Investigation of the methane potential of horse manure

Matthias Mönch-Tegeder*, Andreas Lemmer, Hans Oechsner, Thomas Jungbluth

(*University of Hohenheim, State Institute of Agricultural Engineering and Bioenergy, Garbenstraße 9, 70599 Germany*)

Abstract: During recent years the renewable energy production with agricultural biomass became more and more important. The increased use of agricultural products instead for nutrition aroused a debate. Therefore, the utilization of agricultural byproducts and residuals for anaerobic digestion is the essential step for the future sustainable energy production. One available substrate would be horse manure, but literature is still lacking information about gas potential and digestibility of horse manure in biogas plants. This work aims at investigating the suitability of horse manure with different bedding materials and to produce standard values for different horse manure samples. Additionally the methane yields of the components of the horse manure were analyzed. The results of the batch digestion test showed the highest specific methane yields for straw pellets with 0.247 Nm³ CH_4 kg^{-1} VS. Slightly lower are the values for the straw samples in range of 0.183 to 0.237 Nm³ CH_4 kg^{-1} VS. The digestion of alternate bedding materials like flax and woody materials leads to specific methane values beneath 0.100 Nm³ CH kg^{-1} VS. Based on these results these materials should be avoided for anaerobic digestion. The straw based horse manure produced 0.191 ± 0.02 Nm³ CH_4 kg^{-1} VS in the batch assay. The storage of the manure resulted in significant lower methane yields. Hence, the anaerobic digestion of the straw based horse manure is an efficient conversion pathway and can help to avoid the utilization of acreage for energy production instead of the production of food.

Keywords: biogas, methane yield, horse manure, anaerobic digestion

Citation: Mönch-Tegeder, M., A. Lemmer, H. Oechsner, and T. Jungbluth. 2013. Investigation of the methane potential of horse manure. Agric Eng Int: CIGR Journal, 15(2): 161−172.

1 Introduction

In 2007 the European Renewable Energy Roadmap was published in order to define the objectives for the energy production in 2020 (European Renewable Energy Council, 2007). According to this directive the use of agricultural materials like manure and slurry for biogas production is an important resource for the sustainable energy production (Commission Regulation 2009/152/EC, 2009). The anaerobic digestion of these materials offers many environmental benefits (Nelson and Lamb, 2002; Amon et al., 2007) and is one of the beneficial and advantageous processes in manure treatment (Sakar et al., 2009). The recycling of the animal residues reduces the uncontrolled emissions of CH_4 during the storage and avoided contamination of surface and ground water systems (Romano et al., 2006). Additionally anaerobic digestion leads to a higher fertilizer quality of the manure (Appels et al., 2011). Hence, it can be concluded that the anaerobic treatment of animal byproducts is an environmental friendly, economically viable, and socially acceptable pathway for the energy generation (Wang et al., 2008).

Due to the limited availability of arable land and the increasing use of biogas, it is necessary to develop concepts for disposing the agricultural byproducts in anaerobic digestion (Bauer et al., 2010; Menardo and Balsari, 2012). Furthermore, the economic efficiency of biogas production depends strongly on the substrate costs (Schievano et al., 2009). In the context of increasing prices for agricultural products and increasing environmental requirements the activation of residues for energy production is indispensable. The utilization of liquid manure for biogas production is a widely applied technology in liquid digestions systems (Weiland, 2010),

---

Received date: 2013-02-15 **Accepted date:** 2013-04-19

* **Corresponding author: Mönch-Tegeder, M.,** Email: Matthias.Moench-Tegeder@uni-hohenhe.

but the conversion of higher levels of solid manure into biogas is momentarily unsuitable for the liquid anaerobic digestion (Cui et al., 2011). The large fibrous particles cause many problems like clogging pumps and pipes, and result in scum layers inside the digester (Hashimoto, 1983; Ibrahim et al., 1997; Ward et al., 2008). The availability of appropriate pretreatment steps for fibrous materials like straw leads to a growing interest for solid manure as feedstock for biogas production. However, the decision for the optimal method is crucial. Physical, chemical, physicochemical, and biological processes are subject of a wide range of publications, but in most cases the results are based on lab-scale investigations. Therefore, it is not applicable on large scale practical purposes (Carlsson et al., 2012). A well adapted method for the conditioning of fibrous biomass for anaerobic digestion is a mechanical processing, which can be easily performed for a large-scale biogas plant (Hartmann et al., 2000; Menardo et al., 2012). The application of a mechanical pretreatment step causes changes in the biomass structure, a particle size reduction and a decrease in cellulose cristallinity (Kratky and Jirout, 2011).

An interesting substrate with a large potential for anaerobic digestion is horse manure. In Germany more than one million horses produce about eight million tons manure per year (Garlipp et al., 2011; Deutsche Reiterliche Vereinigung, 2012). Furthermore the disposal of horse manure became increasingly difficult for the owners during the last years due to the lack of arable land and its low fertilizer quality. Additionally equitation becomes more and more popular in urban areas. This leads to an increase in horse barns and an excess of horse manure in these regions, which causes a sharp rise in manure removal costs. The composition of horse manure is dependent on the bedding material and the frequency of stall cleaning. Straw is the most widely used bedding material for horse stalls, however in view of increasing costs for straw and sanitary aspects, other materials such as sawdust, wood pellets and flax straw are gaining importance (Cui et al., 2011). The investigation of the horse manure production across the federal state of Baden-Württemberg in southern Germany shows that 48.9% of the horse farms use only straw, 33.7% straw and sawdust and 15.2% use wood shavings as bedding material (Hess et al., 2004). The digestibility of straw and solid straw manure is well described in the literature (Møller et al., 2004; Tait et al., 2009). However the results on the usability of woody materials for anaerobic digestion are contradictory. For the processing of woody biomass in liquid digestion systems no advantages should be expected, because there is no large scale pretreatment step available for increasing the methane yield.

The digestibility of horse manure with different bedding materials was reported in literature (Kalia and Singh, 1998; Kusch et al., 2008; Cui et al., 2011; Wartell et al., 2012). However, previous research approaches were focused on solid digestion and the estimation of the maximum methane potential. Hence, there is a lack of standard values for the processing of horse manure in liquid digestion systems.

The aim of this study was to investigate the usability of different bedding materials for the anaerobic digestion and to produce standard values of the methane yield for different horse manure samples. Another aspect was to test the effect of storage to the methane yield of the horse manure and the proposal of an efficient conversion pathway. Additionally the chemical compositions of the horse manure samples were analyzed in order to determine if the horse manure inhibits the digestions process or offers some beneficial effects.

