

Effect of Cow Manure to Rice Straw Ratio on Methane Production in Batch Anaerobic Co-Digestion of Concentrated Cow Manure and Rice Straw.

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ABSTRACT

Anaerobic digestion (AD) of biowastes is the most conventional way to produce methane-rich biogas, which has great potential to replace the fossil fuels used in multiple applications, like vehicular transportation. Many countries and companies are involved in the design and construction of AD systems. Both efficient and economical, AD performances are extremely important to promote worldwide adoption of this technology. Using the laboratory-scale batch experiment, anaerobic co-digestion of concentrated cow manure (CM) with rice straw (RS) at five CM to RS volatile solid (VS) ratios was evaluated. The experiment was performed at National Centre for Energy Research and Development, University of Nigeria, Nsukka.

The maximum cumulative biogas yield obtained during the experiment was 293.9L. The pH of the system fluctuates between 6.6 to 8.4. The highest specific CH₄ yields obtained were 15.6L CH₄/g at a CM to RS ratio of 5:1. The results show that it is feasible to co-digest cow manure (CM) and rice straw (RS) when CM/RS VS ratios are not less than 1:1. The maximum atmospheric temperature recorded during the experiment was 41°C. It was found that the organic loading rate, OLR, affected the digester performance more than the dried RS proportion in the feedstock. Tripling the OLR increased the volumetric methane yields by 88% but decreased the specific methane yields by 38%.

(Keywords: bio-waste, rice straw, cow manure, anaerobic digestion, biogas)

INTRODUCTION

Anaerobic digestion is a process that converts organic matter into a gaseous mixture mainly

composed of methane and carbon dioxide through the concerted action of a close-knit community of bacteria [1]. Anaerobic digestion has also been considered as waste-to-energy technology, and is widely used in the treatment of different organic wastes [2]. It has been traditionally used for waste treatment but there is also considerable interest in plant-biomass-fed digesters, since the produced methane is a useful source of energy [3]. The most common reactor type used for anaerobic digestion of wastewaters is the continuously stirred tank reactor (CSTR). The main problem of this reactor type is the fact that the active biomass is continuously removed from the system leading to long retention times. This has been overcome in a number of systems based on immobilization of the active biomass, henceforth referred to as high rate systems.

To date, there is little information on the effects of the cow manure (CM) to rice straw (RS) ratio on the methane production potential and the stability of anaerobic co-digestion of cow manure (CM) and rice straw (RS) [3]. This information would be beneficial to determine the maximum amount of RS to co-digest with CM. In the present study, anaerobic co-digestion of RS and CM was investigated in batch experiments at various CM to RS ratios to examine: (i) the process stability, (ii) the system performance in terms of specific methane yield (SMY) and VS reduction, and (iii) kinetics of hydrolysis.

Waste biomass, such as rice straw, can be converted to fuel through biological or thermochemical processes [4]. Biological processes utilize bacteria to convert the biomass into fuel either through anaerobic digestion of organic matter generating methane or through saccharification and fermentation of sugars [5] producing ethanol. Utilizing rice straw for ethanol production has been investigated [6], and the global production potential was estimated to be

205 ggaliters (GL), which could replace approximately 147 GL of gasoline. Aerobic composting of rice straw has been evaluated with various other substrates for its use as a fertilizer [7]. Thermochemical processes such as pyrolysis [8], combustion, and gasification have also been evaluated as treatment methods of rice straw [9]. One way that biomass can be converted into energy is through anaerobic digestion.

Anaerobic digestion is a natural process in which a variety of microorganisms degrade organic matter into several intermediate products that are converted into a renewable energy source known as methane (CH₄). The stages of anaerobic digestion and general classifications of microorganisms involved are very important. Depending on the total solids (TS) concentration of the waste material, anaerobic digestion can be applied in wet (< 15% TS), semi-dry (15-20% TS) or dry (>20%TS) conditions [10]. The anaerobic digestion of lignocellulosic biomass like rice straw occurs faster in wet conditions, but the overall methane yield and digestibility of the straw is essentially the same in both wet and dry systems [11].

