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ORIGINAL ARTICLE

Evaluation of pig farming residue as substrate for biomethane production via anaerobic digestion

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Abstract

Livestock farming and manure management contribute substantially to greenhouse gas (GHG) emissions in agriculture. Anaerobic digestion (AD) of manure is a promising strategy for mitigating these emissions. This study aimed to assess the biomethane potential (BMP) of various types of pig slurry, investigate factors that influence biomethane production, analyze degradation kinetics, and propose AD process optimization approaches. Thus, substrate analysis, BMP tests in batch assays, kinetic modeling, and principal component analysis (PCA) were conducted. In order to further quantify the effects of different substrate qualities in full-scale operation, biomethane production was simulated under steady-state conditions. Results indicated that piglet slurry had the highest volatile solids (VS)–specific BMP (203 ± 72 L kg^{-1} VS), followed by mixed slurry (202 ± 132 L kg^{-1} VS), fattening pig slurry (117 ± 56 L kg^{-1} VS), and sow slurry (86 ± 17 L kg^{-1} VS). The PCA revealed different substrate types and significant roles for VS, crude fat, volatile fatty acids concentration, and the carbon/nitrogen ratio in achieving high BMPs. First-order two-step kinetic modeling identified hydrolysis as the rate-limiting step, showing a determinant of rate-limiting step of < 0 for each sample. The simulation of continuous operation revealed notable differences in daily biomethane production (36.7–42.7 L day^{-1}) between the different slurries at the same hydraulic retention time and BMP. This research underscores the variability in pig slurry characteristics, exemplified by a total solids range of 1.4–12.1%, and provides crucial insights for optimizing AD processes in livestock waste management.

Keywords Anaerobic digestion · Biogas technology · Energetic utilization · Greenhouse gas mitigation · Kinetic modeling · Pig farming

1 Introduction

Energy consumption worldwide accounts for 75% of the total greenhouse gas (GHG) emissions; it is followed by agriculture, which accounts for 12% (5.86 Gt carbon dioxide [CO_2] equivalent) [1]. Pig farming and manure management contribute to GHG emissions in the agricultural sector [2–4]. The anaerobic digestion (AD) of pig slurry as an effluent management technology offers environmental benefits, as it mitigates GHG emissions by reducing methane (CH_4) and nitrous oxide emissions and replacing fossil fuels in the energy sector [5–8]. AD plants are usually realized as continuously stirred tank reactors (CSTRs) operating at mesophilic conditions (35–40 °C) and hydraulic retention times (HRTs) of more than 30 days [9–12].

The energetic utilization of manure, which is often diluted and thus not ideal for long-distance transportation or mono-digestion, can be achieved through anaerobic co-digestion

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(AcoD) [6]. Therefore, carbon (C)–rich co-substrates with large amounts of easily biodegradable organic matter (for maximizing CH_4 production) are commonly used for animal manure AD [13, 14]. The advantages of AcoD are the sufficiency of macro- and micronutrient supply, a balanced ratio of C to nitrogen (N), reduction of inhibitory effects through dilution, enhancement of process kinetics, and good buffer capacity [15, 16]. However, inappropriate substrate compositions and operating conditions may lead to unstable process conditions and reduced CH_4 production [15, 17, 18]. Another approach to the energetic utilization of manure is the use of high-rate reactors (e.g., upflow-anaerobic-sludge-blanket, or expanded-granular-sludge-bed reactors) for anaerobic digestion [19–21]. However, substrate quality is crucial for the economic feasibility of AD using pig farming residue in different reactor setups, as BMP directly influences revenue. The properties of animal manure are volatile, depending on the applied technology and the animal breed, sex, age, health, nutritional status, and housing conditions [22, 23]. Additionally, manure management involves storage conditions, storage durations, and the use of pretreatment technologies [24–26].

In Europe, the biomethane potential (BMP) of sustainable feedstocks (e.g., waste and residue) excluding energy crops (e.g., mono-cropped maize) derived via AD will be $3.8 \cdot 10^{10}$ m^3 in the year 2030. Animal manure accounts for the largest share of this potential (32%), followed by agricultural residue (24%) and sequential crops (21%) [27]. From a worldwide perspective, the BMP estimated by Chávez-Fuentes et al. [28] is $63.95 \cdot 10^{10}$ m^3 a^{-1}. Therefore, using animal manure in AD plants to generate biomethane reduces GHG emissions in the energy and agricultural sector and may be necessary to mitigate climate change.

Nardin and Mazzetto [29] investigated livestock manure management in a biorefinery approach that includes AD as a process step; they focused on nutrients, particularly N. The determined BMPs of piglet manure, fattening pig manure, and sow manure were 417, 345, and 213 L kg^{-1} of volatile solids (VS), respectively. A study comparing weaner and finisher slurries showed differences in total solids (TS), which ranged from 13.0 ± 3.2 g L^{-1} to 18.0 ± 10.7 g L^{-1} for $n = 10$, and COD, which ranged from 27.7 ± 18.0 g L^{-1} to 33.1 ± 13.7 g L^{-1}. However, only the slurry from the finishers was utilized in BMP tests, which showed an average BMP of 215–240 L kg^{-1} VS at different inoculum to substrate ratios (ISRs) [30].

To ascertain which characteristics of animal manure impede the economic viability of using animal slurry as a feedstock, Triolo et al. [31] studied 20 farms in Denmark, focusing on the BMP of slurries from pig farming. The study covered four piglet slurries (PSs), three slurries consisting of sow and piglet manure, two fattening pig slurries (FPSs), and two sow slurries (SSs). With dry matter (DM) contents ranging from 5.4% ± 3.1% (PS) to 7.9% ± 4.3% (SS), the overall BMP range (including dairy cow and cattle manure) was 170–400 L kg^{-1} VS. The DM content was found to be more important than VS-specific CH_4 potential; DM showed larger variation, resulting in higher fresh matter (FM)–specific CH_4 production using full-scale digesters. Linear relationships were identified for FM-specific BMP with DM content, with a reported coefficient of determination (R^2) of 89.61%. Regarding VS-specific BMP, a negative linear relationship based on lignin (% of VS), a positive relationship based on volatile fatty acids (VFA; % of VS), and a combination of lignin and VFA were derived. Hilgert et al. [24] found a correlation between BMP and VFA. Samples were obtained from the barn, intermediate storage, and external storage of two farms specializing in fattening pigs. A 39.5% reduction in BMP was found for FPS (intermediate storage vs. external storage), which is associated with loss of degradable organic material. Examinations on the impact of different manure management strategies revealed that the VS-specific BMP is reduced from 158 to 24 L kg^{-1} VS by centrifugation and 42 L kg^{-1} VS by decantation. Nevertheless, a mixture of raw slurry and solid fraction from decantation offered the highest BMP of 351 L kg^{-1} VS [32].

To our knowledge, researchers have focused either on the influence of different types of manure [29–31] or on the influence of manure management [24, 32]. However, as described above, in practice both factors exert an influence, resulting in different substrate qualities available for biomethane production. This practical interaction has so far been understudied. Therefore, the objectives of this study are as follows:

- To determine the BMP range for different types of pig slurry that are available for biomethane production
- To investigate parameters that influence biomethane production
- To assess substrate degradation kinetics and its repercussions on continuous operation
- To provide recommendations for improving the BMP of pig slurry

BMP tests were performed, and the different parameters influencing the AD process were determined (e.g., TS, VS, VFA, and nutrient composition). As the findings of this study are intended for implementation by the agricultural sector, the selected approach is oriented toward practical application and existing systems in the German biogas sector.

2 Materials and methods

The various available residues from pig farming and the conditions under which they were sampled are described in the following. Subsequently, the substrate properties are presented, the experimental setup for the BMP tests is described, and finally the application of kinetic models is explained.

2.1 Substrate types

The different stages of pig production can be separated into functional groups, from mating within the breeding process (to obtain piglets) to fattening within the finishing phase. From this, four types of pig production systems are differentiated, as shown in Fig. 1. The first is farrow-to-finish operation, where every production stage is completed in one piggery. The entire process is allocated by splitting the operation into farrow-to-feeder and feeder-to market (or weaner) piggeries. The farrow-to-feeder production system includes the entire breeding process and, in some cases, weaners. However, weaning can also be done in individual piggeries or within the feeder-to-market production system [23, 33]. Within this framework, different types of slurry can be obtained. SS, PS, FPS, and mixed slurry (MS) are obtained from the partial joint storage of slurries from different functional units; they are shown on the right-hand side of Fig. 1. Manure is usually stored beneath the barn in intermediate-storage facilities called slurry cellars (SCs). From there, slurry can be transferred to external storage (elevated tank [ET]) at different intervals, depending on the manure removal system used.

The different types of slurry and the sampling point in each agricultural enterprise included in this study are summarized in Table 1.

2.2 Substrate properties

Sampling was conducted in the Muensterland region, Germany, where livestock farming is as concentrated as in Lower Saxony and Schleswig–Holstein [6]. The implementation period was from November 2022 to March 2023. Sampling was performed following Mybrack et al. [34]. Sufficient mixing of the slurry storage facilities was ensured; in cases where this was technically impossible, samples were obtained from different heights to generate composite samples. pH measurements were performed after sampling on site. The samples were then transported to the Laboratory for Environmental Engineering and Wastewater Treatment, Muenster University of Applied Sciences, and stored in closed vessels at 4 °C.