2 Materials and methods

2.1 Sample collection and preparation

For the investigation of the methane potential, different kinds of unused bedding material, fresh horse manure, stored horse manure and fresh horse manure without bedding (horse dung) were collected at ten horse barns in the region of Stuttgart, Germany. Five barns used only straw as bedding material. The other types of beddings were straw-pellets, a mixture of flax and straw, flax, wood-pellets and sawdust. The barns and the type of bedding are listed in Table 1.

After collecting 500 g of the fresh horse manure samples, the samples were frozen and the trace element composition was analyzed at IS Forschungsgesellschaft

GmbH (Wahlstedt, Germany). Therefore, the substrate samples were dried for 48 h at 60℃ in a drying chamber. To guarantee homogenous samples for the following batch-test and analyses the dried substrates were grinded with a cutting mill Pulverisette 19 (Fritsch, Idar-Obenstein, Germany) to a particle size of 1 mm.

Table 1 Summary of the barns and bedding materials

Barn	Bedding material
A – E	Straw
F	Straw-pellets
G	Straw/flax
H	Flax
I	Wood-pellets
J	Sawdust

2.2 Chemical composition analyses

The fresh samples were analyzed for total solids (TS), volatile solids (VS), ammonium nitrogen content (NH_4) and total nitrogen content (TN) in the laboratory of the State Institute of Agricultural Engineering and Bioenergy (Stuttgart, Germany) according to the guidelines of the Federation of German Agricultural Investigation and Research Institutes (VDLUFA, 2007). To determine the concentrations of crude ash (XA), crude fat (XL), crude protein (XP), crude fiber (XF), nitrogen free extracts (NfE) and total carbon content the prepared samples were analyzed by the State Institute of Agricultural Chemistry (Stuttgart, Germany) according to the European regulations for the Weender feed analysis (Commission Regulation 2009/152/EC, 2009). The concentrations of cell-wall fractions, neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL) were also analyzed at the State Institute of Agricultural Chemistry using the standard methods described by the VDLUFA (2007). The determination of the trace element composition of the fresh horse dung samples were carried out at the ISF GmbH laboratory (Wahlstedt, Germany) using inductively coupled plasma optical emission spectroscopy as published by Vintiloiu et al. (2012).

2.3 Batch digestion test

The methane and biogas potential of the samples were determined by the Hohenheimer Biogas Yield Test (HBT). The HBT is a highly reproducible and efficient patented laboratory batch method (Helffrich, 2005) according to the guidelines of the VDI 4630 (VDI-Society Energy and Environment, 2006) and was previously described by Helffrich and Oechsner (2003). This procedure enables the investigation of 129 samples at the same time. Briefly, the digestion of the substrates is carried out in 100 mL glass syringes (flask sampler) with a 1/1 graduation and a capillary extension. The flask samplers are used as digestion chambers and gas-holders. The flask samplers were inserted into a motor-driven rotor for constant agitation conditions. The rotor is located in an incubation chamber which ensures a constant temperature of digestion of 37 ± 0.5℃. Generally, the batch-test is conducted for 35 days under mesophilic conditions. The determination of the gas volume takes place between one and four times per day according to the amount of produced gas. The volume is recorded with an accuracy of 1 mL and the methane content is measured manually in Vol % using a gas transducer AGM 10 (Pronova Analysetechnik, Berlin, Germany). The analyzer is calibrated with a CH_4 calibration gas (60.5% CH_4) before and after the measurements. The measured gas amounts had to be corrected to standard conditions (0℃, 1013 hPA).

In this experiment each flask was filled with 30 g of inoculum and 600 mg of the sample. The inoculum used for the digestion assay is the standard substrate for the digestion tests at the State Institute of Agricultural Engineering and Bioenergy. In this work the assay was conducted in triplicates. For the correction of the gas production the inoculum was tested without other substrates. To quantify the test conditions a hay and concentrate standard were used. The cumulative biogas and methane production of the samples were calculated to the specific yields, relating to kg VS.

2.4 Calculations and statistical analyses

For the estimation of the energy recovery of the substrates, the obtained energy of the digestion was divided by the Gross Energy (GE) content of the substrate. The GE content of the different substrates were calculated using the results of the Weender feed analysis with the following Equation (1) (Society of Nutrition Physiologie, 2001):

$$GE\text{(MJ/kg)}=0.0239gXP+0.0398gXL+0.0201gXF+0.0175gNfE \quad (1)$$

For determination of the methane yield potential the cumulative specific methane production was fitted to the modified Gompertz Equation (2) (Nopharatana et al., 2007; Budiyono et al., 2010) assuming that the CH_4 production is a function of bacterial growth:

$$M = P \times \exp\left\{-\exp\left[\frac{R_m \times e}{P}(\lambda - t) + 1\right]\right\} \quad (2)$$

where, M is the cumulative methane production (Nm³ kg^{-1} VS); P the methane production potential (Nm³ kg^{-1} VS); R_m the maximum daily methane yield (Nm³ kg^{-1} VS *d); λ the duration of lag phase (d) and t the duration of the assay (d). The parameters P, R_m and λ are constants and can be determined by using non linear regression.

The statistical analyses were performed using the statistical software R (R Core Team, 2012) to determine if there were significant differences in cumulative methane production for the different substrates. The significance test was based on Tukey's studentized range test.

3 Results and discussion

3.1 Chemical composition

The compositions of the different bedding materials are shown in Table 2. The bedding material used by the barns A to F is based on straw. The average ADL fraction of this kind of bedding material is 76.0 ± 14.35 g kg^{-1} TS. For the flax bedding the ADL fraction is 210.0 g kg^{-1} TS. A further increase could be observed for the wood-based beddings to a maximum of 238.0 g kg^{-1} TS. The XF concentrations of the materials increase in a similar manner. The calculated energy content of the beddings ranged from 16.3 ± 0.3 MJ kg^{-1} TS for the straw to 16.7 MJ kg^{-1} TS for flax. The estimation of the energy content of the woody materials failed. The contents of XP and XL in these materials are beneath the detection limits. A large variation was observed for the carbon to nitrogen ratio (C/N ratio) in the straw beddings (67.9 ± 28.0). The wood-based beddings had the highest C/N ratios with 642.55 for the sawdust and 722.63 for the wood-pellets, respectively. In comparison to the optimum C/N ratio of 20-30 (Weiland, 2010; Horan et al., 2011), the values of the wood-based beddings are deviate strongly from this range. The ADL concentrations in the horse dung samples (95.20 ± 1.12 g kg^{-1} TS) are higher than in the straw beddings (Table 3). This is in agreement due to the use of fibrous materials for the horse feeding. The XF values are slightly lower for the horse dung samples. On the other hand we detected higher levels of XP, XL and nitrogen in the dung, which caused a lower C/N ratio (29.57 ± 5.27). Whether the digestion by the horses causes a degradation of the ADL fraction could not be determined. According to Triolo et al. (2011), animal digestion leads to an accumulation of lignin. The calculated energy content (16.44 ± 0.6 MJ kg^{-1} TS) does not differ from the energy content of the bedding material. The energy content values for fresh horse manure samples are listed in Table 4. In comparison to the previous results there is a mixing of the horse dung and bedding material distinguishable although there was no artifical mixed manure tested. Only the GE content of the straw-based fresh manure samples are slightly higher (16.5 ± 0.4 MJ kg^{-1} TS). A large impact of horse dung on the content of digestible components in flax- and wood-based manure samples was observed, resulting in an increased level of digestible compounds. For the quantification of storage effects on the horse manure, samples that were at least stored for four weeks beforehand were analyzed.

