly show a wide variation. This should be a focus of future research.

The results of the full-scale BP study show values more than 100% for most of the BPs when the BMP, the FOM, the EFOM and the literature value of the KTBL are used as determination methods for the SMP of the substrates. These results indicate a systematical measurement error. Underestimation by the methods based on the batch-test seems to be the reason. Most of the methods were investigated for the first time in this research. Further investigations need to be done to optimize the fermentation coefficient for the FOM and the EFOM method. The tE and the adE methods show more reliable results, but the sensitivity is very low. The CE of the tE method is useful to compare the efficiency of BPs with other industrial processes and to show the potential of further bioeconomic concepts. The CE of the adE seems to be useful to determine the additional anaerobic digestible potential of further pretreatment, especially by comparing the values with the CE of the BMP. However, the adE method only roughly predicts the lignin content, so more detailed research is needed.

The BMP and the impact of the digestion system and the inoculum are investigated in this thesis. A coefficient variation of up to 12.8% with different digestion system and of up to 4.8% when using different inocula can be reported. In terms of biological yield efficiency, 64% of the investigated German BP are in this range. Based on these results, stricter guidelines for the use of different digestion systems and the use of a well-known inoculum are essential.

In contrast, studying different BPs in the same laboratory allows the comparison of the data, as the standard deviation in one laboratory is only 1-7%.

Overall, the efficiency analysis as well as the determination of the biological efficiency can contribute to the improvement of the BP as shown for the US BP. However, certain factors lead to a low measurement accuracy, which reduces the benefit of the analysis of German BP. Further research is needed in the area of measurement accuracy in the laboratory and at full-scale biogas plants and the quality of data collected at the BPs needs to improved.

6 Summary

Biogas is a renewable energy source with main advantages compared to other renewable energy sources. The advantages include the use of organic waste as a substrate, local power and heat production, rural job creation, the possibility of a flexible gas production and a product which can easily stored and transported in a gas grid or on the roof of a digester.

However, the development of the biogas sector is highly dependent on the costs of producing gas, electricity and heat. The production costs are higher than the costs for other energy sources. Growth of the biogas sector is therefore only possible if there is political promotion for biogas as there was in Germany through the EEG. Nowadays, due to the reduction of bonus payments in the EEG 2017 and EEG 2021 in Germany as well as the lack of policy promotion in several other countries, lower production costs based on a higher efficiency are essential to help the biogas sector grow further. In order to achieve higher efficiency and to tap the full potential of biogas, the efficiency has to be determined, which is done in this thesis.

The method developed in this thesis uses only the parameters which have high measurement accuracy at German BPs. The system boundary includes only the gas-tight digester to determine the efficiency of the biological system. The output is the produced gas, which is calculated based on the produced power. This is necessary since this value has the highest accuracy and availability at German BPs.

The input methane potential is determined using 6 different methods. These methods are compared on the basis of an investigation of 33 German agricultural BPs as well as one German and one US BP using food waste as feedstock. The four methods based on the batch test show a high sensitivity. Unfortunately, they also show efficiencies greater than 100% for most BPs, clearly indicating an underestimation of the degradable potential. Only for the US BP can an efficiency less than 70% be reported. This result is probably based on the lack of heating system corresponding to the lack of promotion of heat recovery in the US. The CE according to the BMP method also reveals an average efficiency of 95% for the German BPs. The values of the two gross calorific value-based methods show efficiencies below 100%, but with low sensitivity. The results of these methods can be used to determine the further potential of a bioeconomic process and to compare the biogas process with other industrial processes.

There are several impact factors that affect the accuracy of the efficiency measurements. The installed meters are not frequently calibrated at most BPs. Also, some meters are almost completely missing, as only few BPs in Germany have a gas flow meter. Thus, assumptions and calculations are required to determine the efficiency. In the developed method, the gas flow must be calculated from the amount of the power production, the calorific value, the gas quality,

the CHP unit efficiency and the conversion loss at the transformer. The last two values must be assumed, even if the database is small. Another important parameter is the feeding mass. It is measured by the German BPs, but in some cases, the data quality is low. For example, different crops are mixed in the silos and measurement of each substrate is not possible. This leads to measurement errors shown by the organic dry matter mass balance, which has a residual value of up to 24%, while only 11% can be occur based on water incorporation into the ODM.

Another factor having an impact is the sampling. The results of a monthly sampling throughout the year show a fluctuation in the DM/ODM values. This clearly reveals the impact of the frequency and timing of sampling.

To investigate the accuracy of the methods used to determine the SMP of the substrate, the biochemical methane potential test is examined in detail. The BMP consists of the used inoculum, the substrate, the digestion system and the calculation. The impact of the used inoculum and the digestion system is investigated by using different inocula in one digestion system as well as by using the same inoculum in multiple digestion systems. The inocula used in this thesis are well-known and have been used in interlaboratory tests for several years. Thus, outliners were excluded. A CV of 4.8% can be reported between the different inocula, which is lower than reported in most other publications before. The use of different digestion systems shows a higher CV of up to 12.8%. For the inoculum and the digestion system, the deviation varies strongly and no clear correlation can be identified. Therefore, a correction of this effect is not possible. The biological yield efficiency of 21 of the investigated BPs is in the range of 100 ± 12.8%. This reveals the need of stricter rules for the digestion system. All digestion systems used in this thesis are described in the German guideline VDI 4630. The calculations were also done according to the German guideline VDI 4630. An influence can be neglected. However, if the results of a measurement with already dried gas are compared with the results of a calculation according to VDI 4630, which is based on the measurement with wet gas, a discrepancy can be found.

