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The Influence of CO_2 Injection into Manure as a Pretreatment Method for Increased Biogas Production

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Abstract: Manure is considered a by-product or organic waste in cattle, pig, chicken or other animal breeding farms, which can be a valuable product as compost or feedstock for biogas production. The production of biomethane from biogas always copes with the formation of carbon dioxide (CO_2) as a by-product. This CO_2 may be recycled through the feedstock as a pretreatment to maximize homogeneity, and improve biogas yield and biogas quality. The CO_2-pretreatment process of cow manure (CoM), chicken manure (ChM) and pig manure (PM) was performed in the continuously fed agitated reactor at 25 °C temperature and ambient barometric pressure. Biogas yield and composition exploration were performed in an anaerobic continuous feeding digester with controlled mesophilic (37 °C) environmental conditions. The CO_2 pretreated PM, CoM and ChM yielded 234.62 ± 10.93 L/kg$_{VS}$, 82.01 ± 3.19 L/kg$_{VS}$ and 374.53 ± 9.27 L/kg$_{VS}$ biomethane from feedstock volatile solids, respectively. The biomethane yield from CO_2 pretreated CoM, ChM and PM achieved was higher over untreated manure by +33.78%, +28.76% and +21.78%, respectively. The anaerobic digestion process of tested feedstocks was stable, and the pH of the substrate was kept steady at a pH of CoM 7.77 ± 0.02, PM 8.07 ± 0.02 and ChM 8.09 ± 0.02 during all the experiment. The oxidation-reduction potential after pretreatment was within the optimal range (−255 ± 39.0 to −391 ± 16.8 mV) for anaerobic digestion. This process also had a positive effect on the energy generated from the feedstock, with ChM showing the greatest increase, from 2.38 MJ/kg to 3.06 MJ/kg.

Keywords: biomass treatment; carbon dioxide injection; feedstock; anaerobic digestion; droppings; biomethane

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1. Introduction

In recent years, the development of international trade and the demand for livestock-sourced foods has been increasing rapidly, resulting in the rapid expansion of large-scale intensive breeding farms. Livestock organic waste can become a valuable product as compost or feedstock for biogas production if it is managed correctly. Usually, manure is considered a by-product or organic waste in cattle [1–3], pig [4,5], chicken [6,7] or other animal breeding farms. This leads to the idea that it is not a residue, but rather that manure should be considered a valuable product because of its nutrient [8] and biogas potential [9]. Considering that manure may be a source of renewable energy when properly treated makes it essential to improve manure-handling technologies.

Due to the amount of biogas produced and the possibility of applying a closed-loop organic farming model, anaerobic digestion (AD) is one of the most suitable technologies for treating agricultural organic waste such as manure [10], green organic waste [11] and unconditional-expired products [9]. Manure utilization and environmental pollution can both be solved by AD in biogas plants [12]. AD produces nutrient-rich digestate in addition to methane (CH_4) production and electricity generation. Compared to raw untreated manure, digestate contains nitrogen (N) and phosphorus (P) compositions with higher availability for crops. The mineralization of organic matter during biogas production is more intense than in the field [13] and presents higher sorption rates, primarily because the form and proportion in which it is present has been altered during the AD process [14,15].

Currently, the fixation and conversion of carbon dioxide (CO_2) is an emerging area of interest [16]. Various technologies for raw biomass feedstock pretreatment, such as thermal [17], chemical [18], biological [19] and physical [20] are available. The production of biomethane from biogas always involves the formation of CO_2 as a by-product, which ranges from 15 to 60% of the amount of biomethane produced [21]. This by-product CO_2 may be recycled through the feedstock supplied to the bioreactor as raw material. The use of biological-origin CO_2 gained from the biomethane purification process as a carbon source for biomass fermentation might be a concept for reusing CO_2 while minimizing its emissions to the atmosphere [22]. The further implementation of closed-loop CO_2-based processes still requires significant research efforts to result in robust and cost-competitive technologies [23]. Intensification of feedstock pretreatment processes with carbon dioxide is performed to maximize homogeneity (structure), improve biogas output and improve biogas process kinetics (reduce feedstock retention time in the bioreactor).

As an alternative to the use of chemical solvents for biomass fractionation or pretreatment, use of CO_2 could be considered as a more sustainable option [23]. Today, the development of new biomass-based technologies is considered one of the most important factors driving our society toward a more sustainable future due to their applications and benefits. By developing biotechnologies, greenhouse gas emissions are expected to be reduced, and natural resources will be used more efficiently [9].

According to Fu et al. [24], in situ bioconversion of CO_2 to methane (CH_4) can take place in three pathways: directly through hydrogenotrophic methanogenesis, indirectly through homoacetogenic acetate formation followed by acetolactic methanogenesis or directly via electron transfer. The direct hydrogenotrophic methanogenesis pathway is driven by hydrogenotrophic methanogenic archaea using H_2 as an electron donor to directly reduce CO_2 into CH_4. The indirect pathway contains CO_2 conversion to acetate and then its degradation to CH_4 by acetolactic methanogenic archaea [24].