The substrate samples were evaluated in detail by measuring their physical and chemical properties. TS (VS) were determined according to the DIN EN 15934 (DIN EN 15935) standard [35, 36]. A remediation of TS concerning volatile compounds was applied [37]. The VS enhancement (% FM) amounted to 1% per 10 g L^{-1} acetic acid equivalent. This amendment was necessary, as BMP was expressed as L kg^{-1} VS and VFA. As for the anaerobic process, relevant substrate constituents would have been detected as water if

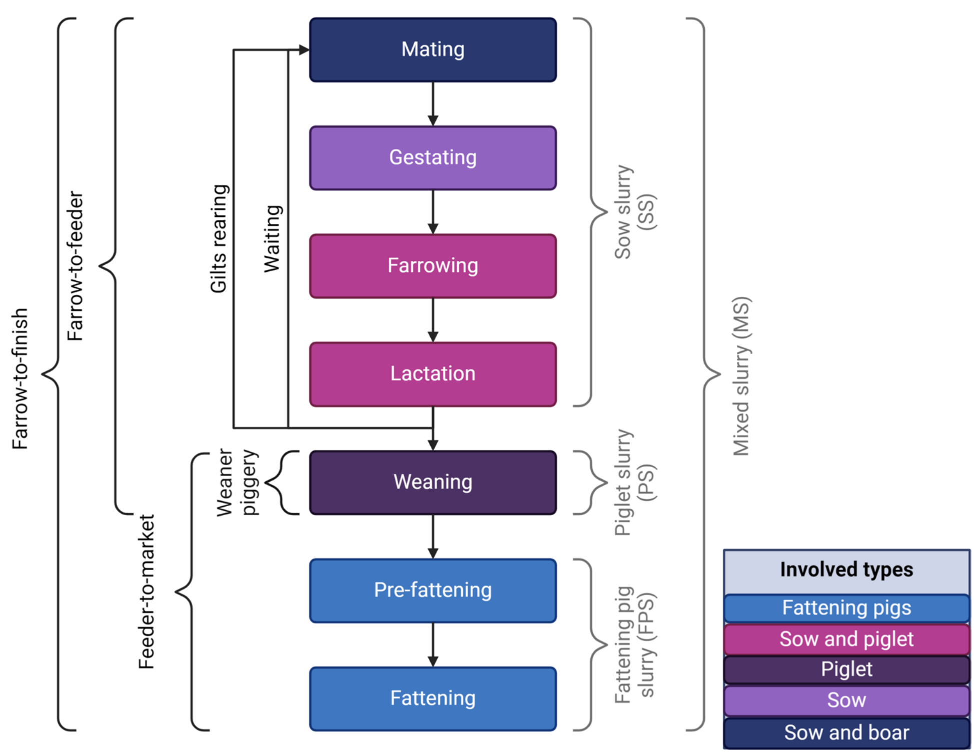


Fig. 1 Typical pig production systems and obtained slurries analyzed in this study

Table 1 Substrate types, sampling points, and remarks of substrate samples from agricultural enterprises with *AE1–AE19*, abbreviations referring to agricultural enterprises; *ET*, elevated tank; *SC*, slurry cellar; *DS*, Danish system; *MS*, mixed slurry; *PS*, piglet slurry; *FPS*, fattening pig slurry; *SS*, sow slurry; *PFS*, prefattening pig slurry

Sample	Agricultural enterprise	Sampling point	Slurry type	Remark
AE1-ET1-MS1	AE1	ET	MS	PS, SS, and FPS; thick phase after sedimentation
AE1-ET2-MS2	AE1	ET	MS	PS, SS, and FPS; thin phase after sedimentation
AE1-SC2-PS	AE1	SC	PS	
AE1-SC3-MS3	AE1	SC	MS	PS and PFS
AE1-SC1-FPS	AE1	SC	FPS	Thick phase
AE3-ET-FPS	AE3	ET	FPS	
AE4-SC1-PS	AE4	SC	PS	
AE4-SC2-SS	AE4	SC	SS	
AE5-SC-MS	AE5	SC	MS	PS and FPS
AE8-SC-PS	AE8	SC	PS	
AE8-ET-MS	AE8	ET	MS	PS and slurry from the farrowing stable
AE9-SC-SS	AE9	SC	SS	
AE10-SC1-PFS	AE10	SC	PFS	
AE10-SC2-FPS	AE10	SC	FPS	
AE14-SC-MS	AE14	SC	MS	PS and FPS
AE15-SC-FPS	AE15	SC	FPS	
AE17-SC-FPS	AE17	SC	FPS	
AE18-SC1-PS	AE18	SC	PS	
AE18-SC2-SS	AE18	SC	SS	Thick phase
AE19-DS-MS1	AE19	DS	MS	SS and PS; thick phase from external sedimentation pit
AE19-DS-MS2	AE19	DS	MS	SS and PS
AE19-DS-MS3	AE19	DS	MS	SS and PS; thin phase from external sedimentation pit

only the DIN EN 15936/15935 standard were used. Thus, an exact VS-specific BMP could be reported. Cuvette tests (LCK 014/LCK 914, Hach Lange GmbH, Duesseldorf, Germany) were used to determine the chemical oxygen demand (COD). The volatile organic acids (VOA) and total inorganic C (TIC) were determined by centrifuging the samples (10 min at 2000 rpm) and subjecting the supernatant to potentiometric titration using an autotitrator (AT1222, Hach Lange GmbH, Düsseldorf, Germany). The VFA concentrations were assessed through ion chromatography using an 882 Compact IC Plus (Metrohm AG, Herisau, Switzerland). For this analysis, a polymer-based cation exchanger column (Metrosep Organic Acids—250/7.8) was used in combination with a conductivity detector. Subsequently, the samples were centrifuged for 10 min at 5000 rpm. The filtered samples were passed through syringe prefilters with pore sizes of 1.0 and 0.45 mm. The temperature and pH were measured on site using a mobile pH meter (Multi 3630 IDS, WTW, Weilheim in Oberbayern, Germany). Phosphorus pentoxide, potassium oxide, magnesium oxide, calcium oxide, copper, manganese, zinc, and sulfur were measured via inductively coupled plasma optical emission spectroscopy in accordance with the DIN EN ISO 11885 standard [38]. Ammonium nitrogen was determined as per DIN 38406–5 [39], and the total N was measured in accordance with the VDLUFA [40]. Weender analysis was conducted according to Commission Regulation (EC) No. 152/2009 for the official control of feed [41]. Table 2 details the properties of the analyzed samples (additional measurements are shown in Appendix Table 7).

2.3 Experimental setup

The test setup used to determine the BMP of the slurries is shown in Fig. 2. The procedure is based on the VDI 4630 test standard [37]. The tests were conducted in 1000-mL glass vessels (no. 7 in Fig. 2) with an ISR of 2 to prevent inhibition. The inoculum was from an agricultural biogas plant (BP) in the Muensterland region and consisted of energy crops (maize silage and corn cob mix), pig slurry, and cattle manure as substrates. If necessary, the vessel was filled with warm water up to a reaction volume of 800 mL. Each vessel was homogenized and then connected to a 1000-mL eudiometer tube (no. 3 in Fig. 2) using polyvinyl chloride hoses (no. 5 in Fig. 2). At the start of the experiment, the eudiometer tubes were purged with N gas to create anaerobic conditions; then, daily monitoring involving gas quantity and

Table 2 Physical and chemical properties of substrate samples with sample designation according to Table 1 with *TS*, total solids; *FM*, fresh matter; *VS*, volatile solids; *COD*, chemical oxygen demand; *VFA*, volatile fatty acids; *VOA*, volatile organic acids; *TIC*, total inorganic carbon; *C/N*, carbon-to-nitrogen ratio; *n.a.*, not analyzed; *n.d.*, not detectable

Sample*	pH (-)	TS (% FM)	VS (% TS)	COD (mg L^{-1})	VFA (g L^{-1})	VOA (mg L^{-1})	TIC (mg L^{-1})	VOA/TIC (-)	C/N (-)
AE1-ET1-MS1	7.9	3.4	64.4	25,700	n.d	1836	10,045	0.18	5
AE1-ET2-MS2	8.1	3.0	60.7	7800	n.d	1505	9330	0.16	1
AE1-SC2-PS	7.6	5.5	72.8	10,300	2.36	3777	8511	0.44	5
AE1-SC3-MS3	7.9	8.5	78.5	76,500	8.82	12,616	5849	2.16	7
AE1-SC1-FPS	7.4	11.7	72.7	41,900	n.d	2056	11,607	0.18	7
AE3-ET-FPS	7.9	2.1	51.1	7900	n.d	1948	9988	0.20	3
AE4-SC1-PS	7.2	2.4	71.6	24,400	0.67	2098	5946	0.35	7
AE4-SC2-SS	7.9	1.8	58.3	49,600	n.d	1272	6095	0.21	4
AE5-SC-MS	8.1	12.1	41.6	21,100	n.d	1918	10,938	0.18	4
AE8-SC-PS	7.8	1.7	51.0	13,000	0.26	2184	9528	0.23	5
AE8-ET-MS	7.9	1.4	43.9	13,700	n.d	1817	10,342	0.18	2
AE9-SC-SS	8.0	2.1	63.3	19,000	n.d	1110	6791	0.16	6
AE10-SC1-PFS	8.0	10.0	77.9	6380	0.10	1565	8703	0.18	7
AE10-SC2-FPS	7.5	7.1	76.1	5230	n.d	1249	8857	0.14	8
AE14-SC-MS	8.0	6.9	68.8	51,800	2.43	6185	15,941	0.39	5
AE15-SC-FPS	7.9	5.1	67.5	49,600	3.87	7788	11,413	0.68	4
AE17-SC-FPS	6.9	3.4	59.5	19,000	0.16	2860	12,283	0.23	3
AE18-SC1-PS	7.3	11.9	72.3	n.a	0.51	2023	5057	0.40	8
AE18-SC2-SS	7.2	9.8	65.2	n.a	n.d	776	2760	0.28	9
AE19-DS-MS1	6.9	11.5	83.9	10,481	0.27	11,141	5437	2.05	12
AE19-DS-MS2	7.9	8.7	80.5	6079	n.d	1124	8623	0.13	6
AE19-DS-MS3	7.3	1.7	63.9	10,511	0.11	5231	4500	1.16	1

quality measurements was performed. The barrier fluid (no. 4 in Fig. 2) consisted of water and 5 wt.% sulfuric acid and sodium sulfate (7.5 wt.%) to prevent the entry of CO_2 from the produced biogas into the barrier liquid.

The gas composition, namely, CH_4, CO_2, oxygen (O_2), and hydrogen sulfide (H_2S), was determined. All measurements were performed using an infrared sensor and an electrochemical sensor (Multitec 540, Hermann Sewerin GmbH, Guetersloh, Germany).