Although, the CV using only one digestion system and one inoculum is only 1-7%. A comparison of the efficiency of different BPs by using the same inoculum and digestion system is hence recommended.

7 Zusammenfassung

Biogas ist eine erneuerbare Energie, die gegenüber anderen erneuerbaren Energien eine Vielzahl von Vorteilen bietet. So können z.B. organische Abfälle zur Energieproduktion genutzt und eine dezentrale Stromversorgung ermöglicht werden, die zusätzlich Arbeitsplätze außerhalb der Städte generiert. Des Weiteren kann Biogas flexibel und dauerhaft produziert und an der Biogasanlage oder im Gasnetz gelagert werden, um anschließend beim Verbraucher umgewandelt zu werden.

Der Nachteil von Biogas ist, dass die Produktionskosten im Vergleich zu fossilen Energieträgern sehr hoch sind. Daher rentiert sich die Produktion von Biogas nur, wenn Zuschüsse vom Staat geleistet werden oder wenn durch eine CO_2-Steuer die fossilen Energieträger entsprechend der langfristigen Folgen ihrer CO_2-Emissionen verteuert würden. Dies ist der vorrangige Grund dafür, dass der Ausbau von Biogas im Vergleich zu anderen erneuerbaren Energien in vielen Ländern bisher gering ist. In Deutschland wird die Biogasbranche durch das EEG gefördert, doch im Zuge des EEG 2012, EEG 2017 und EEG 2021 sind die Bonuszahlungen deutlich reduziert worden, was den weiteren Ausbau der Produktion zum Erliegen gebracht hat und einen Rückbau der Anlagen in den kommenden Jahren wahrscheinlich macht. Um dies zu verhindern sowie einen Ausbau in anderen Ländern zu fördern, ist eine Verringerung der Produktionskosten beispielsweise mittels höherer Effizienz notwendig.

Um die Effizienz zu steigern und Optimierungspotential zu entdecken, ist der erste Schritt, eine solche Effizienz zunächst zu definieren und eine robuste Methode zur Bestimmung dieser festzulegen. Eine solche Methode sollte in dieser Arbeit entwickelt und anschließend ihre Genauigkeit bestimmt werden.

Die Methode in dieser Arbeit wurde so entwickelt, dass damit möglichst viele stromerzeugende Biogasanlagen in Deutschland untersucht werden können. Zudem sollten möglichst nur zur Kostenabrechnung wichtige und somit häufig kalibrierte Messdaten verwendet werden. Die Systemgrenze wurden so gewählt, dass sie alle gasdichten Behälter beinhaltet. Als Output wurde das Potential im produzierten Gas gewählt, das allerdings über den produzierten Strom ausgerechnet werden musste, da viele Biogasanlagen in Deutschland keine Gaszähler besitzen oder diese nicht regelmäßig kalibriert werden. Als Input wurde das Potential vom Substrat gewählt. Dieses Potential kann mittels unterschiedlicher Methoden bestimmt werden. Sechs dieser Methoden wurden in der vorliegenden Arbeit an 33 landwirtschaftlichen Biogasanlagen und an zwei Biogasanlagen (eine in Deutschland und eine in den Vereinigten Staaten von Amerika), die unter anderem Lebensmittelreste als Substrat verwenden, untersucht und

untereinander verglichen. Vier der untersuchten Methoden beruhen auf Ergebnissen aus Batch-Tests. Für diese Methoden konnte eine hohe Sensitivität ermittelt werden. Jedoch wurden für die meisten Biogasanlagen biologische Ausbeuteeffizienzen von mehr als 100% errechnet, was physikalisch nicht plausibel ist und auf eine Unterschätzung des Biogaspotentials der Substrate schließen lässt. Die beiden Methoden, die auf Heizwerten basieren, zeigen hingegen eine geringe Sensitivität, dafür jedoch Effizienzen kleiner als 100%. Die Ergebnisse der beiden Methoden können in Zukunft für die Abschätzung des Potentials weiterer Bioökonomieprozesse sowie zum Vergleich mit anderen Industrieprozessen genutzt werden.

Auf Basis der Konversionseffizienz, die auf dem Biogasertragstest basiert, kann für die deutschen Biogasanlagen eine hohe Effizienz von 95% gezeigt werden. Für die amerikanische Biogasanlage hingegen kann lediglich eine Effizienz von weniger als 70% festgestellt werden. Dies zeigt deutlich den Einfluss der Politik auf die baulichen und somit auch auf die prozesstechnischen Parameter der Biogasanlagen. In Amerika wird beispielsweise in den meisten Staaten die Nutzung von Wärme nicht gefördert, weshalb keine Heizung im Fermenter eingebaut und kein Block-Heizkraftwerk installiert ist.