Several studies have shown promising data when CO_2 injection is used as a pretreatment method in fermentation processes. CO_2 can engage in multiple biochemical reactions of the AD process, such as the carbonic acid equilibrium [25]. The final step (methanogenesis) involves the conversion of simple organic molecules, such as short-chain fatty acids, along with CO_2 and hydrogen into biogas. This step can therefore be stimulated using methanogens, and conditions can be provided for CO_2 to be converted to biogas. As a consequence, it is possible to stimulate this step and to provide conditions for the conversion of CO_2 to biogas using methanogens. Alimahmoodi and Mulligan [26] studied the effects of adding CO_2 to the influent in a laboratory-scale upflow anaerobic sludge blanket reactor. The influent storage tank was maintained at a pressure of 1.01×10^5 Pa to increase CO_2 dissolution. It was estimated that 69–86% of the CO_2 dissolved could be utilized in the process, measuring a 25% increased specific CH_4 yield when continuously injecting CO_2 at a load rate of 0.49 m^3/d into the 0.85 m^3 volume first-stage reactor of a two-phase anaerobic digestion process at 25 °C. Salomoni et al. [27] found that an average amount of 229 L/d of CO_2 was absorbed by injection in the first-phase feedstock pretreatment reactor, equivalent to 46% of input. Bajón Fernández et al. [28] found that CH_4 production increased by up to 13% and 138% for food waste and sewage sludge, respectively, when batch anaerobic digesters were enriched with CO_2.

Circulating CO_2 through feedstock as the pretreatment method increases hydrolysis efficiency, which results in acidogenesis and pH degradation [29]. The acids formed during hydrolysis accumulate in the reactor and degrade the pH as well as the solubility of CO_2 in the substrate [30]. The acids formed during hydrolysis may increase methanogenesis biogas yield [25]. Part of the CO_2 generated during hydrolysis dissolves spontaneously in the substrate, dissolving into carbonic acid ($HCO_3{}^-$) and, at pH > 8.5, further dissociating into carbonate ($CO_3{}^{-2}$) and an H^+ proton. During dissociation, H^+ protons are released and the pH of the medium increases. Muntau et al. [25] examined the evolution of the pH value on CO_2-injected municipal sludge pretreatment. This research did not reveal any significant deviations between CO_2-pretreated and raw sewage sludge. The pH value during the period of 453 days remained stable at 7.5 ± 0.1. Nevertheless, they concluded that acidification caused by increased dissolved CO_2 concentrations can be excluded due to the buffering properties of the sludge.

Once dissolved, CO_2 can also react with aqueous ammonia, which leads to additional CO_2 dissolution and the formation of ammonium aerated compounds, which are industrially used in processes aimed at capturing CO_2 to reduce carbon dioxide [31]. In reaction products, ammonium salts of bicarbonate, carbamate and carbonate are the most likely to occur, the relative abundance of which largely depends on the pH and the free ratio of NH_3 to absorbed CO_2 [32].

Mixed anaerobic population (e.g., methanogenic bacteria, acetogenic bacteria, acidogenic bacteria, *Actinobacteria* and *Crenarcheota*) perform gas fermentation through different CO_2 fixation pathways: the Wood–Ljungdahl, the reductive Tricarboxylic acid cycle, the reductive acetyl-CoA, the dicarboxylate-4-hydroxybutyrate and the 3-hydroxypropionate bicycle, depending on the microbial taxa [33]. Acetogenic bacteria (*Clostridium* and *Acetobacterium*) can be highlighted as the potential for the conversion of CO_2 to CH_4, since they are able to process alternating gas compositions with high metabolic efficiency [34].

Oxidation-Reduction Potential (ORP) is a useful tool for controlling anaerobic digesters as it provides an accurate measurement of oxidation-reduction reactions in an aqueous environment. ORP is used to monitor the microorganisms' activity and maintain favorable conditions for their growth in the anaerobic digestion system. If the ORP is too low, it may indicate that there is not enough oxygen present to support the microorganisms, which can result in reduced biogas production. On the other hand, if the ORP is too high, it may indicate that there is an excess of oxygen, which can be toxic to the microorganisms and also lead to reduced biogas production. ORP values in anaerobic digestion are within the −100 to −300 mV range [35]. The measure of ORP plays a significant role in determining the relationship between mandatory anaerobic bacteria and facultative anaerobic bacteria in microbial communities during anaerobic fermentation [36]. Vongvichiankul et al. [35] researched the ORP and pH reliance. The ORP and pH were related to the volatile fatty acids' (VFA) concentration and type of fermentation. When the pH values varied from 5.5 to 6.0, ORP values ranged from −300 mV to −130 mV. ORP can also serve as a monitoring indicator for anaerobic digesters, as CH_4 production primarily occurs at ORP values between −175 and −400 mV, while acidogenesis takes place at ORPs between −250 and −300 mV [35]. The research of Vongvichiankul et al. [35] shows that the optimal methanogenesis ORP is between −300 and −360 mV so that no oxidizing products (especially O_2) can enter the biogas reactor. The biogas production rate was higher in the butyric acid−type fermentation that occurred in the acidogenic phase than compared to mixed acid−like fermentation. The optimum ORP and pH during the methanogenesis phase were −335.63 ± 28.97 mV and 7.49 ± 0.24, respectively. Consequently, Vongvichiankul et al. concluded that the control of ORP and pH is critical in the production of biogas in anaerobic conditions [35].