The advantages of dry systems opposed to wet systems include water savings, elimination of wastewater disposal, and reuse of the solid residues as fertilizer. Anaerobic digestion systems can be designed as either batch reactors in which all the substrate/inocula mixture is added at the beginning, or continuously-fed reactors in which the substrate/inocula mixture is added incrementally over time. Batch reactors are much simpler and less expensive (40%), but they have larger volume requirements and need a larger area footprint to place the reactors [12]. Biogas generated from the anaerobic digestion process consists primarily of CH₄ (50 to 65%) and carbon dioxide (35 to 40%), with a balance of nitrogen and trace amounts of hydrogen sulfide and water vapor.

CH₄ can be used directly as fuel for cooking and heating, converted into electricity by a combustion engine, or compressed and used as an alternative fuel for motor vehicles [13]. In 2011, 57% of the biogas produced in Europe (*i.e.* 10.1 million tons of oil equivalent) was from biomass sources including decentralized agricultural plants, household wastes and green waste methanation plants or centralized co-digestion facilities. The production of biogas through anaerobic digestion is considered to be one of the cleanest approaches to recovering energy from biomass [14].

Agricultural biogas plants are increasing (especially in Germany), however, the majority of them use food-based or energy crops such as cereals and maize. Using food crops for energy production is controversial because the demand for food is expected to increase in the future and food prices are likely to rise as a result [15].

Food security is a top global priority and using lignocellulosic materials such as rice straw for energy production does not interfere with that priority. The use of agricultural waste products is more desirable because of high availability and reduced greenhouse gases released into the atmosphere when the waste products are utilized rather than left in the field to decompose. When compared with six other lignocellulosic biomasses (wheat straw, oat straw, barley straw, sorghum straw, corn stover, and sugar cane bagasse), rice straw was selected as the most favorable feedstock for energy production primarily because of the quantity available. Though the organic matter is not completely converted by the anaerobic digestion of rice straw, the remaining residues can be used as topsoil maintenance or sustainable growth for biomass. When considering factors such as purchase price, potential fuel yields, and environmental concerns, cellulosic biomass can significantly contribute to energy sustainability and security [16].

The methane potential, however, of untreated rice straw is on the lower end when compared to other agricultural biomasses and agro-industrial by-products. The potential methane production from anaerobic digestion of rice straw has been evaluated under many different conditions in the context of bottle tests, batch reactors and pilot-scale studies. Several studies have been conducted to determine the ultimate methane yield of rice straw with various inocula, and the results range from 92 to 404 L/kg of VS added at ambient and mesophilic temperatures. There is considerable variation in methane yield of straw depending on the type of pretreatment, if any and the digestion conditions [17].

Optimum pH and Buffering Capacity

During anaerobic digestion, organic matter is first converted into sugars, fatty acids, and amino acids in the hydrolysis stage. Acidogenic and acetogenic bacteria further break down these substances and the resulting intermediates are acetic acid, hydrogen and carbon dioxide [18]. The methanogenic bacteria then convert the intermediates into methane and carbon dioxide.

During the anaerobic digestion of rice straw, in particular, approximately 80% of the methane is formed from acetic acid and 20% comes from the conversion of hydrogen and carbon dioxide. The rate limiting step in biogas production varies depending on the substrate and conditions. In the digestion of lignocellulosic biomass such as rice straw, the rate-limiting step has been defined as the hydrolysis of cellulose [18]. With higher (i.e. thermophilic) temperatures, the rate limiting step is the conversion of acetate to methane by acetoclastic methanogens, which are known for their slow metabolism and growth rate. Thus, if the system does not have sufficient buffering capacity, methane production will be inhibited by a rapid and overproduction of acetic acid.

Although the acidogenic/acetogenic bacteria can function normally over a broad pH range of 6 to 10 [20], methanogens are far more sensitive to pH. The ideal pH for rice straw digestion was determined by one author to be 7.5 to 8.0, although several batch experiments with rice straw have been successful in pH ranges of 6.5 to 7.3. When acid accumulation created low pH environments (i.e. < 6.0), the methanogens were inhibited and gas production ceased.