The results of the chemical analyses are shown in Table 5. As expected, the storage of the manure shows clearly losses of the digestible components and an increase in ADL content compared to fresh manure and dung samples. The loss of N and NH_4-N in the stored manure underlines the need to revise the existing system of manure storage in field-clamps. Long storage periods of horse manure should be avoided in order to prevent the reduction of easily degradable compounds and negative environmental effects. A positive effect of the storage period to the degradability of the lignin and an increase of the methane yield of the manure will not observed.

Table 2 Chemical compostion of the bedding materials

Barn	Bedding	TS /% FM	VS /% FM	TN /g kg^{-1} TS	NH$_4$ /g kg^{-1} TS	C/N Ratio	XP /g kg^{-1} TS	XL /g kg^{-1} TS	XF /g kg^{-1} TS	NDF /g kg^{-1} TS	ADF /g kg^{-1} TS	ADL /g kg^{-1} TS	NfE /g kg^{-1} TS	GE /MJ kg^{-1} TS
A	Straw	81.77	75.61	9.68	0.94	42.55	54	9.1	415	747	502	88	366.6	16.41
B	Straw	89.5	83.93	4.41	0.8	96.5	25	12	442	805	553	67	365.9	16.36
C	Straw	90.57	85.47	8.13	0.03	53.62	29	12	457	797	528	96	363.4	16.72
D	Straw	90.98	85.12	4.02	0.05	105.6	26	10	421	778	530	74	382.2	16.17
E	Straw	85.32	80.54	10.8	0.3	39.26	52	12	397	728	467	75	348	15.79
F	Straw-pellets	90.03	85.14	6.06	0.11	69.59	36	8.5	346	753	443	56	464.6	16.28
G	Straw/Flax	72.69	67.76	7.65	0.14	57.49	65	11	464	762	395	119	100.6	13.08
H	Flax	85.05	83.21	5.31	0.26	85.01	27	7.7	592	829	657	210	220.7	16.71
I	Wood-pellets	89.32	87.45	0.63	0.05	722.63	n.a.	n.a.	624	839	684	228	n.a.	n.a.
J	Sawdust	83.2	82.9	0.71	0.04	642.85	n.a.	8.7	651	862	719	238	n.a.	n.a.

Note: TS = total solids; VS = volatile solids; TN = total nitrogen; NH$_4$ = ammonium nitrogen; C/N ratio = carbon/nitrogen ratio; XP = crude protein; XL = crude fat; XF = crude fiber; NDF = neutral detergent fiber; ADF = acid detergent fiber; ADL = acid detergent lignin; NfE = nitrogen free extracts; GE = gross energy.

Table 3 Chemical composition of the horse dung samples

Barn	TS /% FM	VS /% FM	TN /g kg^{-1} TS	NH$_4$ /g kg^{-1} TS	C/N Ratio	XP /g kg^{-1} TS	XL /g kg^{-1} TS	XF /g kg^{-1} TS	NDF /g kg^{-1} TS	ADF /g kg^{-1} TS	ADL /g kg^{-1} TS	NfE /g kg^{-1} TS	GE /MJ kg^{-1} TS
A	23.19	20.51	14.23	0.50	29.94	74.00	29.00	334.00	668.00	456.00	100.00	378.80	16.27
B	21.53	18.22	17.52	0.42	23.57	117.00	41.00	282.00	615.00	432.00	92.00	333.70	15.94
C	22.84	18.92	17.25	0.37	23.71	96.00	30.00	333.00	681.00	462.00	92.00	317.90	15.74
D	22.87	20.71	11.72	0.51	37.11	75.00	26.00	369.00	710.00	465.00	87.00	393.70	17.13
E	20.67	18.85	18.68	1.37	22.64	83.00	18.00	344.00	673.00	446.00	88.00	335.70	15.49
F	26.60	23.47	13.07	0.41	32.66	77.00	31.00	337.00	673.00	458.00	104.00	396.20	16.78
G	23.30	21.10	16.12	1.53	27.12	79.00	32.00	346.00	701.00	430.00	82.00	389.60	16.93
H	22.75	20.18	11.76	0.37	36.57	70.00	22.00	361.00	708.00	496.00	117.00	381.00	16.47
I	23.51	21.46	13.03	0.28	32.78	68.00	20.00	350.00	720.00	433.00	91.00	383.80	16.17
J	27.30	24.72	15.04	2.33	29.59	85.00	37.00	344.00	687.00	449.00	99.00	404.60	17.50

Note: TS = total solids; VS = volatile solids; TN = total nitrogen; NH$_4$ = ammonium nitrogen; C/N ratio = carbon/nitrogen ratio; XP = crude protein; XL = crude fat; XF = crude fiber; NDF = neutral detergent fiber; ADF = acid detergent fiber; ADL = acid detergent lignin; NfE = nitrogen free extracts; GE = gross energy.