To improve the efficiency of biogas production, it is especially imperative to choose the right value of ORP at the initial stage of fermentation. Su et al. [37] kept the initial value of ORP in the range from −400 mV to −300 mV, and then consistently maintained in the range from −230 mV to −180 mV. As a result, the production of acetic acid increased significantly, and the largest increase was 53%. There was also no obvious difference observed in biogas production when the pH was controlled between 5.5 and 6.7. The loading volume and ORP control had a more significant effect on biogas production, whereas the pH range had no obvious influence on biogas production.

Su et al. [37] performed research on citrus waste via biodegradation pretreatment and subsequent optimized fermentation. Scientists have concluded that the interaction of ORP, pH and loading volume affects the fermentation rate and type of acid production. A further Su et al. [37] in-depth study has shown that the increase in biogas correlates with the ORP ratio to pH value and the volume load, determined by the optimized fermentation process. It was decided that a study should be undertaken to find the relation between the CO_2 treatment, the pH and the ORP. For this research, cow (CoM), chicken (ChM) and pig (PM) manure were selected as feedstock to study the concept of CO_2 injection as a pretreatment method for biomass fermentation. Applying CO_2 injection as a feedstock pretreatment method with the main aim of increasing biogas plant productivity and yield was reviewed, and the result of the research is presented and discussed.

2. Materials and Methods

Raw manure (RM) feedstocks were placed in digesters until stable biogas yields and compositions were achieved. After the biogas yield from raw untreated manure is stabilized, the second part of the experiment is carried out. The second part comprises biogas yield and composition research performed in anaerobic continuously fed digesters with controlled mesophilic environmental conditions (37 °C). CO_2-pretreated manure is loaded into the same raw feedstock biogas digester until a stable biogas yield and composition are reached. CoM, ChM and PM were pretreated with CO_2 in a continuously fed, agitated and temperature-controlled pretreatment reactor. More details are presented in Section 2.1. The effectiveness of CO_2 pretreatment was evaluated by comparing the results of raw and pretreated feedstock. Analysis of biogas composition, methane concentration in biogas, biogas and biomethane yield and uniformity of the process was conducted in order to determine the effectiveness of the feedstock pretreatment process.

2.1. Feedstock Characteristics and Pretreatment

Three types of manure were selected as experimental feedstocks for this research. CoM was taken from a litterless industrial scale farm in the Kaunas region in the summer of 2021. PM was taken from a Raseiniai region farm in autumn 2021. The CoM and PM were liquid enough to use in the experiment without additional dilution. ChM was taken from a farm in the Raseiniai region, where chickens were kept on peat litter in the spring of 2021. The PM was diluted with tap water to up to 85% moisture (15% total solids [TS]) before use. Total solids and volatile solids (VS) contents were determined gravimetrically via drying at 105 °C and subsequent ashing at 550 °C. Total carbon (TC) was determined by ISO 10694:1995 [38]; total nitrogen (TN)—by EN 13654–1:2001 [39]. Table 1 shows the characteristics of raw untreated feedstocks used for pretreatment and digestion experiment.

Table 1. Characteristics of raw manure feedstocks used in the experiments.

Feedstock	CoM	ChM	PM
Total solid, %	7.42	37.75	7.5
Volatile solid, %	5.83	26.46	5.33
Total carbon, % in TS	34.3	26.8	28.9
Total nitrogen, % in TS	0.39	2.36	0.691
Carbon/nitrogen ratio (C/N)	87.9	11.4	41.8

All the feedstocks were homogenized with an industrial blender and sieved through a 5 mm sieve to remove large particles and nonbiodegradable material that may come with the manure and affect the research results because of particle size. All the collected manure samples were stored in airtight containers of 20 L and stored in a refrigerator at 5 °C to be protected from environmental influences throughout the study.

The first pretreatment experiment was prepared using CoM as a feedstock. At the start of the experiment, the pretreatment reactor was loaded with three days' total cumulative feedstock at a weight of 1371 g CoM. The TS content in cow manure was 7.42% (Table 1) and dilution with tap water was not necessary. The further daily input to the pretreatment reactor in the continuous experiment mode consisted of 457 g of litterless cow manure. The retention time in the pretreatment reactor was set to three days. The volumetric and hydraulic organic loading rate (OLR) to the pretreatment reactor was set according to anaerobic digestion process parameters with OLR 1.4 kg VS/(m^3·d) with all tested feedstocks (Table 2). The OLR for the pretreatment reactor compared to the digester is high (OLR for CoM pretreatment is 8.86 kg VS/(m^3·d) because of its low volume. The continuous experiment of the anaerobic digestion with CoM took 49 days. Raw CoM was used until the stable biogas yield and composition were observed for three days. Later, the second part of the experiment started with CO_2-pretreated CoM. The biogas yield and composition were stable for seven days. ChM and PM experimental data are given in Table 2. The feedstock for the pretreatment reactor was prepared on the same day as the biogas reactor was fed.

Table 2. The daily feedstock characteristics for pretreatment reactor, digester load rate and experiment duration.