The Appropriate Balance of Nutrients

The appropriate balance of nutrients is a critical factor in the anaerobic digestion process and optimum carbon to nitrogen (C:N) ratios range from 25 to 35 [21]. Untreated rice straw has a very low concentration of total nitrogen (i.e., < 1% on a dry basis), and even less total phosphorus (i.e. 0.044% on dry basis). A typical C:N ratio for untreated rice straw is approximately 80 and therefore an external source of nitrogen is essential for effective digestion. Rice straw with a C:N (non-lignin carbon to Kjeldahl-nitrogen) ratio of 31 produced 4.5 times more biogas than rice husks with a C:N ratio of 81 [22]. The significantly lower gas yield was attributed to the lower nitrogen concentration and higher lignin content in the rice husks compared to the rice straw.

Rice straw digested with cattle manure performed best with a C:N (non-lignin carbon to Kjeldahl-nitrogen) ratio of 25 (versus 12.3, 20, 30, 35, and 40), yielding the highest methane production and lignin reduction. When straw is co-digested with animal manure, appropriate nutrient balance compositions are established and the synergistic effects produce higher methane yields. The biogas production increased by 9% when rice straw was co-digested with cattle dung compared to rice straw alone. Total biogas yield increased

by 30% when rice straw was co-digested with pig manure compared to rice straw alone, although the ratio of straw to manure (i.e. 2:1 versus 1:1) made no difference.

The degradability of rice husks was increased by 10% when they were used as bedding for pigs and lightly soiled with pig manure compared to unused husks. In a study that compared the methane potential of cattle manure to pig manure, ultimate methane yields were 58% higher in pig manure and the methane plateau phase was reached much faster. Besides recycled nutrients within agricultural waste streams, the benefits of co-digestion with animal manure include enhanced production of a carbon-neutral source of renewal energy and reduced greenhouse gas emissions.

The Effects of Temperature

Temperature is a very important variable to consider in the context of rice straw, not only for efficiency and maximizing methane production but also in regards to economical input. The literature reports that the optimum temperatures for methane production from the anaerobic digestion of straw are in the mesophilic range from 35 to 40°C [23], with one of the earliest discoveries made by Richards and Amoores in 1920.

An historical study was conducted in 1934 to evaluate decomposition of rice straw at different temperatures ranging from 20 to 45°C. After 6 months, the highest methane production was observed at 35°C, which was 53% higher than the production at 25°C. In a much more recent study, pretreated rice straw was digested using hogger wastewater as the inoculum [24]. When the temperature of the system was increased from 25°C to 35°C, cumulative methane production increased by approximately 25% for both wet and semi-dry conditions.

A similar study evaluated eight batch reactors containing barley straw (which is analogous to rice straw in the context of anaerobic digestion inoculated with pig wastewater and cow manure at both 25°C and 35°C. It should be noted that the 25°C reactors contained nearly double the amount of pig waste (dry weight) than the 35°C reactors and the experiment simulated a dry digestion process. Methane yields increased by 35% (145 to 222 L/kgVS), 18% (171 to 208 L/kgVS), 17% (156 to 188 L/kgVS) and 4% (151 to 158 L/kgVS) with increasing temperature [25]. The difference in these four sets of batch reactors

was the amount of cattle manure used. The sets of reactors with higher concentrations of cattle manure resulted in more significant changes with increasing temperature.

MATERIALS

Manure was obtained from a farm at the Animal Science Department University of Nigeria, Nsukka. After delivery to the laboratory, cow manure (CM) was sieved through a 2-mm sieve to remove coarse materials thus ensuring that laboratory tubing would not be blocked. The collected CM was dilute due to rain water and settlement in the storage pond, with the total solids (TS) content of 3.7%, volatile solids (VS) content of 2.5% and soluble COD concentration of 33,200 mg/l [26].