Based on the recommendations of Holliger et al. [42, 43], the following requirements/criteria were used to validate each experiment on every tested substrate and ensure basic robustness of the results:

- The BMP of the positive control (microcrystalline cellulose; in triplicate) is 340–395 L kg^{-1} VS and shows a relative standard deviation of < 6% after eliminating a single outlier.
- The BMP of the substrate (in triplicate) has a CV < 10% after deleting a single outlier.
- Tests are completed when a daily biomethane production of < 1% is observed for three consecutive days.
- Abrupt or nonmonotonic outliers require individual analyses.

2.4 Kinetic modeling

First-order process models (Fig. 3) were used to assess the CH_4 production kinetics in the BMP tests.

One- and two-step models were used to describe the degradation process. The two-step model determines the hydrolysis rate constant (k_{hyd}; day^{-1}) and VFA degradation (k_{VFA}; day^{-1}) individually. The model equations are summarized in Table 3.

The Nash–Sutcliffe efficiency (NSE) was used to assess the goodness of fit. The NSE is widely used in the field of hydrology and enables comparisons of parameters at different dimensions. However, the original NSE is highly sensitive to individual outliers [46, 47]. Thus, a modified NSE (NSE_M) was used in this study, and it is defined as follows:

$$NSE_M = 1 - \frac{\sum_{i=1}^{n} \left| X_{obs}^{i} - X_{sim}^{i} \right|}{\sum_{i=1}^{n} \left| X_{obs}^{i} - \overline{X} \right|}, \quad (3)$$

where X_{obs} is the observed value and X_{sim} is the simulated value.

Hydrolysis was assumed to be the limiting step of the degradation process of pig slurry [48, 49]. This assumption

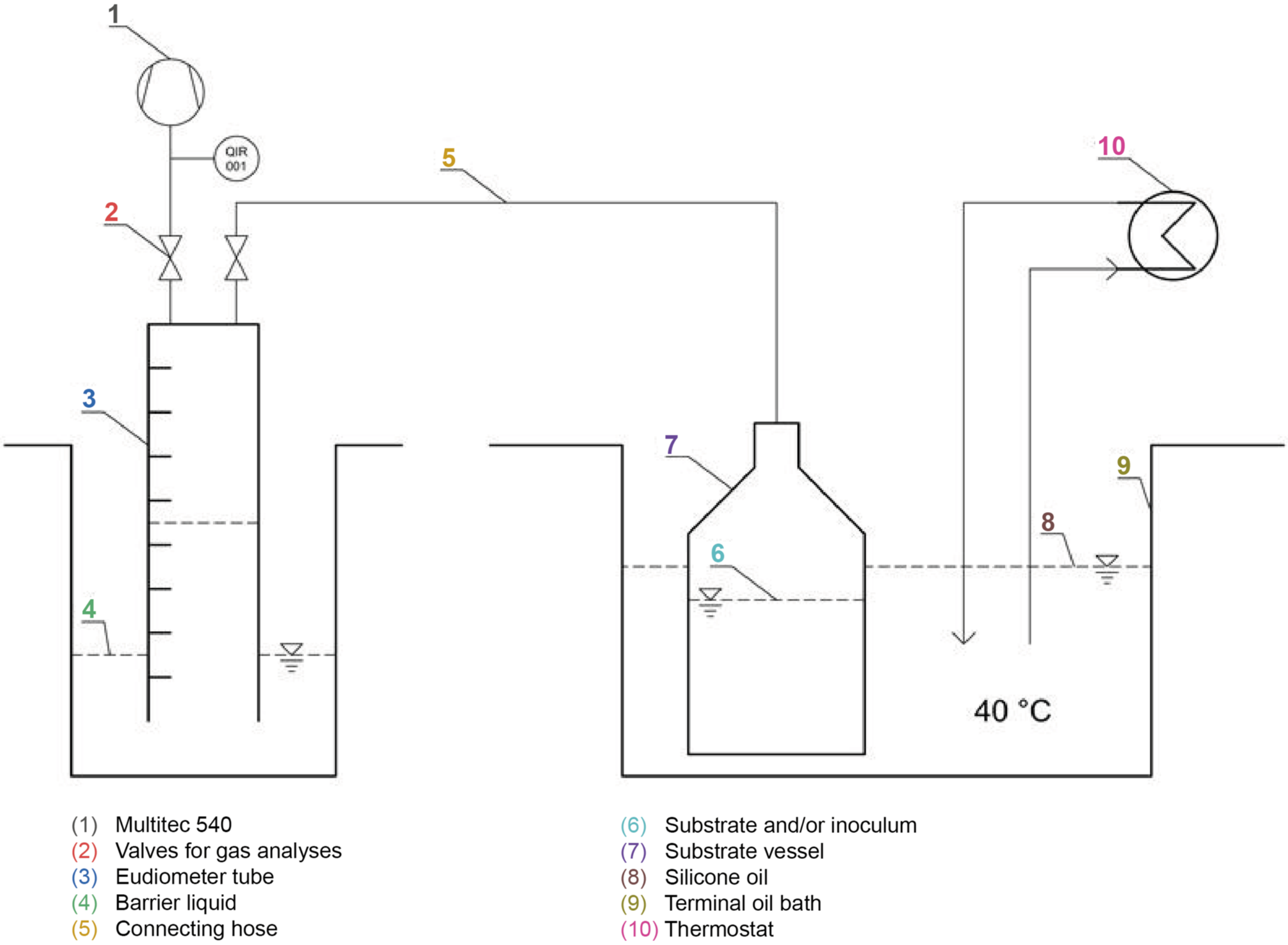


Fig. 2 Reactor setup of batch tests to determine the biomethane potential

Fig. 3 Structures of first-order one-step and two-step models (based on Brulé et al. [44])

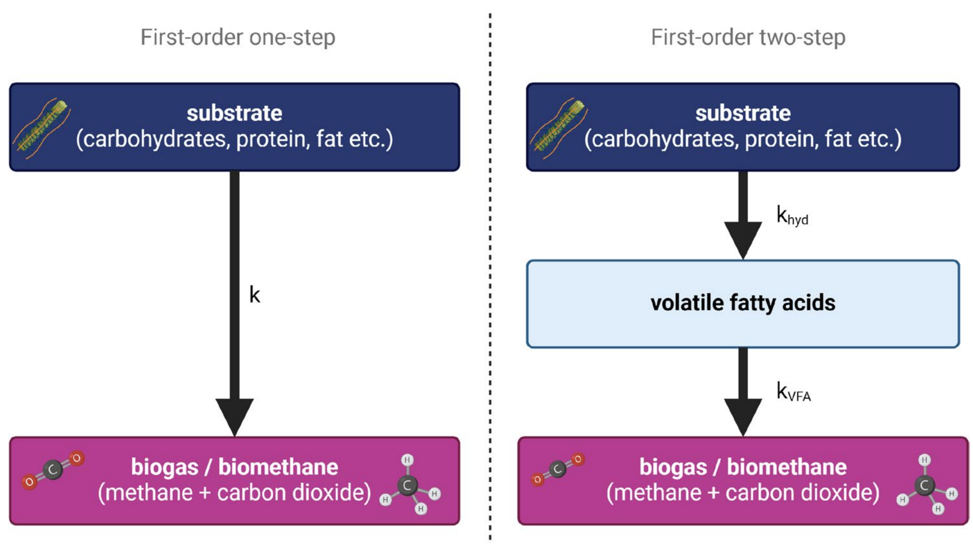


Table 3 Models describing BMP curves with $BMP(t)$, biomethane potential (L kg^{-1} VS) at a given time t; BMP_{max}, maximum biomethane potential (L kg^{-1} VS); k, first-order one-step constant (day^{-1}); t, time (day); k_{hyd}, first-order two-step constant for substrate degradation (day^{-1}); k_{VFA}, first-order two-step constant for VFA degradation (day^{-1})

Model	Equation	Reference
First-order one-step	$BMP(t) = BMP_{max} \cdot (1 - e^{-k \cdot t})$ (1)	[45]
First-order two-step	$BMP(t) = BMP_{max} \cdot (1 + \frac{k_{hyd} \cdot e^{-k_{VFA} \cdot t} - k_{VFA} \cdot e^{-k_{hyd} \cdot t}}{(k_{VFA} - k_{hyd})})$ (2)	[44]

was verified using the determinant of rate-limiting step (DR), defined by Shin and Song [50] as follows:

$$DR = \ln \frac{k_{hyd}}{k_{VFA}}. \tag{4}$$

A negative (positive) DR value indicates that substrate degradation (acetoclastic CH_4 production) is the rate-limiting step [50]. For a negative DR value, a first-order kinetic, as described by Mata-Alvarez [51], can be applied as follows:

$$\frac{dS}{dt} = -k \cdot S, \tag{5}$$

where S is the concentration of biodegradable solids (g L^{-1}) and k is the first-order hydrolysis constant (day^{-1}). The S value under steady-state conditions during continuous operation was derived via CSTR mass balancing [52].

$$\frac{dS}{dt} V = S_0 \cdot Q_{in} - S \cdot Q_{out} - k \cdot S \cdot V = 0, \tag{6}$$

where S_0 is the input concentration of biodegradable solids (g L^{-1}), Q_{in} is the input flow (L day^{-1}), Q_{out} is the output flow (L day^{-1}), and V is the reactor volume (L). Under ideal conditions and $Q_{in} = Q_{out}$, Eq. 6 can be transferred to Eqs. 7 and 8.

$$\frac{dS}{dt} = \frac{1}{HRT} \left(S_0 - S \right) - k \cdot S = 0, \tag{7}$$

where HRT is the hydraulic retention time (HRT; day).

$$S = S_0 \cdot \frac{1}{1 + k * HRT} \tag{8}$$

Based on the available BMP, the specific biomethane yield (BMY) under steady-state conditions was expressed using the input and output concentrations (S_0 and S, respectively) of biodegradable solids.

$$BMP_{max} \cdot \left(S_0 - S \right) = BMY \cdot S_0, \tag{9}$$

where BMY is the biomethane yield under steady-state conditions (L CH_4 kg^{-1} VS). Thus, the specific BMY was derived by combining Eqs. 8 and 9.

$$BMY = BMP_{max} \cdot \frac{k \cdot HRT}{1 + k * HRT} \tag{10}$$

Equation 7 was extended using the input mass flow of VS ($\dot{m}_{vs}$; kg VS day^{-1}) to calculate the absolute daily CH_4 yield of a full-scale digester operating in steady state (BMY_{FS}).

$$BMY_{FS} = \dot{m}_{vs} \cdot BMP_{max} \cdot \frac{k \cdot HRT}{1 + k \cdot HRT}, \tag{11}$$

where $\dot{m}_{vs}$ is the input mass flow of VS (kg VS day^{-1}) and BMY_{FS} is the biomethane yield of a full-scale digester in steady state (L day^{-1}).