Characteristic	CoM	ChM	PM
Daily mass of the feedstock loaded in the digester, g	457	74.2	500
Water amount used for dilution, g	0	240.7	0
Stable biogas yield and composition research duration with raw feedstock, days	3	6	6
Stable biogas yield and composition research duration with CO_2-pretreated feedstock, days	7	11	9
Total biogas yield and composition research duration, days	49	80	56
Pretreatment reactor organic load rate, kg VS/(m^3·d)	8.86	14	8.88
Pretreatment reactor hydraulic load rate, kg/m^3	152	166	166
Digester organic load rate, kg VS/(m^3·d)	1.4	1.4	1.4
Digester hydraulic load rate, kg/m^3	24.1	28.5	26.3

Every following feeding material for experiments with ChM and PM was prepared by the same methodology, except that the ChM needed extra dilution with tap water in the amount of 240.7 g.

The pretreatment reactor was custom-made for research on gas injection to feedstock. The CO_2-pretreatment process for manure was performed in a continuously stirred gas-tight vertical cylindrical pretreatment reactor with a total volume of three liters (Figure 1).

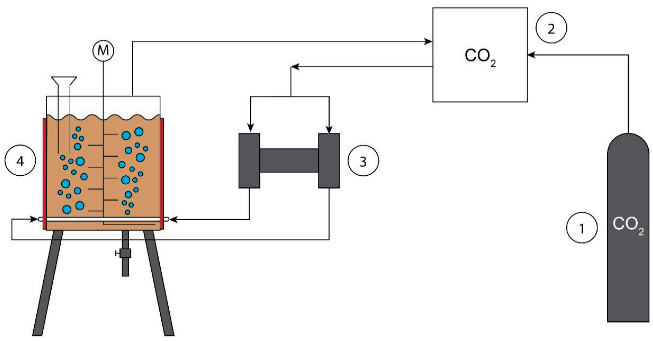

Figure 1. CO_2-pretreatment reactor technological scheme: 1–compressed CO_2 gas cylinder (200 bar) with pressure reducer, 2–Restek gas sampling bag, 3–precision gas pump, 4–pretreatment reactor with mechanical agitator, temperature control and gas injection tubes.

The manure pretreatment process technological scheme consists of a gas sampling bag (2), gas cylinder (1), gas circulation pump (3) and reactor (4). The 25-L (Restek, Bellefonte, PA, USA) gas sampling bag (2) was filled from a compressed CO_2 gas cylinder (1) (BIOGON® C, Linde) via a pressure reducer, and the system was prepared for continuous 24 h circulation. The feedstock was continuously circulated with 100% CO_2 via a precision gas pump (3) at a flow rate of 6.5 L/min from the Restek 25-L gas sampling bag with inlet and outlet valves. Atmospheric pressure was maintained in the pretreatment reactor tank. A lower mesophilic temperature of 25 ± 0.5 °C was maintained using thermostatic control and an electric heating pad. After 24 h of the pretreatment process, the bioreactor was gas-flushed with fresh CO_2 from the cylinder, and fresh CO_2 was injected into the gas sampling bag again. The feedstock retention time in the pretreatment process is 72 h. The injected CO_2 gas circulated in a closed cycle to determine the effect on CO_2-pretreatment dynamics in the long-term pretreatment experiment.

The top part of the pretreatment reactor (4) is made of polycarbonate, allowing us to see the agitating efficiency in the pretreatment process. The reactor (4) parts are sealed together with screws and O-ring gaskets to ensure anaerobic conditions. Reactor mechanical stirrer lower blades are designed to clean the bottom of the reactor (to prevent the formation of sediments). The stirrer is controlled via a time relay. The temperature was set and operated by a programmable logic controller and the pH of the substrate was measured daily. Integrated diffuser tubes are perforated with 1 mm holes and installed in the base of the bioreactor for closed-loop CO_2 gas circulation. In order to ensure anaerobic conditions and dispose of oxygen at the beginning of the experiment, the headspace of the pretreatment reactor gas was flushed with CO_2 gas from cylinder (1). The acidogenic fermentation occurrence was determined by hydrogen presence and concentration that was measured using an ETG biogas analyzer (ETG Risorse e Tecnologia S.r.l., Chivasso, Italy) in the off-gas after 24 h of continuous circulation.

Samples of the feedstock were weighed on electronic scales KERN EG4200-2NM (Kern&Sohn, Germany), measuring range 0–4200 g, accuracy ±0.02 g, resolution 0.01 g. The pH of the raw material and the pretreated samples were determined daily during each loading with a Hanna pH-213 m (Hanna Instruments, Smithfield, VA, USA) with a measuring range from 2.00 to 16.00, accuracy ±0.01, resolution 0.01. Analyses of the raw material's weight, temperature, pH and ORP were performed daily for the purpose of observing feedstock characteristics. In total, 49 measurements were made for CoM, 80 measurements were made for ChM and 56 measurements were made for PM.

2.2. Anaerobic Digestion Process

At the start of the experiment, digesters were filled to working volume with fresh CoM, ChM and PM inoculum from continuously operating laboratory continuous-flow stirred tank digesters. The inoculum was prepared by feeding separately the same CoM, ChM and PM to the digesters for 30 days before the experiment. This was done in the biogas laboratory at Vytautas Magnus University in Lithuania. The inoculum was sieved through a 5 mm sieve to remove large particles and nonbiodegradable material.