The CM was then concentrated by sieving through a 0.5-mm sieve. The CM fraction passing the sieve was settled in a container for 2 hours before some supernatant was removed from the container. The solid fraction remaining on the sieve was then added to the container and mixed evenly with the mixed liquor, to form concentrated CM. The concentrated CM had a TS content of 12.6% and VS content of 9.3%. This CM was used to simulate CM with high TS contents and CM concentrated with the separation process. RS was manually cut to less than 20 mm by a knife.

The sieved CM and cut RS were then frozen to prevent biological decomposition. To freeze RS was in accordance with the protocol used by Lehtomaki, et al. [27]. Prior to commencement of the experiment, the frozen CM and cut RS were transferred to a refrigerator at 4 °C for one day.

Biological Methane Production Potential (BMP) Tests

The biological methane production potentials (BMPs) of the CM-RS mixtures were examined at five CM/RS VS ratios - 1:1 (Treatment A), 2:1 (Treatment B), 3:1 (Treatment C), 4:1 (Treatment D) and 5:1 (Treatment E) - in 50-litre digesters made from mild steel. Each digester had two ports on the cap, one for liquid sampling and the other for gas sampling. The volume of VS of CM/RS added to each 1-litre digester for ratios A, B, C, D and E were respectively 1 / 1, 2/1, 3 /1, 4/1 and 5/1 . Each digester was inoculated with 500 ml of mixed liquor (inoculums) taken from laboratory-scale continuously stirred digesters treating mixtures of CM and RS at a CM to RS ratio of 4:1.

The inoculum contained 240.5 g/l of total suspended solids (TSS) and 150.6 g/l of volatile suspended solids (VSS) [28]. Tap water was added to each digester to give a working volume of 17L. The initial pH of the mixed liquor in each digester was adjusted to 7.5±0.1 by using 1 M HCl or 1 M NaOH [28]. Finally, the digesters were flushed with N₂, and then sealed with the caps.

The digesters were placed in a shaker incubator at 35 °C. The methane content in the head space and the methane volume produced from each digester were measured once daily. The specific methane yield (SMY) of each mixture was calculated by dividing the cumulative volume of methane produced after anaerobic degradation was complete by the total mass of VS initially added [28]. Complete anaerobic degradation was assumed when there was minimal methane production observed for 30 days. No supplemental nutrients were added to the substrate. There were two replicates for each CM to RS ratio.

ANALYTICAL METHODS

The liquid samples were taken from digesters once every three days using 5-ml syringes. After immediate measurement of pH, the samples were then centrifuged at 1,700 g for 10 min and then at 21,912 g for 20 min at 4°C.

The supernatants were tested for soluble COD. For analysis of volatile fatty acids (VFAs), the supernatants were further filtered through 0.45 cm cellulose nitrate membrane filter paper (Whatman, England), and then VFAs were measured with high performance liquid chromatography (HPLC, Agilent 1200, Agilent Technology, USA) using a UV index detector and an Aminex HPX-87H column (Bio-Rad, USA) [29]. Separation during HPLC measurement was achieved using a mobile phase of 1% H₂SO₄ at a flow rate of 0.6 ml/min and the column temperature of 65 °C. The detector temperature was 40 °C. The VFA mix containing acetic, propionic, isobutyric, butyric, isovaleric and valeric acids, each of 10 mM (Sigma–Aldrich, USA) was used for HPLC calibration.

Total solids, VS, soluble COD and alkalinity were analyzed according to standard methods (APHA, 1995) [29]. The NH₄-N concentration in the liquid samples was analyzed using a nutrient analyzer (Konelab, Thermo Clinical Labsystems, Vantaa, Finland). The volume of biogas was measured by displacement of water, and was then converted to the biogas volume under standard temperature

and pressure (STP) conditions of 0°C and one atmosphere. The CH₄ content in biogas was measured using a 7890A gas chromatograph (GC, Agilent Technology, USA) with a thermal conductivity detector and a 45–60 mesh, matrix molecular sieve 5A column (Sigma–Aldrich, USA). Helium gas was the carrier gas at a flow rate of 30 ml/min. The temperature of the injection inlet, oven and detector was 100 °C, 60 °C and 105 °C, respectively [29].