Table 4 Chemical composition of the fresh manure samples

Barn	Bedding	TS /% FM	VS /% FM	TN /g kg^{-1} TS	NH$_4$ /g kg^{-1} TS	C/N Ratio	XP /g kg^{-1} TS	XL /g kg^{-1} TS	XF /g kg^{-1} TS	NDF /g kg^{-1} TS	ADF /g kg^{-1} TS	ADL /g kg^{-1} TS	NfE /g kg^{-1} TS	GE /MJ kg^{-1} TS
A	Straw	53.38	46.65	14.78	5.47	27.13	72.0	12.0	372.0	714.0	482.0	87.0	367.40	16.10
B	Straw	36.27	31.94	10.07	2.02	40.12	52.0	16.0	427.0	745.0	529.0	105.0	309.50	15.88
C	Straw	51.58	46.38	14.60	1.68	29.05	71.0	18.0	380.0	712.0	470.0	75.0	385.80	16.80
D	Straw	46.73	42.81	11.82	1.92	35.53	61.0	13.0	381.0	732.0	479.0	69.0	395.70	16.56
E	Straw	33.49	30.40	18.95	0.56	22.63	60.0	15.0	399.0	743.0	480.0	83.0	398.20	17.02
F	Straw-pellets	40.54	35.01	12.29	0.04	33.13	73.0	18.0	358.0	719.0	490.0	101.0	389.90	16.48
G	Straw/Flax	31.60	28.72	18.68	0.07	22.80	59.0	18.0	379.0	735.0	489.0	77.0	404.00	16.81
H	Flax	25.70	22.18	15.51	2.13	26.06	72.0	27.0	349.0	708.0	492.0	107.0	355.10	16.02
I	Wood-pellets	47.23	42.48	11.39	0.13	37.76	74.0	13.0	443.0	757.0	560.0	170.0	333.00	17.02
J	Sawdust	49.14	45.36	11.34	0.83	38.45	54.0	10.0	499.0	799.0	580.0	157.0	309.00	17.12

Note: TS = total solids; VS = volatile solids; TN = total nitrogen; NH$_4$ = ammonium nitrogen; C/N ratio = carbon/nitrogen ratio; XP = crude protein; XL = crude fat; XF = crude fiber; NDF = neutral detergent fiber; ADF = acid detergent fiber; ADL = acid detergent lignin; NfE = nitrogen free extracts; GE = gross energy.

Table 5 Chemical composition of the stored manure samples

Barn	Bedding	TS /% FM	VS /% FM	TN /g kg^{-1} TS	NH_4 /g kg^{-1} TS	C/N Ratio	XP /g kg^{-1} TS	XL /g kg^{-1} TS	XF /g kg^{-1} TS	NDF /g kg^{-1} TS	ADF /g kg^{-1} TS	ADL /g kg^{-1} TS	NfE /g kg^{-1} TS	GE /MJ kg^{-1} TS
A	Straw	24.13	21.24	16.27	7.43	25.57	83.0	16.0	413.0	725.0	529.0	117.0	324.30	16.60
B	Straw	28.79	24.08	10.54	0.13	37.97	61.0	14.0	446.0	731.0	568.0	127.0	260.60	15.54
C	Straw	25.73	23.19	9.90	0.19	41.92	63.0	7.80	445.0	748.0	571.0	116.0	334.00	16.61
D	Straw	25.56	21.17	11.61	0.05	34.97	74.0	6.70	360.0	742.0	575.0	149.0	354.60	15.48
E	Straw	21.59	17.97	14.44	0.46	30.20	76.0	11.0	385.0	727.0	544.0	130.0	343.10	16.00
G	Straw/Flax	22.45	20.47	9.21	0.07	46.26	60.0	18.0	403.0	761.0	517.0	94.0	384.30	16.98
H	Flax	24.44	20.83	19.41	2.35	21.12	69.0	23.0	409.0	726.0	535.0	142.0	303.70	16.10
I	Wood-pellets	26.43	22.37	17.09	0.41	23.58	78.0	8.60	388.0	681.0	527.0	167.0	273.20	14.79
J	Sawdust	76.70	67.51	14.21	0.61	29.77	71.0	n.a.	542.0	754.0	671.0	231.0	n.a.	n.a.

Note: TS = total solids; VS = volatile solids; TN = total nitrogen; NH_4 = ammonium nitrogen; C/N ratio = carbon/nitrogen ratio; XP = crude protein; XL = crude fat; XF = crude fiber; NDF = neutral detergent fiber; ADF = acid detergent fiber; ADL = acid detergent lignin; NfE = nitrogen free extracts; GE = gross energy.

3.2 Trace elements

In general the use of animal residues has a beneficial effect on the digestion process. The manure contains a large amount of essential trace elements and nutrients for an optimal and stable digestion process. Additionally the manure offers a good pH buffer system and helps to prevent an acidification of the digester while feeding with a high organic loading rate (Oechsner et al., 2011). In order to determine if the horse manure offers the same advantageous effects for the biogas process, the trace-element concentrations of the fresh horse manure samples were analyzed. The trace element compositions of the straw based fresh horse manure in comparison to values from maize- and grass silage as well as some manure samples are shown in Table 6. Obviously the micronutrient concentrations of the fresh manure are considerably lower than the levels of the other animal manures. Relating to the optimum values of the digestate (IS Forschungsgesellschaft, 2011) the horse manure cannot provide sufficient amounts of trace elements for a stable biogas process. In comparison with the silages, the concentrations of the micronutrients are equal to the ones for grass silage. Thus, it can be stated that the beneficial effect due to the trace element supply of the digestion process cannot be fulfilled by the horse manure.

Table 6 Trace element composition of the straw based fresh horse manure samples

Element /mg kg^{-1} TS	Fresh horse manure			Maize silage	Grass silage	Cattle liquid manure	Pig liquid manure	Pig solid manure	Optimum values (IS Forschungsgesellschaft, 2011)
		±	STD	(Kimmich and Slotyuk, 2011)			(Sager, 2007)		
Ni	1.80	±	0.74	0.2	2.0	6.3	12.5	8.9	16
Fe	810.67	±	621.22	64.6	879.4	1970.0	2080.0	2680.0	2400.0
Co	0.37	±	0.28	0.0	0.5	2.1	4.0	2.3	1.8
Mn	89.00	±	23.83	18.4	78.9	180.0	358.0	317.0	300.0
Mo	1.48	±	0.85	0.4	1.3	3.5	5.3	2.1	4.0
Se	0.27	±	0.12	0.3	0.3	0.6	3.4	1.4	0.5

Note: TS = total solids.

3.3 Methane production

The cumulative methane yields of all samples are shown in Figure 1. The pretreatment of the inhomogeneous materials was a necessary tool to generate homogenous samples and results and to obtain an acceptable variation coefficient for all substrates.