Raw CoM, ChM and PM was used in the first part of the experiment until stable daily biogas yield and composition were reached. In the second part, CO_2-pretreated CoM, ChM and PM was used until stable biogas yield and composition were reached. The biogas yield and composition experiment took place in the continuous feeding BTP-2 laboratory biogas reactor (Umwelt und Ingenieurtechnik GmbH, Dresden, Germany).

The laboratory digester system (Figure 2) consists of a 15-L glass vertical type reactor 1, with biomass heating mat and an electric mixer 3, a biogas drum type flowmeter 5 (Ritter Apparatebau GmbH & Co, Bochum, Germany) and a biogas storage bag 6. The biogas digester maintains a mesophilic 37 ± 0.5 °C temperature. The temperature and operation of the reactor mixing system are processed by a process controller 4. The agitation cycle and temperature of the biogas reactor substrate are controlled automatically. The agitation intensity was set at 60 s agitating with a 300 s resting period. The feedstock is loaded into the digester via inlet valve 9 and discharged from the digestate valve number 10. All data were collected and analyzed on a personal computer 8. The collected biogas was analyzed with an Awite Bioenergie GmbH AwiFlex (Germany) biogas analyzer 7. The gas analyzer measures methane (CH_4), carbon dioxide (CO_2), hydrogen sulfide (H_2S) and oxygen (O_2) in the biogas. For this experiment, CH_4 and H_2S concentrations were continuously monitored throughout the study. The CH_4 measurement range is 0–100%, accuracy ±3%, resolution of 0.1%; the H_2S measurement range is 0–3000 ppm, accuracy ±3%, resolution of 1 ppm. The pH of the raw material and the digestate was determined daily during each loading with a Hanna pH-213 m (Hanna Instruments, USA) with a measuring range from 2.00 to 16.00, accuracy ±0.01, resolution 0.01.

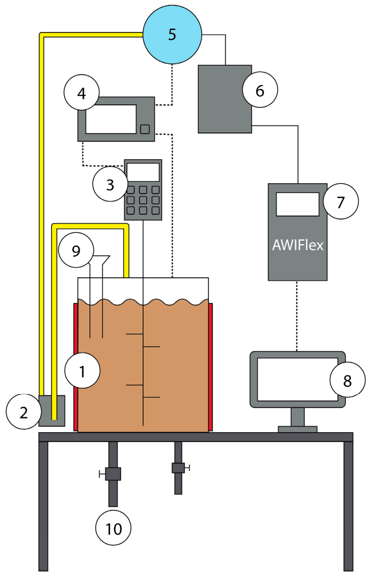

Figure 2. Scheme of the laboratory biogas digester. 1–digester with heating mat, 2–moisture from biogas collector, 3–reactor agitator controller, 4–data logger, 5–Ritter gas volume flowmeter, 6–biogas storage tank, 7–biogas analyzer, 8–personal computer for data analysis, 9–feedstock inlet, 10–digestate discharge valve.

For the observation of the anaerobic-processing process, several parameters are usually used, such as temperature, pH, organic load and hydraulic load. For the long-term CO_2 pretreatment study on CoM, ChM and PM, a pH and ORP analysis of the raw material was performed daily. During anaerobic processing, the pH has the greatest impact on the activities of the community of acidic and methanogenic microbes. Just as pH measures proton activity and assigns a value to the acidity or alkalinity of a system, ORP measures electron activity and assigns a value to the oxidizing or reducing nature of a system. It reflects a solution's tendency to either accept or donate electrons and affect the suitability of water for supporting life and its corrosiveness. Based on the ORP range, the authors defined as toxic, anoxic and anaerobic conditions, when ORP > 0 mV, −50 < ORP < −200 mV and ORP < −350 mV, respectively [38]. A Mettler Toledo ORP sensor was used for online ORP measurements, over the range of −500 to +500 mV.

The influence of feedstock pretreatment for anaerobic digestion was evaluated using the following indicators: intensity of biogas production, biogas yield from raw and pretreated feedstock (B_M), biogas yield from raw and pretreated feedstock total solids (B_{TS}), biogas yield from raw and pretreated feedstock volatile solids (B_{VS}) and energy value from raw and pretreated feedstock obtained at anaerobic conversion (e_M). The calculations were made using the following equations [19]: $B_M = b_{dt}/m$; $B_{TS} = b_{dt}/m_{TS}$; $B_{VS} = b_{dt}/m_{VS}$, where b_{dt} is the volume of produced biogas during the time interval dt, l; m is the mass of the sample, kg; m_{TS} is the mass of total solids of the sample, kg; and m_{VS} is the mass of volatile solids of the sample, kg. The most valuable component in biogas is methane, which indicates the energy value of the biomass obtained at anaerobic digestion (e_M). The energy obtained from the biomass is determined by the equation [19]: $e_M = B_M \cdot e_b$, where (e_b) is the energy value of biogas that depends on the methane concentration in the biogas, MJ/l. The energy value of the biogas is determined by the equation [19]: $e_b = 0.0353 \cdot C_{CH4}/100$, where C_{CH4} is the methane concentration in biogas, %.