2.5 Implementation

The models were implemented in Python 3.11, mainly using the numpy, pandas, and scipy packages. For first-order one-step modeling, BMP_{max} and k were fitted; for first-order two-step modeling, BMP_{max}, k_{hyd}, and k_{VFA}. For the initial guess of BMP_{max}, the maximum experimental value for each batch assay was considered. Fixed values were used for the initial guesses of the kinetic parameters ($k = 0.0001$ day^{-1}, $k_{hyd} = 0.0001$ day^{-1}, and $k_{VFA} = 0.0002$ day^{-1}). In general, fitting was performed to the cumulative BMP curve using the optimize.curve_fit function in the scipy package. This function solves a given nonlinear least-squares problem (in this case using Eqs. 1 and 2 [Table 3]) using the trust region reflective algorithm and a maximum of 10,000 iterations [53, 54].

Overall, the robustness of the results is strengthened by using a heterogeneous sample set, applying triplicates within the BMP test setup and indicating standard deviations (in Fig. 4 and Fig. 6). Furthermore, the first-order two-step model is applied as a more complex alternative to the first-order one-step model, and using NSE_M to assess the goodness of fit. Finally, the results are discussed in the context of literature.

3 Results

The sample set contained 22 different slurries representing the production stages of pig farming. It begins with sows producing piglets, which are raised to a specific weight and undergo the fattening phase, where various feeding strategies are used, depending on the animal weight. Furthermore, different management strategies are included, such as slurry sedimentation and use of storage facilities (e.g., an ET or under the barn) [55]. The pH ranged from 6.9 to 8.1 at TS contents of 1.4–12.1% FM. The FPSs had the highest average TS content in a slurry category (TS = 6.6% ± 3.4% FM), followed by the MSs (TS = 6.4% ± 3.9% FM), PSs (TS = 5.4% ± 4.0% FM), and SSs (TS = 4.6% ± 3.7% FM).

The average C-to-N (C/N) ratio was 5.4 ± 2.6 (range of 1–12), matching the C/N ratio reported by Hjorth et al. [56]. Given that the optimal C/N ratio is 15–40, the substrates did not correspond to the properties needed for optimal degradation in anaerobic digestion processes [10, 57–59].

COD measurements showed high variability (5230–76,500 mg L^{-1}). These differences in substrate properties reflected the findings of Miroshnichenko et al. [22] and Kirchmann and Witter [60]. In the following, the results of the BMP tests are presented, which are then incorporated into the context of kinetic modeling and PCA. Finally, the examination of continuous operation under steady-state conditions at full scale is shown.

3.1 Slurry BMPs

Batch experiments were performed as described in Sect. 2.3, and the referenced general requirements and validation criteria for BMP tests were applied on the dataset. The progression of discontinuous CH_4 production for the different slurries is shown in Fig. 4.

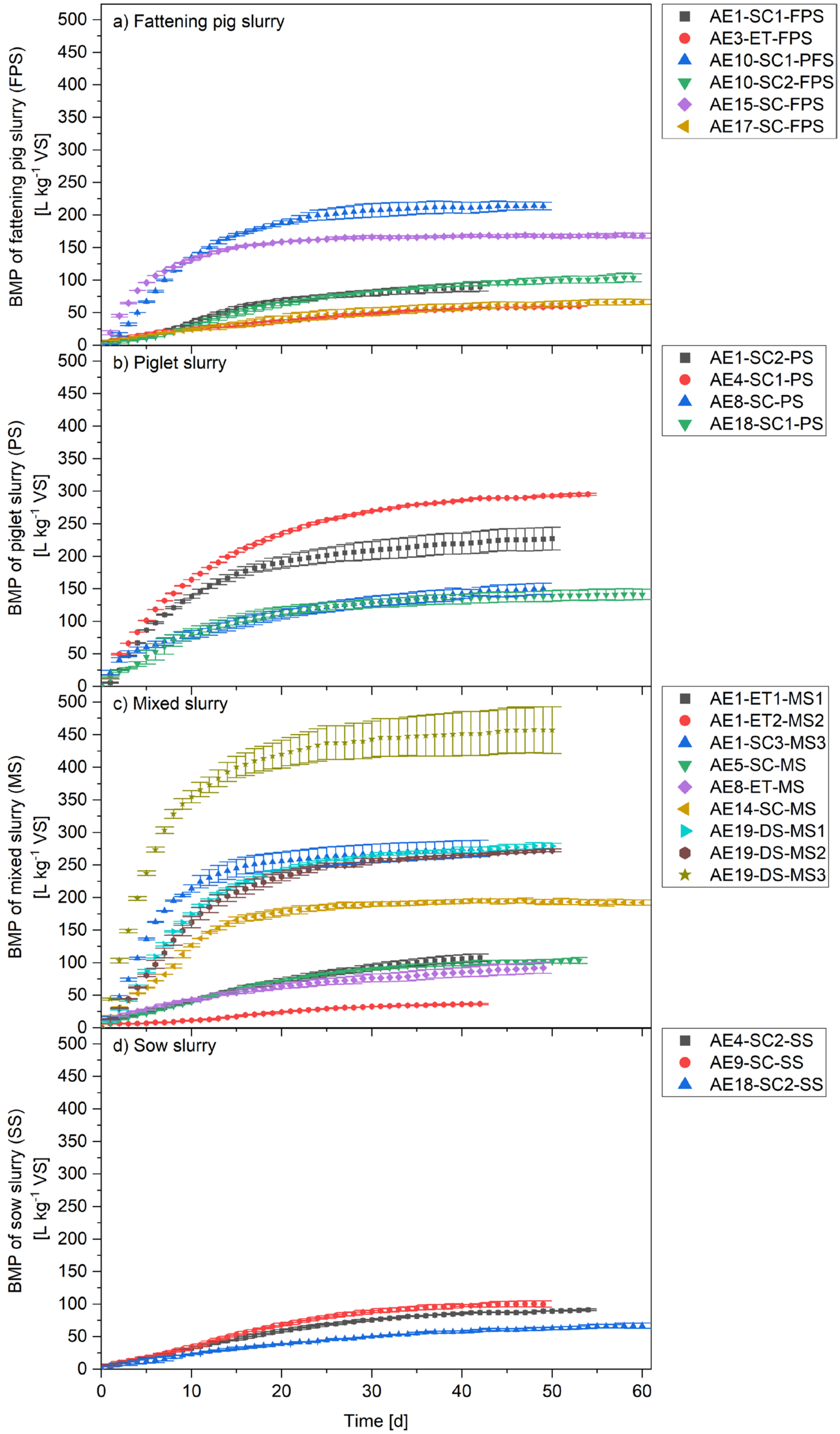
The highest BMP, 457 ± 35 L kg^{-1} VS, was obtained from AE19-DS-MS3, which consisted of PS and SS, was the thin phase of AE19-DS-MS2 and thus significantly higher than the expected BMP for pig slurry. This BMP corresponded to a high CH_4 content in the BMP test. One explanation for this result could be a low content of carbohydrates, which generally promote a lower CH_4 content than fats or proteins [61]. However, the concentration of crude fat was not distinctly high. As no further anomalies were detected, the sample was included in the sample set. The BMP of the raw slurry from the barn of this enterprise was 272 ± 2 L kg^{-1} VS, and that of its thick phase was 280 ± 4 L kg^{-1} VS. In comparison to the overall dataset, high BMPs were obtained from this enterprise. This was due to its dung removal system (Danish system [DS]), where the slurry is cooled under the barn and frequently pumped out. This permanently drains the external sedimentation pit of the slurry [62]. In terms of FM, the external sedimentation pit increased biomethane production by 42% for the thick phase compared with the raw slurry. AE1-SC3-MS3 (MS from SC no. 3 at AE1) had a similarly high BMP of 276 ± 13 L kg^{-1} VS and a correspondingly high COD of 76,500 mg L^{-1}. Four more slurries from this agricultural enterprise were sampled. Two of them were obtained from different ETs and contained MS. The facility exploits the settleability of pig slurry [63]. All slurries are transferred to one of these tanks (ET2), and the bottom layer is pumped into a second ET (ET1). Therefore, thin slurry was obtained from ET2, and thick slurry was obtained from ET1. However, these ETs contained not only the stable slurry AE1-SC3-MS3 but also SS and FPS. This procedure was done because DM and nutrients (especially phosphorus) are more likely to be found in the thick phase; these nutrients can then be transported more efficiently to faraway fields or BPs [56]. The BMP of the thickened slurry was 108 ± 6 L kg^{-1} VS, which was higher than that of AE1-ET2-MS2 (37 ± 1 L kg^{-1} VS). The TS and VS of AE1-ET1-MS1 were also higher than those of AE1-ET2-MS2, resulting in higher CH_4 production in terms of FM. Between these two samples were the MS samples AE5-SC-MS and AE8-SC-MS. In addition, the composition of AE14-SC-MS was comparable to that of AE1-SC3-MS3 (PS and FPS [or prefattening slurry (PFS)]). AE14-SC-MS, a mixture of PS and FPS, had a BMP of 195 ± 4 L kg^{-1} VS.