RESULTS AND DISCUSSIONS

Process Stability

Key factors measured to assess AD process stability were pH, VFA/alkalinity ratio, and concentrations of ammonium/free ammonia.

pH

The pH of the slurry was analyzed with pH meter in the laboratory after every 3 days. The maximum pH obtained was 8.4 while the minimum obtained during the experiment was 6.6. In Treatment E (CM: RS = 5:1), pH fell immediately after the commencement of the experiment and reached a pH value of 6.6 on Day 27 (Figure 1).

The low pH value in Treatment E brought methane production to a complete halt. In Treatments A, B, C and D, pH values over 90 days were in the range of 6.6 - 8.4. The lowest values in Treatments A, B, C and D were 7.3 (Day 10), 7.2 (Day 9), 7.2 (Day 8) and 7.1 (Day 10), respectively. After the lag phase (about 20 days) of biogas production, pH values in Treatments A, B, C and D rose and remained in the range of 7.0 to 7.8 till the end of the experiment.

These findings are compatible with the normal growth of anaerobic microorganisms (Raposo et al., [30]. Higher pH values during the lag phase reflected the higher proportion of CM in the feedstock since the pH value of raw CM material was 7.4 and of raw RS material was 4.5. While the pH values at the four CM/RS ratios (Treatments A, B, C, D and E) were very close after the lag phase.

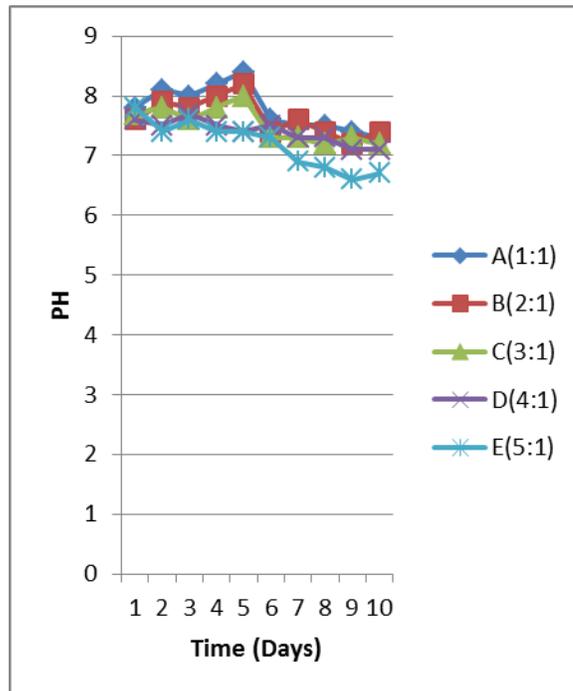


Figure 1: Variation of pH with Time at Different Manure to Grass Silage Ratios (1:1 (A), 2:1 (B), 3:1 (C), 4:1 (D) and 5:1 (E)).

VFA/Alkalinity

The maximum total VFA (TVFA) concentrations were obtained on Days 6, 24, 21, 16 and 24 in Treatments A, B, C, D and E, and were 130.5 g/l, 170.1 g/l, 170.3 g/l, 149g/l and 160.2 g/l, respectively. The accumulation of TVFA demonstrates the inhibition of the methanogenesis process, Siles et al., [31]. TVFA concentrations were almost zero after Day 27, Day 20, Day 25 and Day 29 in Treatments A, B, C and D, respectively.

In Treatment E, the maximum TVFA concentration was 150.9 g/l occurring on Day 17 and then levelled off (data not shown). When the VFA/alkalinity ratio was less than 0.3–0.4, the AD process was stable without an acidification risk (Borja et al., 2004). On Day 12, the ratios were 2.25, 2.30, 2.00, 2.88 and 2.23 in Treatments A, B, C, D and E, respectively, which were quite high and considered to inhibit the activity of methanogens Borja et al. [32]. By Day 23, the ratios were 0.65, 0.37, 0.37, 0.82 and 5.15 in Treatments A, B, C, D and E, respectively.