3. Results and Discussion

3.1. CO_2 Pretreatment Influence on Feedstock pH and ORP

During the process of CO_2 pretreatment, continuous temperature was maintained, and the pH and ORP of the feedstock were measured daily (Table 3). The acidogenic fermentation occurrence was determined by hydrogen presence in the gas of the pretreatment reactor. The hydrogen concentration for ChM in feedstock pretreatment off-gas was 456 ± 15 ppm, in CoM was 245 ± 35 ppm and in PM was 823 ± 43 ppm.

Table 3. The influence of CO_2 pretreatment on feedstock pH and ORP.

Indicator	PM	CoM	ChM
pH of raw feedstock	8.24 ± 0.14	7.91 ± 0.1	6.33 ± 0.04
pH of pretreated feedstock	7.3 ± 0.04	7.25 ± 0.05	5.72 ± 0.09
Influence of pretreatment on feedstock pH, %	−11.4	−8.4	−9.6
pH of the digestate using raw feedstock	8.03 ± 0.02	7.79 ± 0.03	7.95 ± 0.05
pH of the digestate using pretreated feedstock	8.07 ± 0.02	7.77 ± 0.02	8.09 ± 0.02
Influence of pretreatment on substrate pH, %	0.42%	−0.26%	1.7%
ORP of raw feedstock, mV	−413.4 ± 12.8	−227 ± 25	54.2 ± 67.6
ORP of pretreated feedstock, mV	−391 ± 16.8	−313 ± 20	−225 ± 39

In the experiment on PM, before the pretreatment process, the pH of the raw feedstock was 8.24 ± 0.14, and after pretreatment the pH decreased to 7.3 ± 0.04. In a study on CoM, the pH value in the raw material was 7.91 ± 0.1 and after pretreatment decreased to 7.25 ± 0.05. In terms of the third raw material, ChM, this feedstock had a pH of 6.33 ± 0.04 before treatment, and after pretreatment with carbon dioxide, it became even more acidic with a pH value of 5.72 ± 0.02 [40].

Manure consists of organic components with different hydrolysis rates and biodegradability. VFAs are significant intermediate products of anaerobic digestion and can serve as indicators of hydrolysis [41]. The greatest influence of pretreatment on raw feedstock pH was achieved on pig manure. The pH of the pig manure decreased by 11.4%, while the influence of CO_2 pretreatment for raw chicken manure pH was 9.6%. The lowest influence of pretreatment on feedstock pH was achieved on cow manure at 8.4%. The first factor used to assess the effectiveness of CO_2 pretreatment is the pH decrease of pretreated feedstock, as explained in the literature that the hydrolysis and acidogenesis processes reduce pH in the pretreated substrate [42].

The steady anaerobic digestion process of all tested types of manure (indicated by the pH of the digestate) was evenly retained with raw and previously CO_2-pretreated manure at pH 7.77–8.09. The pH in the digestate typically varies from 6.5 to 8.2, [40] with optimal values for anaerobic digestion producing methane of 6.8–7.2 [43]. An increase of the pH in the digestate contributes to the disturbance of the ammonia (NH_3) balance, beginning with the conversion of ionized $NH_4{}^+$, which is not volatile, to NH_3, with lower solubility and higher evaporation [44–46]. The ChM usually contains a large amount of ammonia, which may inhibit the biogas methanogenesis process. In our research, the pH of the digestate was higher than was suggested in Ward's research [40] as ideal conditions for anaerobic digestion (pH 6.8–7.2). It is therefore appropriate to inject CO_2 to the pretreatment process of raw feedstocks to accelerate hydrolysis and to intensify anaerobic conditions. Pretreatment with CO_2 may increase volatile fatty acid content available to methanogens and acidify the raw materials, while at the same time increasing the source of H_2 and CO_2 for hydrogenotrophic pathway methanogenesis [47].

The ORP of raw PM were relatively stable at −413.4 ± 12.8 mV. The pretreated PM feedstock showed more acceptable results for further anaerobic treatment of PM at −391 ± 16.8 mV. The most promising data of pretreatment on ORP was achieved on ChM. The ORP of untreated ChM was 54.2 ± 67.6 mV with great variation in the substrate and faraway for AD suitable feedstock ORP value of less than −250 mV. The ORP of pretreated ChM was −255 ± 39 mV with less deviation in the data and more acceptable results for further AD. The ORP value of pretreated CoM became more stable and decreased from −227 ± 25 mV to −313 ± 20.9 mV. Samani et al. [48] reported that the hydrolysis, acidogenesis and acetogenesis phases are compatible with ORP at −320 mV. The results of the Vongvichiankul et al. [35] study indicated that the optimum ORP and pH during the acidogenesis phase were −284 ± 32.71 mV and 5.76 ± 0.24, respectively. The optimum ORP and pH during the methanogenesis phase were −335.63 ± 28.97 mV and 7.49 ± 0.24, respectively. Based on the results and the information available in the literature, it can be concluded that CO_2-pretreated feedstocks are more convenient for biogas production compared to untreated feedstocks.