The FPSs showed CH_4 potentials ranging from 60 ± 1 L kg^{-1} VS (AE3-ET3-FPS) to 214 ± 6 L kg^{-1} VS (AE10-SC1-FPS). The PSs had high BMPs (average BMP = 203 ± 72 L kg^{-1} VS). As for the PS of AE8, where MS from an ET was also examined, the BMP was 150 ± 9 L kg^{-1} VS, which was distinctly higher than that of AE8-ET-MS. The lower CH_4 potentials of slurries from the same agricultural enterprise and different storage tanks can be attributed to substrate handling in practice and substrate quality degradation caused by aging [24]. Two different pig slurries from AE10 were also sampled. Its PFS (AE10-SC1-PFS) had a higher BMP (214 ± 6 L kg^{-1} VS) than its FPS (AE10-SC2-FPS; 104 ± 6 L kg^{-1} VS).

For the SSs, the obtained BMPs were similar: 91 ± 1 L kg^{-1} VS for AE4-SC2-SS, 100 ± 5 L kg^{-1} VS for AE9-SC2-SS, and 67 ± 4 L kg^{-1} VS for AE18-SC2-SS. However, the number of samples for this type of slurry was smaller compared with the numbers of MS or FPS samples.

With individual BMP measurements structured according to their origin, the PSs had the highest VS-specific BMP (203 ± 72 L kg^{-1} VS), followed by the MSs (202 ± 132 L kg^{-1} VS), which included six high-BMP slurries containing PS (AE1-SC3-MS3, AE5-SC-MS, AE14-SC-MS, and AE1-DS-MS1-3) and had a large variation in general. They were followed by the FPSs (117 ± 56 L kg^{-1} VS) and SSs (86 ± 17 L kg^{-1} VS). This ranking was consistent with the results of Nardin and Mazzetto [29], although they did not study MSs and obtained higher BMPs. Hilgert et al. [24] investigated the CH_4 potentials of indoor- and outdoor-stored pig slurries with regard to their chemical compositions and storage conditions. In their study, FPS samples from two different farms showed TS contents of 1.12–4.00% FM and yielded BMPs of 166–313 L kg^{-1} VS (estimation based on a modified Gompertz model). Samples were obtained from

Fig. 4 Experimentally obtained VS-specific BMPs for (a) fattening pig slurry (FPS), (b) piglet slurry (PS), (c) mixed slurry (MS), and (d) sow slurry (SS); AE1–AW19, abbreviations referring to agricultural enterprises; ET, elevated tank; SC, slurry cellar; DS, Danish system; PFS, prefattening pig slurry



barns, intermediate storage, and outdoor storage; the intermediate and outdoor-storage facilities appeared to be equivalent to the SCs and ETs in the current study, respectively. However, a reduction in BMP was detected from the barn samples to the intermediate-storage and outdoor-storage samples. This trend was also observed in AE1-ET1/ET2-MS1/MS2 and AE8-ET-MS relative to the other samples from these enterprises. Nevertheless, the sample from the ET at AE8 also contained slurry from a farrowing stable; at AE1, the thick phase (ET1) and thin phase (ET2) from FPS and SS were also present in these repositories, so a tendency was evident, but no general conclusion could be made about the amount of BMP reduction. Regarding slurry management at AE1, sedimentation improved the BMP. A comparatively small difference (0.5%) in DM content was accompanied by a significantly higher BMP of 108 ± 5 L kg^{-1} VS at ET1 compared with that at ET2 (37 ± 1 L kg^{-1} VS).

3.2 Modeling results

Individual parameter estimates of the applied process models are summarized in Table 4, which shows the NSE_M statistics and the parameters BMP_{max} k, k_{hyd}, and k_{VFA}. Additionally, the BMP test results are given. For the first-order one- and two-step models, NSE_M > 0.8 for each sample, indicating that the experiments agreed satisfactorily with the simulations.

For the first-order two-step model, extremely high k_{VFA} values (> 10 day^{-1}) were calculated in some cases. Meanwhile, k_{hyd} was similar to the kinetic parameter k of the first-order one-step model, and the same NSE_M values were calculated. Thus, VFA degradation occurred instantaneously, and the kinetic description of the additional process phase of acetoclastic CH_4 formation was not required in this case.

All samples had negative DR values, so hydrolysis was the rate-limiting step, as illustrated in Table 4. The kinetic description of VFA utilization was not of any significance at high k_{VFA} values (> 10 day^{-1}), so the process could be described with the same precision using the one-step kinetic model. Although 10 samples did not require the application of the two-step kinetic model, it performed equally well as a one-step first-order model and even better when k_{VFA} was within a reasonable range. Therefore,

Table 4 Experimentally estimated BMPs and corresponding model parameters (BMP_{max}, k, k_{hyd}, and k_{VFA}) with NSE_M, DR, and sample name (according to Table 1)

Sample	Experiment	First-order one-step model			First-order two-step model				
	BMP (L kg^{-1} VS)	BMP_{max} (L kg^{-1} VS)	k (day^{-1})	NSE_M (-)	BMP_{max} (L kg^{-1} VS)	k_{hyd} (day^{-1})	k_{VFA}* (day^{-1})	DR (-)	NSE_M (-)
AE1-ET1-MS1	108	136	0.038	0.97	136	0.038	> 10	− 20	0.97
AE1-ET2-MS2	37	58	0.026	0.88	58	0.026	> 10	− 19	0.88
AE1-SC1-FPS	90	109	0.045	0.88	91	0.093	0.226	− 1	0.94
AE1-SC2-PS	227	226	0.093	0.95	224	0.100	1.942	− 3	0.95
AE1-SC3-MS3	276	274	0.143	0.92	270	0.176	1.018	− 2	0.95
AE3-ET-FPS	60	67	0.044	0.91	67	0.044	> 10	− 19	0.91
AE4-SC1-PS	295	298	0.079	0.98	298	0.079	> 10	− 19	0.98
AE4-SC2-SS	91	105	0.041	0.93	102	0.045	1.307	− 3	0.94
AE5-SC-MS	103	114	0.050	0.93	111	0.055	1.266	− 3	0.94
AE8-ET-MS	92	94	0.059	0.90	94	0.059	> 10	− 21	0.90
AE8-SC-PS	150	147	0.077	0.84	147	0.077	> 10	− 20	0.84
AE9-SC-SS	100	124	0.038	0.90	109	0.061	0.294	− 2	0.95
AE10-SC1-PFS	214	220	0.091	0.91	214	0.121	0.560	− 2	0.98
AE10-SC2-FPS	104	122	0.035	0.89	107	0.062	0.205	− 1	0.97
AE14-SC-MS	195	198	0.102	0.88	194	0.149	0.403	− 1	0.94
AE15-SC-FPS	169	167	0.159	0.95	167	0.159	> 10	− 17	0.95
AE17-SC-FPS	66	74	0.040	0.95	74	0.040	> 10	− 20	0.95
AE18-SC1-PS	141	141	0.084	0.95	140	0.085	> 10	− 5	0.95
AE18-SC2-SS	67	76	0.036	0.97	76	0.036	> 10	− 19	0.97
AE19-DS-MS1	280	283	0.092	0.92	276	0.118	0.624	− 2	0.97
AE19-DS-MS2	272	276	0.087	0.92	270	0.110	0.632	− 2	0.97
AE19-DS-MS3	457	451	0.148	0.94	450	0.156	3.665	− 3	0.94

* k_{VFA} values exceeding 10 were considered negligible due to the instantaneous metabolization of intermediate products

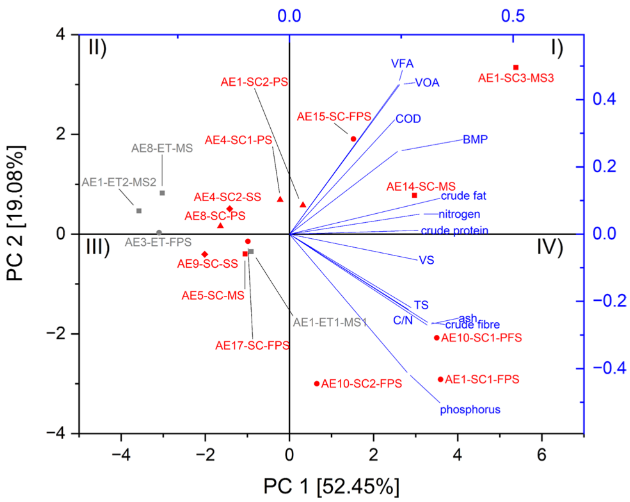


Fig. 5 Biplot for BMPs and substrate properties; sample names as per Table 1; rectangles: MS; circles: FPS; triangles: PS; rhombi: SS; gray: storage in ET (external storage) and indication of quadrant

the effects on the full-scale operation of BPs with different substrate qualities were determined using the kinetic parameters of the first-order one-step model [48].

3.3 Principal component analysis (PCA) between BMP and substrate properties

PCA is used to reduce the dimensionality of large datasets containing different variables and to increase interpretability while minimizing information loss [64]. Figure 5 shows a biplot where the substrate properties and BMPs are the variables. The samples from AE19 were excluded because its husbandry system differs from those of the other enterprises and comparability was not justified. PC1 (PC2) represented 52.45% (19.08%) of the variances in the dataset. Regarding the variables, N and protein charged PC1 to the same extent due to the analytical method of protein. This was also reflected in the correlation matrix (Appendix Figure 7), with r = 0.99 between these two parameters. The VFA and VOA also affected PC1 and PC2 similarly. Given these examinations, the same parameters were determined using two methods. The VOA were determined within the context of VOA/TIC determination according to the Nordmann method, where sulfuric acid consumption is measured to estimate the concentration of acetic acid equivalents in each analyzed sample [65]. The individual C2–C6 carboxylic acids were determined within VFA determination; they can be reported as a sum parameter, as is the case here [66]. Therefore, VOA determination can also be used to assess pig slurry as an AD substrate. In addition, ion chromatography offers deep insights into the acid spectrum and is used, for example, to monitor BPs and determine the accumulation of propionic acid or its ratio to the present acetic acid [67, 68].

For PC1, the parameters crude fat, crude fiber, and ash content had the highest positive correlation. PC1 did not have a negative correlation with any parameter. Regarding PC2, the VFA, VOA, and COD concentrations had the highest positive correlation, whereas phosphorus, ash content, crude fiber, the C/N ratio, TS, and VS had negative correlations.