The results of the anaerobic digestion of the different bedding materials are shown in Table 7. In this investigation the highest specific methane yield could be determined for the straw-pellets (0.247 Nm^3 CH_4 kg^{-1} VS). The methane yields for the other straw-samples are in the range of 0.183 to 0.237 Nm^3 CH_4 kg^{-1} VS and comparable with the results found in the literature e.g. Amon et al. (2007) and Triolo et al. (2011) who detected values of 0.189 Nm^3 CH_4 kg^{-1} VS and 0.289 Nm^3 CH_4 kg^{-1} VS for wheat straw respectively. An increase in methane yield due to the reducing particle size as reported by Menardo et al. (2012) could not be observed. In consideration of the large variations of the methane potential of straw it must be assumed, that the harvest time and conditions for straw are just as important as for other energy crops. A slight decrease in methane production was observed for the straw/flax bedding (0.156 Nm^3 CH_4 kg^{-1} VS). Similar results were found for the digestion of the flax bedding alone with a cumulative methane yield of 0.067 Nm^3 CH_4 kg^{-1} VS. After the digestion time of 35 days, the methane production of the wood-pellets and sawdust beddings showed the lowest yields with 0.021 and 0.017 Nm^3 CH_4 kg^{-1} VS. These results match previous work results by Tong et al. (1990) who reported 0.042 Nm^3 CH_4 kg^{-1} VS for white fir. In the investigation of softwood bedding material by Wartell et al. (2012) the measured methane yields were lower than 0.010 Nm^3 CH_4 kg^{-1} VS. According to these results, the use of woody biomass for anaerobic digestion is an inefficient pathway for energy production. In contrast to that, the use of straw materials for the biogas production offers an efficient conversion to energy. Thus the calculated energy recoveries of the straw beddings are in the range of 42.15 to 57.05% and comparable with the digestibility in ruminants. For the other materials the combustion seems a more preferable method for energy production.

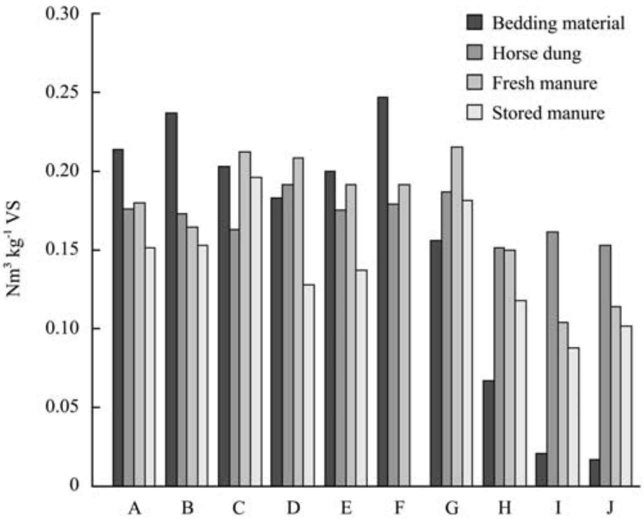

Figure 1 Cumulative methane production (Nm^3 kg^{-1} VS) of the different samples

Table 7 Cumulative methane yield of the bedding materials

Barn	Bedding	Specific methane yield /Nm^3 CH_4 kg^{-1} VS	Variation coefficient /%	Methane energy /MJ kg^{-1} VS	Energy recovery /%	P	R_m	λ	R^2
A	Straw	0.214	1.82	8.51	47.95	0.203	0.0143	0.57	0.989
B	Straw	0.237	2.36	9.44	54.11	0.231	0.0173	1.53	0.994
C	Straw	0.203	0.55	8.09	45.68	0.194	0.0130	0.83	0.983
D	Straw	0.183	4.16	7.29	42.15	0.174	0.0165	3.33	0.925
E	Straw	0.200	2.48	7.96	47.58	0.191	0.0139	1.01	0.989
F	Straw-pellets	0.247	2.14	9.82	57.05	0.238	0.0175	1.33	0.993
G	Straw/Flax	0.156	1.33	6.22	44.36	0.150	0.0133	0.85	0.986
H	Flax	0.067	1.31	2.66	15.56	0.063	0.0072	0.44	0.972
I	Wood-pellets	0.021	11.30	0.83	n.a.	n.a.	n.a.	n.a.	n.a.
J	Sawdust	0.017	12.51	0.66	n.a.	n.a.	n.a.	n.a.	n.a.

Note: VS = volatile solids; P = methane production potential, Nm^3 CH_4 kg^{-1} VS; R_m = maximum daily methane yield Nm^3 CH_4 kg^{-1} VS; λ = lag time, d; n.a. = not available.

The methane production yields of the horse dung are listed in Table 8. The observed methane yields after 35 days digestion are in the range of 0.171 ± 0.014 Nm^3 CH_4 kg^{-1} VS and are marginally lower than the reported values from Wartell et al. (2012) with 0.210 Nm^3 CH_4 kg^{-1} VS. Yusuf et al. (2011) determined a biogas yield of 0.257 Nm^3 kg^{-1} VS for horse dung but the methane content of the produced gas was not reported. Overall, the methane production of the horse dung is very inconsistent and is mainly affected by the feeding intensity and of the composition of the forages (Møller et al., 2004; Amon et al., 2007). For this trial the substrates were collected in January. In this season the energy requirements for the horses are low and the feeding intensity is also at lower levels. The lower energy recovery (36.77 ± 3.24%) by the anaerobic digestion of the horse dung in comparison to the straw bedding is expected and within the scope of the roughage level fed the horses.

Table 8 Cumulative methane production of the horse dung samples

Barn	Specific methane yield /Nm^3 CH$_4$ kg^{-1} VS	Variation coefficient /%	Methane energy /MJ kg^{-1} VS	Energy recovery /%	P	R_m	λ	R^2
A	0.176	1.73	7.02	38.20	0.186	0.0083	3.73	0.999
B	0.173	0.68	6.89	36.57	0.180	0.0094	5.16	0.993
C	0.163	5.97	6.51	34.25	0.173	0.0083	4.09	0.996
D	0.191	3.45	7.60	40.18	0.199	0.0097	4.75	0.995
E	0.175	2.98	6.95	40.93	0.186	0.0084	5.03	0.997
F	0.179	1.04	7.13	37.50	0.183	0.0091	4.39	0.996
G	0.187	0.85	7.46	39.92	0.196	0.0096	4.40	0.992
H	0.151	0.48	6.02	32.44	0.159	0.0072	4.54	0.998
I	0.161	5.36	6.41	36.19	0.171	0.0075	3.82	0.997
J	0.153	1.98	6.09	31.51	0.158	0.0071	3.64	0.996

Note: VS = volatile solids; P = methane production potential, Nm^3 CH$_4$ kg^{-1} VS; R_m = maximum daily methane yield Nm^3 CH$_4$ kg^{-1} VS; λ = lag time, d.