3.2. Biogas, Methane Yields and Energy Value

The CO_2-pretreatment process showed promising results for biogas yield with all the tested feedstocks. The CO_2 pretreatment influences the biogas yield and biogas energy value of feedstock (Table 4). The PM and CoM biogas digesters working on organic load 1.4 kg VS/(m^3·d) yielded 21.7 ± 1.1 L/kg and 8.3 ± 0.2 L/kg biogas, respectively. The pretreated PM and CoM increased the biogas yield from feedstock by 18.3% to 26.5 ± 1.2 L/kg and by 19.5% to 10.3 ± 0.2 L/kg, respectively. As in the other biogas digesters, the chicken manure biogas digester in the study worked on the same organic load of 1.4 kg VS/(m^3·d). Biogas yield gained from the chicken manure is the highest in this experiment–raw 123.09 ± 2.35 L/kg and pretreated 137.56 ± 2.94 L/kg, with an increase of 10.5%.

Table 4. The influence of CO_2 pretreatment on feedstock biogas yield and energy value of biogas.

Indicator	Raw PM	Pretreated PM	Raw CoM	Pretreated CoM	Raw ChM	Pretreated ChM
Bioreactor organic load kg VS/(m^3·d)	1.4	1.4	1.4	1.4	1.4	1.4
Biogas yield from feedstock, L/kg	21.66 ± 1.06	26.52 ± 1.22	8.32 ± 0.20	10.34 ± 0.23	123.09 ± 2.35	137.56 ± 2.94
Biogas yield feedstock total solids, L/kg	288.76 ± 14.34	353.60 ± 16.30	112.06 ± 3.05	139.34 ± 3.05	531.52 ± 10.15	593.99 ± 12.68
Biogas yield from feedstock volatile solids, L/kg	406.33 ± 20.17	497.56 ± 22.94	142.87 ± 3.36	177.65 ± 3.89	758.31 ± 14.48	847.44 ± 18.08
Methane concentration in biogas, %	66.69 ± 0.66	66.35 ± 0.34	54.70 ± 0.06	58.40 ± 1.51	54.73 ± 0.70	63.05 ± 0.45
Energetic value of biogas, MJ/m^3	23.54 ± 0.23	23.42 ± 0.12	19.31 ± 0.02	20.77 ± 0.45	19.32 ± 0.25	22.26 ± 0.16
Biomethane yield from feedstock volatile solids, L/kg$_{VS}$	192.64 ± 5.71	234.62 ± 10.93	61.3 ± 1.5	82.01 ± 3.19	290.88 ± 5.74	374.53 ± 9.27
Energy obtained from feedstock, MJ/kg	0.51 ± 0.03	0.62 ± 0.03	0.16 ± 0.01	0.21 ± 0.01	2.38 ± 0.05	3.06 ± 0.08
Influence of the pretreatment on biomethane yield, %	+21.78		+33.78		+28.76	

The methane content in the biogas during the experiment was quite high even with untreated raw materials. The least amount of methane in biogas was observed in the untreated cow manure, and it averaged at 54.7%. The pretreatment process improved methane content in biogas of CoM to 58.4%. The highest methane concentration recorded in the case of pig manure (PM) at 66.6%, and even though it decreased to 66.4% after the pretreatment process, the final biomethane yield was 21.78% higher compared to untreated PM. The greatest impact on biogas methane content was observed in the ChM case. The concentration of methane in biogas from ChM increased from 54.7% to 63.1%.

The biomethane yield from volatile solids rose after carbon dioxide pretreatment with all tested feedstocks. Biomethane yield from PM increased from 192.64 ± 5.71 L/kg$_{VS}$ to 234.62 ± 10.93 L/kg$_{VS}$ using carbon dioxide injection as a feedstock pretreatment method. Liu et al. [49] made an experiment of biological pretreatment of PM with a microbial community cell biocatalyst to accelerate degradation of antibiotics present in PM. The pretreatment method in Liu et al.'s experiments enhanced biomethane content by 93.2% up to 98.7 L/kg$_{VS}$ [49]. Although the yield of biomethane from volatile solids increased by only 21.78% in our research, the pretreated PM biomethane yield was more than two times greater compared to that in the Liu et al. research.

The physiochemical pretreatment research on PM was made by Qiao et al. [50]. The pretreatment was performed in eight stainless steel boilers by heating to 170 °C for one hour. The feedstock had a total solids content of 28.14% and the biogas yield experiment was maintained at a mesophilic temperature of 37 °C. Qiao et al. [50] compared the biogas production from pig manure residues with and without hydrothermal pretreatment.

They achieved a methane productivity of 290.8 L/kgVS, resulting in a 14.6% increase in biomethane content [50]. The increase of biomethane content in biogas in our research was 21.78% at the pretreatment temperature of 25 °C.

Another potential pretreatment method for PM was experimentally tested by Rafique et al. [47]. These researchers performed chemical pretreatment experiment of calcium hydroxide at 70 °C with a retention time of 1 h. During monodigestion, they used sludge from an anaerobic digester from a WWTP as inoculum. After pretreatment, researchers obtained 25% improvements, with a production of 237.5 L/kg_{VS} [47].