BMP showed moderate correlations with the VOA (r = 0.560) and VFA (r = 0.621). This was remarkable because according to VDI 4630 [26], the VS content was corrected to include the VFA organic content lost during TS analysis (sample drying) in the specific BMP. A strong correlation (r = 0.718) was observed for crude fat. Due to the high CH_4 potential and CH_4 content of this macronutrient, low concentrations were assumed to have a substantial influence on the overall BMP [61]. However, difficulties arose during the analysis and subsequent evaluation of the Weender parameter crude fat. Here, a value of 0 was assumed for samples that were below the detection limit of 0.1% FM. Regarding the relationship between the BMP and micronutrient supply of the tested substrates, no conclusions could be drawn from the experimental setup, as all BMP tests were conducted using a well-balanced, micronutrient-sufficient inoculum [37, 69].

The BMP (sample) distribution in the biplot shows four groups in each quadrant. Alongside high BMPs, positive indications for PC1 and PC2 were observed at AE1-SC3-MS3, AE1-SC2-PS, AE14-SC-MS, and AE15-SC-FPS. Quadrant I contained VFA, VOA, COD, crude fat, crude protein, and N alongside high BMPs. This was meaningful because these were identified as value-giving parameters regarding the BMP. The PCA results suggested that the presence and concentration of VFA, VOA concentration (determined in the context of VOA/TIC analytics), crude fat, VS, and the C/N ratio were indicators for high or low BMPs for pig slurry.

3.4 Effects of degradation kinetics on operation of commercial-scale plants

Four clusters of samples in the PCA biplot showed different values for the kinetic parameter of the one-step model. For groups one and two, the average first-order kinetic constants were 0.12 and 0.05 day^{-1}, respectively. A lower kinetic parameter value of 0.04 day^{-1} was determined for group three. Group four showed a kinetic parameter value of k = 0.06 day^{-1}. Hence, the effects of substrate quality were analyzed using exemplary kinetic constants for slow degradation kinetics ($k1 = 0.04$ day^{-1}), moderate degradation kinetics ($k2 = 0.08$ day^{-1}), and fast degradation kinetics ($k3 = 0.12$ day^{-1}). Kafle and Kim [70] conducted BMP tests on pig manure with a TS content of 7.5% FM at an ISR ratio of 1. The determined first-order one-step kinetic constant was $k = 0.045$ day^{-1} at $BMP_{max} = 270.3$ L kg^{-1} COD, which was between $k1$ and $k2$. Sun et al. [71] found faster kinetics ($k = 0.377 \pm 0.006$) for pig slurry with a TS content of 5.1% FM at an ISR ratio of 2 in a batch assay; this value exceeded the first-order constants determined in the present study. However, this kinetic parameter value was determined in the context of $BMP_{max} = 490.6 \pm 1.9$ L kg^{-1} VS.

Hülsemann et al. [72] compared biological efficiency assessment methods and their application to full-scale BPs. The investigation was conducted based on data from Germany's Biogas Measurement Program III and were used in the current study to derive representative configurations of agricultural BPs [73]. The defined plant types were a small manure-based BP (BP1) and moderate- and large-sized BPs using energy crops and manure (BP2 and BP3, respectively). One plant of each type was selected from a database that was also used by Stürmer et al. [74] for an investigation set in the Muensterland region. The exemplary plants are described in Table 5.

The daily biogas production of pig manure in steady state under assumptions of TS = 6%, VS = 65% FM, and BMP = 170 L kg^{-1} VS was calculated using Eq. 11 and the substrate (pig slurry) quantity for each BP (Table 5). This approach was chosen to reflect a realistic BMP based on the results in Sect. 3.1. No information was obtained about the slurry types used in the BPs; BP3 was assumed to use several qualities of pig slurry, as its daily amount of pig slurry exceeds the usual amounts provided by single farms. Moreover, higher BMPs tend to occur in combination with fast degradation kinetics, and only the influence of the latter was to be determined. Three theoretical HRTs oriented toward the real HRTs (Table 4) for the existing plants were investigated to quantify the influence of HRT variations on the BMP. The daily biomethane production from the feeding of pig slurry in each BP is given in Table 6. Given the BMY_{FS} for each scenario, an energy content of 9.97 kWh m^{-3} for CH_4, and the CHP efficiency specified in Table 4, the effects of the investigated substrate degradation kinetics and HRT variation on revenue were determined by calculating the electricity generation over an operating period of 20 years (8760 full-load hours per year). Based on this, the total revenue for the use of pig slurry as a substrate was

Table 5 Representative agricultural BP concepts and characteristics for Muensterland region, Germany with *BP*, biogas plant; *HRT*, hydraulic retention time; *CHP*, combined heat and power plant

Parameter	BP1	BP2	BP3
Type (-)	Small BP using manure	Moderate-sized BP using energy crops and manure	Large BP using energy crops and manure
HRT (day)	100	93	99
CHP capacity (kW$_{el.}$)	75	630	1267
CHP efficiency (%)	39	41	40
Remuneration (€ kWh^{-1})	0.2310	0.2099	0.2099
Feeding of pig slurry (t day^{-1})	7	15	46
Feeding of cattle manure (t day^{-1})	7.5	3	7
Feeding of poultry manure (t day^{-1})	-	1.5	-
Feeding of maize silage (t day^{-1})	-	22	42
Feeding of rye silage (t day^{-1})	-	2.5	-
Feeding of grain (t day^{-1})	-	-	21

Table 6 Daily biomethane production in steady state (BMY_{FS}; m3 day^{-1}) for BP1, BP2, and BP3 and difference in overall revenue ($\Delta_{revenue}$) from AD of pig slurry relative to base scenario ($HRT = 95$ d and $k = 0.08$ day^{-1}) with BP: biogas plant

Scenario		BP1		BP2		BP3	
k(day^{-1})	HRT (day)	BMY_{FS} (m^3 day^{-1})	$\Delta_{revenue}$ (€)	BMY_{FS} (m^3 day^{-1})	$\Delta_{revenue}$ (€)	BMY_{FS} (m^3 day^{-1})	$\Delta_{revenue}$ (€)
0.04	70	34.2	−44,696	73.3	−91,491	224.7	−273,729
	95	36.7	−28,012	78.7	−57,341	241.4	−171,556
	120	38.4	−17,082	82.3	−34,966	252.4	−104,615
0.08	70	39.4	−10,722	84.4	−21,949	258.8	−65,667
	95	41.0	-	87.9	-	269.5	-
	120	42.0	6676	90.1	13,666	276.2	40,887
0.12	70	41.5	3011	88.9	6164	272.5	18,443
	95	42.7	10,844	91.4	22,196	280.4	66,409
	120	43.4	15,624	93.0	31,982	285.2	95,687

determined by multiplying the individual plant revenue and the previously calculated total power production. In Table 6, $k2 = 0.08$ day^{-1} and $HRT = 95$ day are the base scenario from which the differences between scenarios ($\Delta_{revenue}$) were calculated.

BMY_{FS} varied with HRT. It also changed with the kinetic parameter k. With identical assumptions for the BMP, TS, and VS, the daily biomethane production between the BPs depended only on the HRT, k, and substrate quantity. Identical HRTs and kinetic parameters therefore led to the relationship between the daily biomethane production and substrate quantity. Among the different kinetic parameters, the effect of the HRT weakened with an increase in k. For BP1, an increase in HRT from 95 to 120 days at $k1 = 0.04$ day^{-1} led to a 4.54% increase in BMY_{FS}, whereas an increase of only 1.71% was observed at $k3 = 0.12$ day^{-1}. This also applied to HRT reduction. Here, BMY_{FS} was less sensitive to HRT reduction at $k3 = 0.12$ day^{-1}, decreasing by only 2.80%, whereas a 6.93% reduction was seen at $k1 = 0.04$ day^{-1} when HRT was reduced to 70 days. Furthermore, an increase in degradation kinetics, such as from $k2 = 0.08$ day^{-1} to $k3 = 0.12$ day^{-1}, resulted in a higher increase in BMY_{FS} than an HRT increment from 95 to 120 days. For the BMY_{FS} to be equal at $k3 = 0.12$ day^{-1}, HRT should be 143 days at $k2 = 0.08$ day^{-1}. With increases in substrate quantity and CH_4 production, the difference in the BPs' overall revenue varied between scenarios. For example, a decrease in the kinetic parameter to $k1 = 0.04$ day^{-1} reduced the revenue of BP3 by € 171,556. With the HRT reduced at the same time, this reduction increased to € 273,729. Revenue could be increased by € 66,409 by setting $k3 = 0.12$ day^{-1} and keeping HRT constant.

4 Discussion

In Germany, pig slurry is usually collected under the barn and stored for a certain time. When the storage capacity under the barn is reached, the suspension is transferred to an external tank with a larger volume. Then, the slurry is utilized as fertilizer. However, agricultural enterprises must maintain sufficient storage capacity to store all the slurry produced in autumn/winter, where field application of slurry (as fertilizer) is neither allowed nor meaningful [75]. Therefore, they have large storage facilities, and slurry remains in tanks for several months. Without any incentive for livestock farmers, such as profit sharing, equity interest in the BP, or policy measures, the available substrates are likely to be of lower quality in terms of BMP; a 39.5% decrease in the BMP of FPS from SCs to ETs was previously reported [24]. The current study included samples from intermediate and external storage facilities (AE1 and AE8). At AE8, a 42.87% reduction in BMP from the SC to the ET was observed. AE8-ET-MS contained slurry from a farrowing stable, which tends to have low BMPs, VS (% TS), and VS due to VFA [25]. AE1 has different production stages, leading to a mixed ET sample (containing PS, SS, and FPS); thus, drawing a general conclusion was difficult. Furthermore, ET1 and ET2 contained either the thick or thin phase of sedimented slurry, and the FPS from this farm was a thickened phase. Nevertheless, the VS-specific BMP of the thick phase from ET1 was three times higher than that of the thin phase from ET2. Due to the higher DM content of ET1, the FM-specific CH_4 potential was 3.5 times higher. Substrate degradation could be assumed to have already occurred because of the significantly higher BMPs of the slurries from the SCs of this enterprise.