The fresh manure based on straw bedding has slightly lower methane yields (0.191 ± 0.02 Nm³ CH$_4$ kg^{-1} VS) than the raw bedding material (Table 9) but higher yields than the horse dung samples. This diluting effect was already reported earlier by Møller et al. (2004) and Hashimoto (1983), who stated that an increase of straw in solid manure increased the methane yield. The obtained results are in the range of the reported methane values by Kusch et al. (2008) with 0.170 Nm³ CH$_4$ kg^{-1} VS for horse manure and 0.165 Nm³ CH$_4$ kg^{-1} VS for solid cattle manure (Quiñones et al., 2012). An effect of the horse activities to the digestibility of the bedding materials as described by Cui et al. (2011) was not observed because the milling of all materials in advance to the batch-test reduced the effect of micro structural changes of the spent straw. A large effect was observed for the manure samples based on flax and wood. The methane yield for the flax manure is 0.150 Nm³ CH$_4$ kg^{-1} VS, for wood-pellet manure 0.104 Nm³ CH$_4$ kg^{-1} VS and sawdust manure 0.114 Nm³ CH$_4$ kg^{-1} VS. Although the digestibility shows a strong increase, the energy recovery for this three samples (21.88 to 32.23%) is still lower than for the manure based on straw bedding (41.31 ± 4.09%).

Table 9 Cumulative methane production of the fresh manure samples

Barn	Bedding	Specific methane yield /Nm³ CH$_4$ kg^{-1} VS	Variation coefficient /%	Methane energy /MJ kg^{-1} VS	Energy recovery /%	P	R_m	λ	R^2
A	Straw	0.180	6.17	7.18	38.96	0.175	0.0119	1.48	0.996
B	Straw	0.164	1.81	6.53	36.19	0.177	0.0076	2.02	0.858
C	Straw	0.212	1.39	8.44	45.14	0.207	0.0122	1.70	0.997
D	Straw	0.208	3.29	8.27	45.76	0.205	0.0120	2.72	0.998
E	Straw	0.191	2.46	7.59	40.50	0.190	0.0097	2.60	0.997
F	Straw-pellets	0.191	2.43	7.60	39.85	0.192	0.0102	2.03	0.998
G	Straw/Flax	0.215	0.69	8.55	46.19	0.214	0.0124	3.60	0.989
H	Flax	0.150	3.17	5.98	32.23	0.155	0.0072	3.01	0.998
I	Wood-pellets	0.104	2.73	4.14	21.88	0.100	0.0064	1.23	0.991
J	Sawdust	0.114	2.13	4.53	24.41	0.109	0.0078	1.73	0.989

Note: VS = volatile solids; P = methane production potential, Nm^3 CH$_4$ kg^{-1} VS; R_m = maximum daily methane yield, Nm^3 CH$_4$ kg^{-1} VS; λ = lag time, d.

The batch results of the stored manure samples show a decrease in the cumulative methane yields (Table 10). This is caused by the degradation of volatile organic matter during the storage period. For this experiment the samples were collected during the winter period, hence it be can assumed that the energetic losses and greenhouse gas emissions increase in the warmer seasons. To sum up, for the practical application long term storage of the manure should be avoided to maximize the economical and environmental benefit.

Table 10 Cumulative methane production of the stored manure samples

Barn	Bedding	Specific methane yield /Nm³ CH_4 kg^{-1} VS	Variation coefficient /%	Methane energy /MJ kg^{-1} VS	Energy recovery /%	P	R_m	λ	R^2
A	Straw	0.151	2.19	6.02	31.91	0.155	0.0077	2.59	0.997
B	Straw	0.153	1.67	6.10	32.84	0.152	0.0091	2.42	0.998
C	Straw	0.196	0.65	7.83	42.48	0.206	0.0116	3.84	0.988
D	Straw	0.128	1.38	5.08	27.20	0.127	0.0052	1.62	0.986
E	Straw	0.137	0.12	5.44	28.33	0.138	0.0070	2.74	0.995
G	Straw/Flax	0.181	2.41	7.20	38.67	0.188	0.0094	4.89	0.994
H	Flax	0.118	2.02	4.71	24.92	0.117	0.0063	2.21	0.998
I	Wood-pellets	0.088	8.55	3.51	20.09	0.086	0.0060	2.28	0.994
J	Sawdust	0.102	0.79	4.08	n.a.	0.107	0.0063	4.25	0.964

Note: VS = volatile solids; P = methane production potential Nm^3 CH_4 kg^{-1} VS; R_m = maximum daily methane yield Nm^3 CH_4 kg^{-1} VS; λ = lag time, d; n.a. = not available.

In order to investigate the differences in cumulative methane yield between the bedding materials, the horse dung, the fresh and the stored manure respectively and the results of the straw based materials were used (Figure 2). The storage period of the manure resulted in significant lower methane yields than the values of the bedding material and fresh horse manure. Again, for the practical utilization of horse manure for anaerobic digestion, a logistic has to be established to guarantee a rapid reutilization as feedstock.

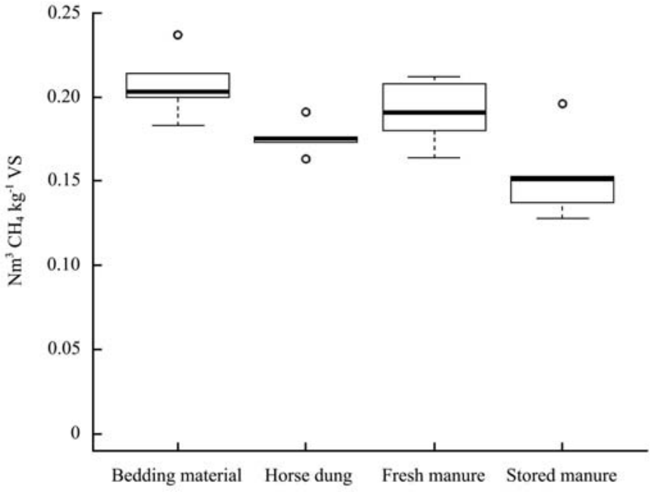

Figure 1 Boxplots of the cumulative methane production Nm^3 CH_4 kg^{-1} VS of the straw based samples

3.4 Degradation kinetics

The aim of this study was not to calculate the maximum methane potential of the substrates for estimating the degradation efficiency of the substrates. In general these values are not reachable in large scale digestion and are not sufficient for investigating the best energetic conversion pathway. For this purpose, the calculated gross energy is the more appropriate tool. For analyzing the degradation kinetics of the different substrates the modified Gompertz equation was used (Table 7, Table 8, Table 9 and Table 10). The results of the calculation show a strong correlation to the cumulative biogas production curves. In this case the lag phase was the most significant parameter for describing the digestibility of the different substrates. The comparison between the lag phase of the bedding materials and the horse dung samples approved the assumption of the loss of easy degradable materials due to the use as feedstock. The same effect can be observed for the fresh and stored manure. The storage of the manure causes an increase of recalcitrant materials and a lagged biogas production.