Hence, after 20 days from the commencement of the experiment, the systems under all CM to RS ratios except Treatment E were stable. Digestion of pure RS (Treatment E) was not stable and failed to produce methane after Day 30. This shows that for successful AD of GS it is necessary to add a source of external alkalinity to increase the buffering capacity. Otherwise, the digestion system would be unstable and even fail.

Ammonium/Free Ammonia

The ammonium ($\text{NH}_4^+ \text{-N}$) concentrations in Treatments A, B, C and D decreased with increasing the fraction of RS in the feedstock [33]. This clearly shows that co-digestion of RS with animal manure can prevent the probable adverse effects of $\text{NH}_4^+ \text{-N}$ on the system stability. The concentration of free ammonia (NH_3) in the liquid phase was dependent on pH and its concentrations during the experiment at the five CM/RS. In this study, free ammonia concentrations were high in Treatments A and B in comparison with Treatment C and D, with the highest levels of 246 and 210 mg/l, respectively. However, no significant inhibition was observed.

The concentrations of $\text{NH}_4^+ \text{-N}$ and free ammonia that cause inhibition of AD vary in different AD systems. For example, 50% reductions in methane production have been found for $\text{NH}_4^+ \text{-N}$ concentrations from 1.7 to 14 g/l Chamy et al., 1998 [34]. The inhibition of free ammonia and $\text{NH}_4^+ \text{-N}$ on AD is reversible. Wu et al. [35] found

that during AD of meat and bone meal, inhibition of methanogens by free ammonia was reversible when the free ammonia concentration was as high as 998 mg/l. The varying inhibition concentrations of free ammonia and $\text{NH}_4^+ \text{-N}$ are attributed to the differences in substrates and inocula, environmental conditions (temperature, pH, etc.), and acclimation periods.

BMP of the Cow Manure CM-RS Rice Straw Mixtures at Different CM to RS Ratios

In Treatments A, B, C and D, the initial methane production was low during the period from Day 1 to Day 6. This was probably due to the low addition of inoculum relative to the substrate, resulting in low initial concentrations of methanogens in the reactors. After Day 6, methane production increased sharply, and consequently pH drop to 7.5 ± 0.2 , indicating the enrichment of methanogens in the reactors.

At the end of the experiment, methane production declined due to the lack of soluble biodegradable organic substances. In Treatment A, methane production ceased till Day 5 due to the accumulation of VFAs and a low pH.

In Treatment A, there were two peaks of the daily methane yield, occurring on Day 20 (7.8L) and on Day 21 (7.8L). In Treatments B, C and D, peaks of the daily methane yield occurred on Day 20 (12.5L), Day 21 (14.0) and Day 29 (15.9), respectively (Figure 2).