The AE19 samples contained SS and PS and showed high BMPs. This was ascribed to the adopted dung removal system. A DS enables continuous removal of slurry and its cooling beneath the barn [76]. The constant removal of slurry facilitates a steady flow through an external sedimentation pit, resulting in a thin phase (BMP = 457 ± 35 L kg^{-1} VS) and a thick phase (BMP = 280 ± 4 L kg^{-1} VS). This approach is highly recommended for supplying BPs with high-BMP substrates.

Substrate quality can also be improved through the individual collection of cleaning water and excrement or the use of constructional feces–urine separation systems, where excrements are not gathered as a mixed suspension with a low TS content. At a TS content of approximately 25.4%, a mean BMP of 275 L kg^{-1} VS was determined for feces from fattening pigs, resulting in a high FM-specific BMP in the BP. The influence of high N concentrations (e.g., 9.03 g L^{-1}), which can inhibit continuous AD, had not been determined at the time of this study. [77] Moreover, advantages in terms of nutrient management can be expected.

Figure 6 shows the average BMP of the different slurry types and sampling points in this study compared to previously reported BMPs at different animal growth stages and approaches in manure management.

The range of values given in this study (minimum BMP at AE1-ET2-MS2 = 37 ± 1 L kg^{-1} VS; maximum BMP at AE19-DS-MS3 = 457 ± 35 L kg^{-1} VS) coincides with the findings of previous studies. However, the average values calculated for the individual slurry types appear to be lower than in previous studies, particularly in comparison to Gopalan et al. [23]. One explanation for this could be that the samples taken by Gopalan et al. [23] originated from barns (except for one) using flush system on a daily basis which results in fresh samples. This is supported by higher VS values (% of TS) and the higher presence/concentration of VFA. A practical realization of this removal frequency is only the case for AE19 in the sampled barns, which is also reflected in the observed BMPs. Nevertheless, a lower BMP is confirmed for sow slurries (dry sow slurry; farrowing

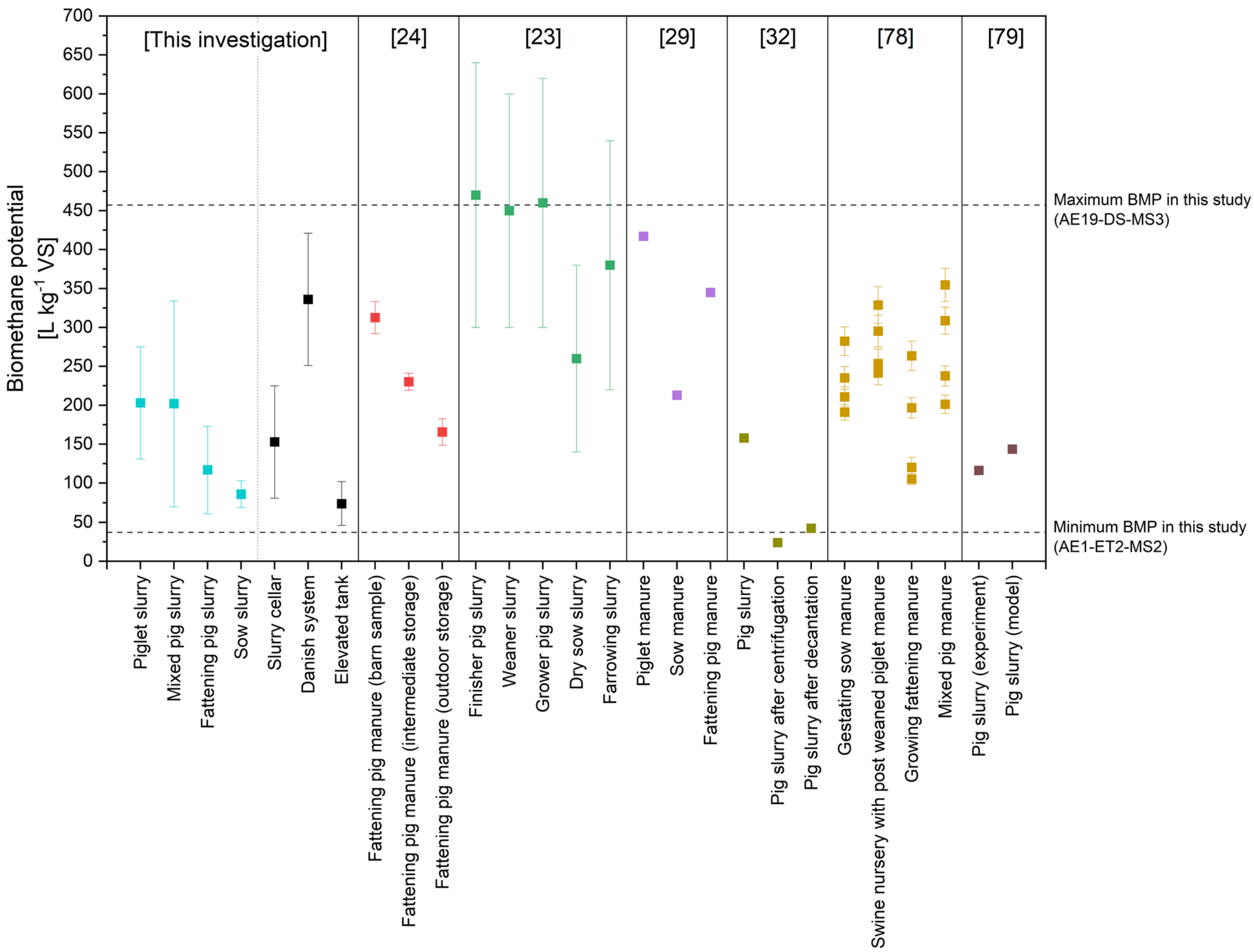


Fig. 6 Average biomethane potential and standard deviation (indicated by upper and lower whisker where applicable) divided by slurry and storage type in comparison to previous results [23, 24, 29, 32, 78, 79]

slurry) in comparison to fattening pigs or piglets. In this regard, the results of this study are also in close accordance with the results of Arhoun et al. [32], Winkler et al. [79], and Hilgert et al. [24]. The reduction of the BMP from intermediate samples (slurry cellars [SCs]) to outdoor-storage samples (elevated tanks [ETs]) found in this study can also be observed in the works of Hilgert et al. [24] in which they investigated the slurry from fattening pigs. Additionally, the results of Nardin and Mazzetto [29] confirm the established order in relation to the BMP of pig slurry types in this study.

The PCA result suggested that the presence of VFA is an indicator for the BMP. Similar findings were obtained by Hilgert et al. [24], who found a reduction in VFA from intermediate to external storage, which they associated with a longer storage period based on the results of Gerardi [80] and Franco et al. [81]. The authors stated that substrate degradation in the form of VFA conversion to acetate, CO_2, and H_2 via acetogenic microorganisms results in CH_4 emissions, which was confirmed by the determined BMPs and corresponding substrate properties in the present study. Thus, in practice, the presence and/or concentration of VFA can be used to assess premature substrate degradation and/or substrate quality, respectively. Additionally it was found that DM content is highly affected by storage time, showing a reduction of 10% at a storage duration of 20 days for swine manure [82]. In addition to the VFA content, the crude fat content, VS, and C/N ratio are meaningful parameters for assessing pig slurry, as confirmed by Gopalan et al. [23] regarding the VS content.

Among other aspects, the modeling results indicated that substrate degradation was the rate-limiting step. This can be prevented, for example, through pretreatment measures or the use of enzymes [49, 83, 84]. Through modeling, the influence of different degradation kinetics can be investigated based on a first-order one-step model with hydrolysis as the rate-limiting step. The calculated daily steady-state CH_4 production using pig slurry via AD in three large-scale plants showed that large differences occurred due to variations in degradation kinetics. For example, gas production using pig slurry in a small manure-based BP varied from 36.7 to 42.7 m^3 day^{-1} at the same HRT. As for plant profitability throughout the operating period, additional (decremental) revenue of € 10,844 (€ 28,012) could be achieved by increasing (reducing) the kinetic parameter relative to moderate kinetics. With higher substrate usage, these values accordingly increased, as shown by the results of BP3, whose revenue declined by € 171,556 with reduced kinetics. Considering the investment costs of the compared BPs (approximately € 0.5 million for BP1, € 1.5–2 million for BP2, and over € 2 million for BP3), kinetics improvement can influence economic efficiency, but it is not the only factor for successful plant operation. Degradation kinetics are improved through good substrate management, as with the BMP and TS/VS content. Therefore, in addition to the quantified influence of kinetics, BMP and TS/VS must be considered in general assessments of plant operation. Furthermore, the determined kinetic parameters in this study will be used in future research to investigate BP networks, which is currently being prepared and are therefore a valuable result of this study. This concept offers higher total profits in comparison to individual solutions with biomethane upgrading plants at each BP [85]. The obtained kinetic constants and described methodology for estimating BMY_{FS} were used to determine the biomethane production of several BPs with different substrates. Based on this, a BP network with different utilization paths (e.g., CHP units, use of biogas in industries, or the upgrade of biogas to biomethane and its utilization as fuel) will be simulated and evaluated in terms of economic efficiency.