4 Conclusions

The aim of this study was to produce fundamentals for the practical application of horse manure for energy production by anaerobic digestion. Thus, there was no need to estimate methane yields, which are in the large-scale digestion inaccessible. Furthermore the harvest conditions have a large effect to the methane yields of straw. A delayed harvest caused by weather conditions leads to a reduction of the straw quality and a decrease in methane yields. Additionally the feeding intensity of the horses is expected to have a large impact on the methane yield of the manure. The results of the batch digestion test shows that the straw based horse manure is a good substrate for the biogas production. It was also observed that the alternative bedding materials have advantages by reducing health risks for the horses, in the absorptive capacity and partly in the lower costs but are inadvisable for the anaerobic digestion. The low methane yields from these bedding materials are not feasible for an economical energy production. Additionally the woody biomass leads to sinking layers in the digester thus causing higher failure rates. Unfortunately the investigations of these negative effects are exceedingly difficult in lab scale tests. Therefore, it can be concluded that for the anaerobic digestion of horse manure, the mixing with other bedding materials than straw should be avoided. For the horse manure with alternative bedding materials the combustion is the favorable pathway. A more detailed examination of the straw based samples revealed that there is no significant difference in the methane production between the bedding material, the horse dung and the fresh manure. However, significant lower values were obtained for stored manure samples. According to these results the storage period of the manure is a critical factor for the economic result. Therefore, the development of a continuous logistic chain is the key for keeping the storage period as small as possible. Furthermore due to the low mass density of the horse manure the average haul distance is an important factor for the economical outcome. In the scope of the results of the batch digestion tests the processing of straw seems to be an interesting alternative. The use of straw for anaerobic digestion can cause a resource competition between energy production and livestock farming. As a consequence of the increasing demand, the costs for straw will rise, affecting the horse owners directly. In the public perception of renewable energies, this context can tighten the negative discussions about the biogas production. Subsequently to the increasing costs of straw the economical benefit will decline. For the anaerobic digestion of horse manure in the biogas plant a mechanical pretreatment step is necessary to avoid swim layers and clogging of pumps and pipes. The mechanical disintegration should take place directly before the processing in the digester. Otherwise the increasing surface area causes an unregulated degradation and loss of energy. Thus, the digestion of horse manure is economically reasonable only if the substrates are free of charge.

A beneficial effect of the horse manure to the anaerobic process concerning the trace-element supply was not observed. Due to the high C/N ratio the horse manure seems to be a good co-substrate for the digestion of nitrogen rich substrates like liquid pig manure and poultry dung.

Further work will include a process scale-up and the optimization of the mechanical pretreatment. Furthermore an evaluation of the measured methane yields of the samples in practical application is necessary.

Acknowledgments

The investigations were funded by the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) within the scope of the project “Horse manure – further development of technologies for the efficient use of horse manure, FKZ 03KB064”.

References

Amon, T., B. Amon, V. Kryvoruchko, A. Machmüller, K. Hopfner-Sixt, V. Bodiroza, R. Hrbek, J. Friedel, E. Pötsch, H. Wagentristl, M. Schreiner, and W. Zollitsch. 2007. Methane production through anaerobic digestion of various energy crops grown in sustainable crop rotations. *Bioresource Technology,* 98(17): 3204-3212.

Amon, T., B. Amon, V. Kryvoruchko, W. Zollitsch, K. Mayer, and L. Gruber. 2007. Biogas production from maize and dairy cattle manure-Influence of biomass composition on the methane yield. *Agriculture, Ecosystems and Environment,* 118(1-4): 173-182.

Appels, L., J. Lauwers, J. Degrve, L. Helsen, B. Lievens, K. Willems, J. Van Impe, and R. Dewil. 2011. Anaerobic digestion in global bio-energy production: Potential and research challenges. *Renewable and Sustainable Energy Reviews,* 15(9): 4295-4301.

Bauer, A., C. Leonhartsberger, P. Bösch, B. Amon, A. Friedl, and T. Amon. 2010. Analysis of methane yields from energy crops and agricultural by-products and estimation of energy potential from sustainable crop rotation systems in EU-27. *Clean Technologies and Environmental Policy,* 12(2): 153-161.

Budiyono, I. N. Widiasa, S. Johari, and Sunarso. 2010. The kinetic of biogas production rate from cattle manure in batch mode. *International Journal of Chemical and Biological Engineering,* 3(1): 39 - 44.

Carlsson, M., A. Lagerkvist, and F. Morgan-Sagastume. 2012. The effects of substrate pre-treatment on anaerobic digestion systems: A review. *Waste Management,* 32(9): 1634-1650.

Commission Regulation 2009/152/EC. 2009. Laying down the methods of sampling and analysis for the official control of feed, Official Journal of the European Union L 54/1.

Cui, Z., J. Shi, and Y. Li. 2011. Solid-state anaerobic digestion of spent wheat straw from horse stall. *Bioresource Technology,* 102(20): 9432-9437.

Deutsche Reiterliche Vereinigung, e. V. 2012. Zahlen, Daten, Fakten Pferdesport 2012. 2012, from http://www.pferd-aktuell.de/shop/index.php/cat/c106_Verband.html.

European Renewable Energy Council. 2007. Renewable energy technology roadmap.

Garlipp, F., E. F. Hessel, and H. F. A. van den Weghe. 2011. Characteristics of gas generation (NH_3, CH_4, N_2O, CO_2, H_2O) from horse manure added to different bedding materials used in deep litter bedding systems. *Journal of Equine Veterinary Science,* 31(7): 383-395.

Hartmann, H., I. Angelidaki, and B. K. Ahring. 2000. Increase of anaerobic degradation of particulate organic matter in full-scale biogas plants by mechanical maceration. *Water Science and Technology,* 41(3): 145-153.

Hashimoto, A. G. 1983. Conversion of straw-manure mixtures to methane at mesophilic and thermophilic temperatures. *Biotechnology and Bioengineering,* 25(1): 185-200.

Helffrich, D. 2005. Laborverfahren zur Bestimmung der Qualität und Quantität des beim anaeroben Abbau organischer Substanzen entstehenden Biogases im Batch Verfahren. German Patent DE 10227685 B4: In German.

Helffrich, D., and H. Oechsner. 2003. The hohenheim biogas yield test - Comparison of different laboratory techniques for the digestion of biomass. *Landtechnik,* 58(3): 148-149.