Angelidaki and Ahring [51] studied the use of B4 bacteria for biological pretreatment to degrade hemicellulose from cow manure. Based on their study results, monodigestion increases methane production by 30%, producing 300 mL CH_4/g as opposed to 200 mL CH_4/g. Cow manure biomethane yield in our experiment increased from 61.3 ± 1.5 L/kg_{VS} to 82.01 ± 3.19 L/kg_{VS} after the pretreatment process. It was the greatest pretreatment impact on biomethane yield at +33.78% compared to all tested feedstocks. It is important to note that even though the amount of biomethane gained from CoM in our research is low in comparison with Angelidaki and Ahring's research, the improvement is still significant. It is possible that the low biomethane gain from CoM can be attributed to the fact that we used CoM and a mesophilic process rather than the thermophilic process used in Angelidaki and Ahring's research.

Ramos et al. [52] considered that the optimal conditions for CoM alkaline pretreatment are based on using sodium hydroxide (NaOH) at a concentration of 6% of total solids with a temperature of 121 °C for 20 min. As a result of co-digesting with sewage sludge, they were able to obtain 168 L/kg_{VS} of biomethane, which represents a 155% increase over the raw CoM samples. It is important to note that even the biomethane yield in our experiment of CoM pretreatment increased from 61.3 ± 1.5 L/kg_{VS} to 82.01 ± 3.19 L/kg_{VS}. The results with Ramos et al.'s [52] research may not be comparable because of co-digestion with sewage sludge and the thermophilic process.

Zahan and Othman [53] conducted chemical pretreatment experiments with chicken litter under alkaline conditions and using an alkaline–acid sequence. For alkaline conditions, researchers pretreated the samples with 5% NaOH at 120 °C for 90 min, while for alkaline–acid conditions, they used 5% NaOH at 120 °C for 90 min and 3% H_2SO_4 at 120 °C for 90 min. An improvement of 50% was observed in the biomethane yield (from 240.7 to 481.5 L/kg_{VS}) after the anaerobic digestion process was completed. The chicken manure (ChM) biomethane yield rose from 290.88 ± 5.74 L/kg_{VS} raw feedstock to 374.53 ± 9.27 L/kg_{VS} after the carbon dioxide–pretreatment process in our experiment and the improvement on chicken manure biomethane yield in our research was +28.76%. The comparison between the biomethane yield in our research and Zahan and Othman's [53] biomethane yield results shows biomethane yield from ChM may vary in a wide amplitude depending on the pretreatment process, which in most cases is beneficial. During the CO_2 pretreatment, the CO_2 and water in the substrate may react with the ammonia in the ChM [54]. The conditions of the CO_2 pretreatment are not optimal for urea formation and could lead to the production of ammonium carbonate/bicarbonate or ammonium carbamate [54]. In addition, the reduction in ammonia content in ChM feedstock contributes to a reduction in ammonia inhibition in the biogas production process.

Costa et al. [55] performed the biological pretreatment of organic poultry manure with *Clostridium cellulolyticum*, *Caldicellulosiruptor saccharolyticum* and *Clostridium thermocellum* as bioaccumulation strains. According to their findings, biologically pretreated manure produces 102 L/kg_{VS} of methane, which represents a 15% improvement over raw manure. The ChM biomethane yield in our research rose from 290.88 ± 5.74 L/kg_{VS} raw feedstock to 374.53 ± 9.27 L/kg_{VS} from pretreated. Compared to our research results, the low biomethane yield in Costa et al. [55] may have been obtained because of inhibition or a large amount of nonbiodegradable materials present in the feedstock.

According to the results of this experiment, pretreatment of feedstocks with CO_2 may facilitate manure solubilization and increase biodegradability as well as biomethane production.

4. Conclusions

Based on experimental studies conducted with CoM, ChM and PM, it has been found that the pretreatment of manure prior to anaerobic digestion is an effective way to reduce ORP levels, resulting in more consistent and desirable outcomes for the anaerobic digestion process. This experiment showed that CO_2 injection pretreatment is an effective method for increasing biogas yield from feedstock. The highest biogas yield of 123 l/kg was achieved with chicken manure, demonstrating the potential of this technique for producing renewable energy.

Energy obtained from feedstock was highest in CoM and lowest in PM. The manure energy value obtained from feedstock after CO_2 pretreatment increased by 21.6–31.2%.

The biomethane yield could be increased by 33.78% compared to untreated manure. Further studies are needed to confirm the benefits of CO_2 pretreatment of manure for the biogas production process in combination with more than one pretreatment condition, such as CO_2 injection pressure and additional heating. Not only the technical but also the economic feasibility and life-cycle analysis of the biogas pretreatment process must be taken into consideration.

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Abbreviations

AD	Anaerobic digestion
CH_4	Methane
ChM	Chicken manure
CO_2	Carbon dioxide
CoM	Cow manure
H_2S	Hydrogen sulfide
HCO_3^-	Carbonic acid
N	Nitrogen
NH_3	Ammonia
O_2	Oxygen
OLR	Organic loading rate
ORP	Oxidation-reduction potential
P	Phosphorus
PM	Pig manure
RM	Raw manure
TC	Total carbon
TS	Total solids
VFA	Volatile fatty acids
VS	Volatile solids

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