The conversion of agricultural waste like pig slurry to biomethane facilitates circular economy principles by providing energy from waste and recycling nutrients back into agricultural systems, thus minimizing environmental impacts while enhancing resource efficiency [86]. For the practical application of pig slurry as a substrate for AD, good slurry management plays a crucial role in enhancing resource circularity by maximizing methane yields while minimizing waste and nutrient loss. This includes reducing storage times; for example, slurry extracted after one fattening interval can be obtained from intermediate storage and instantly used for AD. Storage times can be reduced further using a Danish housing system, where manure is constantly removed from the stable, supporting a more closed-loop system where organic waste is rapidly converted to energy and nutrient-rich digestate. With a BP on the site of the agricultural enterprise, a direct supply can be realized; otherwise, manure can be stored for a short time until the typical volume of a slurry tanker is reached. Another advantage of the DS is slurry cooling, which promotes substrate quality. In addition to the DS, the use of a feces–urine separation system for dung removal can enhance substrate quality for AD. A further increase in substrate quality in current dung removal systems can be achieved through slurry sedimentation. This increases the TS content, and higher FM-specific BMPs can be achieved in BPs [26]. This approach should be implemented and validated in practice, particularly the quantities provided by the agriculturalist, possible emptying cycles (depending on barn size), and the yield increase achieved. In addition, reasonable co-substrates with high C concentrations should be selected for the AD of pig slurry to compensate for the unfavorable C/N ratio of the substrates studied. Another point relates to the selection of pig slurry for AD from the perspective of BP operators. Available slurries should be evaluated regarding their VS, crude fat, VFA, and C/N ratio; only promising slurries should be used in BPs. In this study, PSs and MSs tended to show higher VS-specific BMPs than SSs and FPSs.

In addition to greenhouse gas mitigation and the production of biomethane, the utilization of pig slurry in BPs offers benefits in terms of resource circularity and ancillary services from an energy system point of view. The digestate produced through AD reduces dependance on artificial fertilizers and also recycles essential nutrients like nitrogen and phosphorus into agricultural systems. Technological solutions for processing digestate into composts, biocarbon, nutrient-rich fractions, or fertilizer granules can further promote the implementation [87, 88].[89] This aligns with circular economy goals by transforming waste into a resource that sustains agricultural productivity and reducing environmental impacts [90]. The transportation of substrates from individual farm sites to BPs is seen as an important component in bioeconomy for the current biogas sector in Germany as well as developing markets. A case study for Croatia for example showed that an economic operation is not possible with a transport distance for animal manure of more than 60 km [91]. The simulations carried out by Topić et al. [92] on possible substrate mixtures, taking into account the transportation costs and including the substrate properties (e.g., individual BMP, DM, density) for different substrates, resulted in a maximum transportation distance for pig slurry of 25 km and 91 km for cow slurry, under which economic operation with this feedstocks is possible. This further stresses the importance of carefully implemented bioeconomy policies.

The European Renewable Energy Directive (RED II) [93] and its implementation within the German legislation [94] was considered a driver for improved manure utilization in BPs and biomethane employment in the transportation sector. With rising GHG quota prices, the share of manure in the substrate mixture of BPs is increased, while the specific GHG emissions are reduced. However, it is criticized that the current policy predetermines that the GHG reductions in agriculture are instead counted toward the transportation sector. Additionally, Magnolo et al. [95] highlighted that the current standards applied by the RED II do not cover the entire life cycle of anaerobic digestion of manure. Therefore, it is recommended to implement supportive policies to facilitate investment in digesters and digestate storage, to provide simplified permitting procedures, and to enable cooperative, logistically optimized plant concepts. [96] Furthermore, as one out of five proposed measures for future German biogas policy, Thrän et al. [97] recommend to focus the support schemes on GHG reduction referring to the biofuel sector.

5 Conclusions

The results of this study underscored the variability of the BMP from organic residue, such as pig slurry, ranging from 86 ± 17 L kg^{-1} VS for sow slurry to 203 ± 72 L kg^{-1} VS for piglet slurry. The main conclusions from this substrate evaluation are:

Regarding substrate characterization, the concentrations of VS, crude fat, and VFA and the C/N ratio were determined to be highly influential parameters that can be used to assess the quality of pig slurry in terms of the utilization of energetic potential via AD. By an improved manure management and easy techniques, such as slurry sedimentation, the substrate quality can be further improved. According to the application of the modeling results, in addition to the ultimate BMP, the degradation kinetics of substrates considerably influence CH_4 production during continuous steady-state AD in full-scale BPs. A daily biomethane production from pig slurry at a small scale BP using only manure as a substrate was 42.7 m^3 day^{-1} with fast degradation kinetics, whereas 36.7 m^3 day^{-1} was achieved with slow degradation and the same HRT and BMP.

By exploring the factors influencing the substrate quality of pig slurry and its effects in continuous operation, this work contributes to the following Sustainable Development Goals defined by the United Nations in 2015: (no. 7) Affordable and Clean Energy, (no. 12) Responsible Consumption and Production, and (no. 13) Climate Action. In this way, biomethane, as a renewable and circular resource, plays a crucial role in advancing energy independence and reducing GHG emissions across all economic sectors.

Appendix

Table 7 Additional analysis for substrate characterization

Sample	Nitrogen (% of FM)	Phosphorus (% of FM)	Crude Ash (% of FM)	Crude protein (% of FM)	Crude fat (% of FM)	Crude fiber (% of FM)
AE1-ET1-MS1	0.3	0.2	1.2	2.0	0.1	0.5
AE1-ET2-MS2	0.2	0.0	0.7	1.4	< 0.1	< 0.1
AE1-SC1-FPS	0.5	0.6	2.5	3.1	0.3	1.3
AE1-SC2-PS	0.3	0.1	1.0	2.1	0.2	0.8
AE1-SC3-MS3	0.5	0.2	1.6	2.9	0.5	1.1
AE3-ET-FPS	0.2	0.1	1.1	1.4	< 0.1	< 0.1
AE4-SC1-PS	0.2	0.1	0.8	1.1	0.3	0.7
AE4-SC2-SS	0.2	0.2	0.9	1.1	0.3	0.5
AE5-SC-MS	0.3	0.2	1.4	1.9	0.2	< 0.1
AE8-ET-MS	0.3	0.0	0.9	1.7	0.1	< 0.1
AE8-SC-PS	0.3	0.1	1.0	1.8	0.1	0.5
AE9-SC-SS	0.2	0.1	0.9	1.4	< 0.1	0.4
AE10-SC1-PFS	0.6	0.3	2.0	3.7	0.4	1.4
AE10-SC2-FPS	0.1	0.4	1.7	0.9	0.2	1.5
AE14-SC-MS	0.6	0.2	2.0	3.6	0.3	0.8
AE15-SC-FPS	0.4	0.2	1.5	2.5	0.3	0.5
AE17-SC-FPS	0.4	0.2	1.3	2.5	0.1	0.5
AE18-SC1-PS	0.6	0.6	3.1	3.8	0.6	1.8
AE18-SC2-SS	0.4	0.8	3.4	2.7	0.4	1.1
AE19-DS-MS1	0.4	0.4	1.7	1.6	0.6	2.2
AE19-DS-MS2	0.4	0.3	1.3	0.9	0.6	0.7
AE19-DS-MS3	0.3	0.1	0.5	0.1	< 0.10	0.0

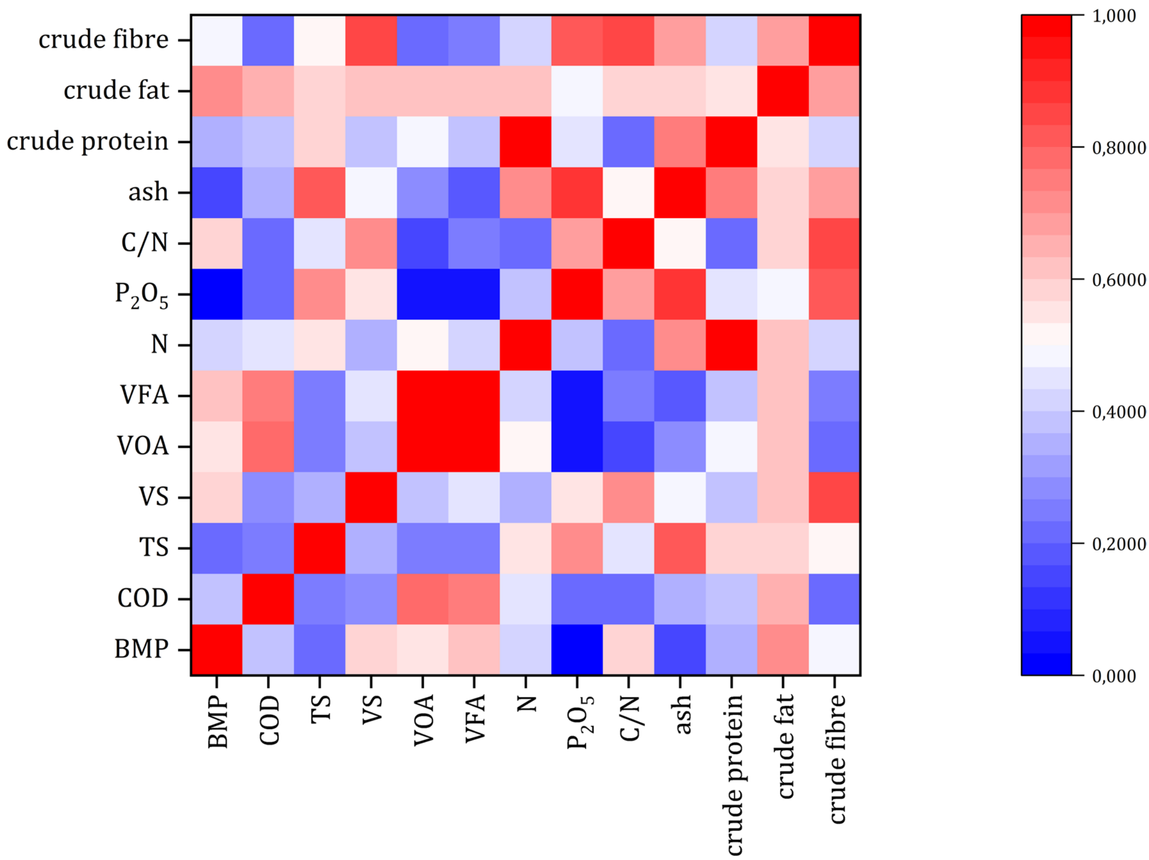


Fig. 7 Correlation matrix; C/N, carbon-to-nitrogen ratio; VFA, volatile fatty acids; VOA, volatile organic acids; TS, total solids; VS, volatile solids; COD, chemical oxygen demand; BMP, biomethane potential

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Declarations

Competing interests The authors declare no competing interests.

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