Hess, C., J. Beck, and T. Jungbluth. 2004. Problematik der Mistverwertung in der Pferdehaltung Baden-Württembergs, Universität Hohenheim: 121.

Horan, N. J., Z. Siqqiqui, and K. Anaman. 2011. Optimisation of C:N ratio for co-digested processed industrial foodwaste and sewage sludge using the bmp. *International Journal of Chemical Reactor Engineering,* 9: in press.

Ibrahim, I. I., G. Guowei, Z. Jinfu, S. A. Tayel, M. F. A. Khairy, and S. A. El-Shimi. 1997. Anaerobic digestion for waste water poultry manure by UBF reactor. *Journal of Environmental Sciences,* 9(2): 149-161.

IS Forschungsgesellschaft. 2011. Process for producing biogas. EP 1 997 901 B1.

Kalia, A. K., and S. P. Singh. 1998. Horse dung as a partial substitute for cattle dung for operating family-size biogas plants in a hilly region. *Bioresource Technology,* 64(1): 63-66.

Kimmich, S., and L. Slotyuk. 2011. Research into the difference in the nutrient content of conventional and ecological produced substrates and their influence on the biogas process, Universität Hohenheim.

Kratky, L., and T. Jirout. 2011. Biomass size reduction machines for enhancing biogas production. *Chemical Engineering and Technology,* 34(3): 391-399.

Kusch, S., H. Oechsner, and T. Jungbluth. 2008. Biogas production with horse dung in solid-phase digestion systems. *Bioresource Technology,* 99(5): 1280-1292.

Menardo, S., G. Airoldi, and P. Balsari. 2012. The effect of particle size and thermal pre-treatment on the methane yield of four agricultural by-products. *Bioresource Technology,* 104(1): 708-714.

Menardo, S., and P. Balsari. 2012. An analysis of the energy potential of anaerobic digestion of agricultural by-products and organic waste. *BioEnergy Research,* 5(3): 759-767.

Møller, H. B., S. G. Sommer, and B. K. Ahring. 2004. Methane productivity of manure, straw and solid fractions of manure. *Biomass and Bioenergy,* 26(5): 485-495.

Nelson, C., and J. Lamb. 2002. Haubenschild farms anaerobic digester: 35.

Nopharatana, A., P. C. Pullammanappallil, and W. P. Clarke 2007. Kinetics and dynamic modelling of batch anaerobic digestion of municipal solid waste in a stirred reactor. *Waste Management,* 27(5): 595-603.

Oechsner, H., A. Lemmer, and D. Preissler. 2011. Spurenelemente in NawaRo-Biogasanlagen zum Ausgleich substratbedingter Mangelerscheinungen und zur Stabilisierung des Gärprozesses. Biogas in der Landwirtschaft: Stand und Perspektiven. Göttingen, KTBL-Schrift. 488**:** 48-61.

Quiñones, T. S., M. Plöchl, J. Budde, and M. Heiermann. 2012. Results of batch anaerobic digestion test - effect of enzyme addition. *Agricultural Engineering International: CIGR Journal,* 14(1): 38-50.

R Core Team. 2012. R: A language and environment for statistical computing. Vienna, Austria, R Foundation for Statistical Computing.

Romano, P. V., U. Krogmann, M. L. Westendorf, and P. F. Strom. 2006. Small-scale composting of horse manure mixed with wood shavings. *Compost Science and Utilization,* 14(2): 132-141.

Sager, M. 2007. Trace and nutrient elements in manure, dung and compost samples in Austria. *Soil Biology and Biochemistry,* 39(6): 1383-1390.

Sakar, S., K. Yetilmezsoy, and E. Kocak. 2009. Anaerobic digestion technology in poultry and livestock waste treatment — a literature review. *Waste Management and Research,* 27(1): 3-18.

Schievano, A., G. D'Imporzano, and F. Adani. 2009. Substituting energy crops with organic wastes and agro-industrial residues for biogas production. *Journal of Environmental Management,* 90(8): 2537-2541.

Society of Nutrition Physiologie. 2001. Energie- und Nährstoffbedarf landwirtschaftlicher Nutztiere , Nr. 8: Empfehlungen zur Energie- und Nährstoffversorgung der Milchkühe und Aufzuchtrinder. Frankfurt a. Main: DLG-Verlag.

Tait, S., J. Tamis, B. Edgerton, and D. J. Batstone. 2009. Anaerobic digestion of spent bedding from deep litter piggery housing. *Bioresource Technology,* 100(7): 2210-2218.

Tong, X., L. H. Smith, and P. L. McCarty 1990. Methane fermentation of selected lignocellulosic materials. *Biomass,* 21(4): 239-255.

Triolo, J. M., S. G. Sommer, H. B. Møller, M. R. Weisbjerg, and X. Y. Jiang. 2011. A new algorithm to characterize biodegradability of biomass during anaerobic digestion: Influence of lignin concentration on methane production potential. *Bioresource Technology,* 102(20): 9395-9402.

VDI-Society Energy and Environment. 2006. VDI 4630: Fermentation of organic Materials - Characterization of the substrate, sampling, collection of material data, fermentation tests.

VDLUFA. 2007. Method Book III - The chemical analysis for feedstuffs. Darmstadt, Germany: VDLUFA Verlag.

Vintiloiu, A., A. Lemmer, H. Oechsner, and T. Jungbluth. 2012. Mineral substances and macronutrients in the anaerobic conversion of biomass: An impact evaluation. *Engineering in Life Sciences,* 12(3): 287-294.

Wang, H., S. L. Brown, G. N. Magesan, A. H. Slade, M. Quintern, P. W. Clinton, and T. W. Payn. 2008. Technological options for the management of biosolids. *Environmental science and pollution research international,* 15(4): 308-317.

Ward, A. J., P. J. Hobbs, P. J. Holliman, and D. L. Jones. 2008. Optimisation of the anaerobic digestion of agricultural resources. *Bioresource Technology,* 99(17): 7928-7940.

Wartell, B. A., V. Krumins, J. Alt, K. Kang, B. J. Schwab, and D. E. Fennell. 2012. Methane production from horse manure and stall waste with softwood bedding. *Bioresource Technology,* 112(1): 42-50.

Weiland, P. 2010. Biogas production: current state and perspectives. *Applied Microbiology and Biotechnology,* 85(4): 849-860.

Yusuf, M. O. L., A. Debora, and D. E. Ogheneruona. 2011. Ambient temperature kinetic assessment of biogas production from co-digestion of horse and cow dung. *Research in Agricultural Engineering,* 57(3): 97-104.