Eine Vielzahl von Parametern beeinflusst die Genauigkeit der Effizienzbestimmung, darunter die geringe Häufigkeit der Kalibrierung oder das Fehlen von Messgeräten. Daher ist es notwendig, zur Berechnung der Werte Annahmen zu treffen. Bei der Rückrechnung von der Strommenge zur Gasmenge sind neben der Strommenge die Gasqualität, der Heizwert von Methan, der Wirkungsgrad des Block-Heizkraftwerks und der Trafoverlust einzurechnen. Werte für die letzten beiden Faktoren sind anzunehmen, wobei es für beide in der Literatur nur wenige Daten gibt, sodass die Annahmen sehr ungenau sind. Ein weiterer wichtiger Parameter ist die Substratmenge. Diese muss zwar laut EEG von jedem Betreiber erfasst werden, doch zeigt die Praxis, dass die Daten recht ungenau sind, beispielsweise da verschiedene Substrate gemeinsam im Silo siliert werden (sogenannte Mischsilagen). Beim Beschicken der Anlage sind die einzelnen Substrate unmöglich unabhängig voneinander zu wiegen. Eine genaue Angabe der Einzelsubstratmassen ist somit unmöglich und kann nur abgeschätzt werden. Diese Beobachtung konnte mittels Aufstellen der organischen Trockenmassenbilanz bestätigt werden. Eine Abweichung des errechneten Input zum Output von bis zu 24% ist festzustellen, wobei Wassereinschlüsse in der organischen Trockenmasse zu Fehlern von ca. 11% in der organischen Trockenmassenbilanz führen können.

Ein weiterer Einflussfaktor ist die Probennahme. Anhand von über ein Jahr monatlich gezogenen Proben konnte gezeigt werden, dass die Werte der Trockensubstanz und der

organischen Trockensubstanz je nach Zeitpunkt der Probennahme stark variieren, sodass bei geringer Anzahl von Probennahmen große Ungenauigkeiten entstehen.

Am Beispiel des Biogasertragstests wurde die Genauigkeit der verwendeten Methoden zur Bestimmung des spezifischen Methanertrags untersucht. Die Hauptbestandteile des Biogasertragstests sind das verwendete Inokulum, das zu untersuchende Substrat, der Versuchsaufbau und die Auswertung. Die Einflüsse des Inokulums und des Versuchsaufbaus wurden in der vorliegenden Arbeit genauer untersucht. Dazu wurden sechs Inokula in einem Versuchsaufbau und jeweils ein Inokulum in unterschiedlichen Versuchsaufbauten untersucht. Es wurden Inokula verwendet, die schon bei mehreren Ringversuchen Verwendung fanden und daher bekannt war, dass verlässliche Ergebnisse mit diesen zu erzielen sind. Dies führte zu einem Variationskoeffizienten von 4,8% zwischen den Methanerträgen bei Verwendung verschiedenen Inokula. Dieser Variationskoeffizient (CV) ist geringer als der CV, der in den meisten anderen Publikationen berichtet wird. Bei der Verwendung unterschiedlicher Systeme, die alle nach der deutschen Richtlinie VDI 4630 zulässig sind, zeigte sich hingegen eine Abweichung der Ergebnisse von 12,8%. In beiden Fällen konnten keine eindeutigen Zusammenhänge zwischen den Inokula und den Systemen bei der Untersuchung von unterschiedlichen Substraten festgestellt werden, sodass eine Korrektur der Ergebnisse nicht möglich ist. Aus 34 untersuchten Anlagen haben 21 eine biologische Ausbeuteeffizienz, die im Bereich von 100% ± 12,8% liegt. Dies verdeutlicht, dass der Messfehler aufgrund des verwendeten Systemaufbaus bereits größer ist als der Unterschied in der Effizienz der meisten Biogasanlagen. Folglich sind striktere Regeln zur Verwendung der Systeme von Nöten. Während des gesamten Versuchs sowie während der anschließenden Auswertung wurde die Richtlinie VDI 4630 befolgt. Trotzdem kam es in zwei Versuchsaufbauten, die sich nur darin unterschieden, dass das Gas beim einen Versuchsaufbau mittels Sicapent® vor der Messung getrocknet wurde, während beim anderen Versuchsaufbau die Messung im feuchten Gas stattfand und der Wasseranteil anschließend nach der VDI 4630 herausgerechnet wurde, zu unterschiedlichen Messergebnissen.

Aufgrund des geringen internen Variationskoeffizienten (1-7%) bei der Verwendung von einem Versuchsaufbau für den Biogasertragstest und einem Inokulum, ist es anzuraten, bei zukünftigen Untersuchungen immer den gleichen Versuchsaufbau und das gleiche Inokulum zu verwenden. Die hieraus gemessene Effizienz der Anlagen kann problemlos untereinander verglichen werden.

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