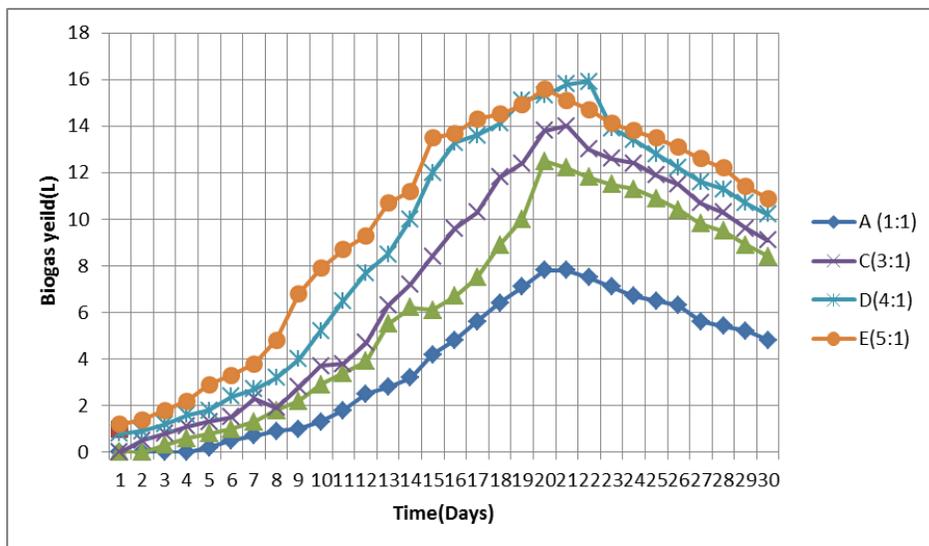


Figure 2: Profiles of the Daily Methane at Different Manure to Grass Silage Ratios (1:1 (A), 2:1 (B), 3:1 (C), 4:1 (D) and 5:1 (E).

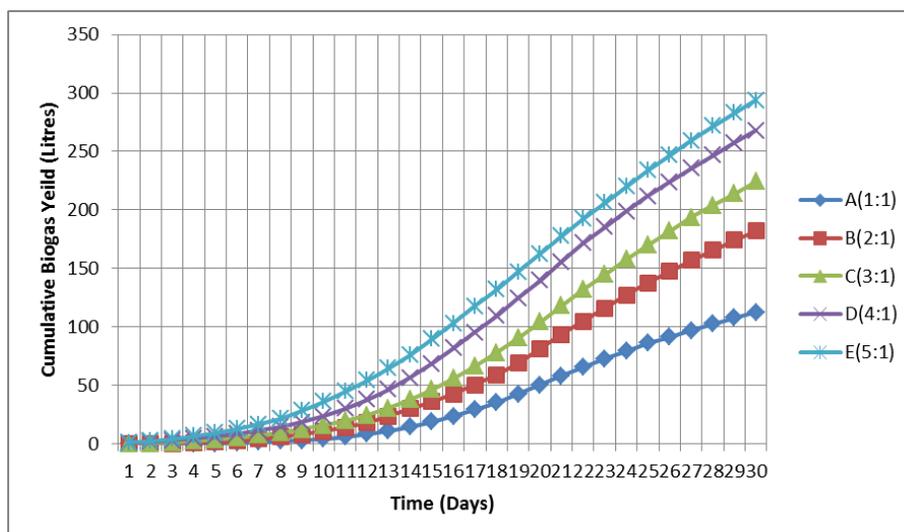


Figure 3: Profiles of the Cumulative Methane at Different Manure to Grass Silage Ratios (1:1 (A), 2:1 (B), 3:1 (C), 4:1 (D) and 5:1 (E)).

The cumulative methane yields in Treatments A, B, C, D, and E were 112.6L, 182.1L, 224.1, 267.7L, and 293.9L, respectively. Thus, the SMYs of the CM-RS mixture in Treatments A, B, C, D and E were calculated as 7.6, 8.4, 10.1, 10.3 and 11.1L CH₄/g VS added, respectively. There was no significant difference in the CH₄ content in biogas at different CM/RS ratios. The methane contents rose from Day 5 to reach a peak of 65%, 70%, 67%, 69% and 60% in Treatments A, B, C, D and E, respectively. Over the periods of Days 10 - 30, the methane contents at all Treatments ranged 55-65%. In the following 30 days, the methane contents decreased steadily to 54%, 54%, 53%, 52% and 52% in Treatments A, B, C, D and E, respectively.

Apart from the SMY and the cumulative methane yield, the duration of the lag phase is also an important factor in determining the efficiency of anaerobic digestion.

The methane production potential P was 112.6L, 182.1L, 224.1L 267.7L and 293.9L in Treatments A, B, C, D and E, respectively. The cumulative methane yields measured in the experiment were up to 94%-99%. The digestion time is a key indicator to substrate biodegradability and the utilization rate, and was thus investigated in this study. The technical digestion time, described with T₈₀, is defined as the time needed to produce 80% of the maximum gas production Palmowski and Muller, [36]. Increasing the RS fraction in the feedstock resulted in a shorter effective biogas production period. In practice, the digestion time, in terms of hydraulic retention time (HRT) and

solid retention time (SRT), can be shortened according to the effective biogas production period.

Co-digesting animal manure that has a low C/N ratio low levels of nitrogen (high C/N ratio) gives more higher methane yield than digesting manure only (likely that the low carbon content and high free ammonia concentrations resulted in relatively low SMY in Treatment (1) during the first 20 days, the system reached a pH inhibited the activity of methane anaerobic digestion of straw RS in the feedstock is too high, it is hard to reach the optimum system per terms of the methane production potential. Lehtomäki et al.[37] investigated anaerobic co sugar beet tops and oat straw crops were up to 30% of the RS ratios in Treatments B and C. VS removals were 60.5%, 63.8%, 64.7%, 65.2% and 59.5% in Treatments A, B, C, D and E, respectively .

Daily yield and cumulative methane yield over 30 days along with feedstock containing more stable operation performance (Callaghan et al.). The reasons for low SMY in Treatment A include: value as low as 6.45; this methanogens; and (2) additional nutrients are required for Scherer et al., [38]. Therefore, when the fraction of co-digestion of cattle manure with RS, straw, and found that the highest BMPs were obtained when the feedstock. This optimal ratio was in the range of CM to AD of RS can only remove 37%-67% (Lehtomaki and Bjornsson; Cirne et al.; Lehtomaki et al), depending on the reactor configuration, temperature, RS type, pre-treatment methods, etc. VS removals during AD

of CM alone or with various agro- industrial wastes range from 42% to 82% (Monou et al.; Panichnumsin et al.).

In this study, the highest VS removals were achieved in Treatments B and C due to the positive synergism between RS and CM, resulting from the provision of balanced nutrients and reduction of inhibitory materials. Thus, the GCM to RS ratio of 5:1 is recommended for application, under the context of the concentrated CM, because of its high methane production potential, short effective biogas production period, and as a result, utilization of a high amount of RS in co-digestion with CM. The optimum VS ratio would depend on the type of animal manure, characteristics of the manure, species and characteristics of co-digested energy crops.

Up to the commencement of methane production there was an accumulation of acetic acid in the reactors. Once obvious methane production started (Day 8, Day 7, Day 6, Day 5, and Day 9 in Treatments A, B, C, D and E, respectively), acetic acid began to decrease. Acetic acid was not detected after Day 26, Day 28, Day 26, Day 25 and Day 24 in Treatments A, B, C, D and E, respectively.

During AD, methane is derived from acetoclastic methanogenesis or from hydrogenotrophic methanogenesis. Accumulation of acetic acid in a digester is the result of a greater production of acetic acid than its conversion to methane and carbon dioxide. It is difficult to quantify how much methane is originated from acetoclastic methanogenesis and from hydrogenotrophic methanogenesis (Mottet et al.). In the present study, the daily methane production was positively related to the acetic acid concentration at all CM to RS ratios. This may indicate that methane was mainly produced via acetoclastic methanogenesis.

Hydrolysis Process

At all CM/RS ratios, soluble COD concentrations increased dramatically in the first 5 days and decreased after Day 18. The highest soluble COD concentrations were 23,960, 23,180, 23,160 and 23,780 mg/l, and declined to 3,220, 2,360, 2,300 and 4,600 mg/l at the end of biogas production in Treatments A, B, C, and D, respectively. The soluble COD removals were 86.6%, 89.8%, 90.1% and 80.7% in Treatments A, B, C, and D, respectively. It is often assumed that the rate-

limiting step in anaerobic digestion of energy crops and crop by-products is hydrolysis of particulate matter to soluble matter.

Increasing the RS fraction in the feedstock resulted in increasing soluble COD concentrations from 8678.6 to 14958.3 mg/l. However, the hydrolysis yields decreased from 59.5% to 50.1% as the RS fraction in the feedstock rose. The soluble COD removal rate increased from 86.6% to 90.1% with the increase of RS fractions up to 50%, and a further increase in the RS fraction resulted in a negative effect and a lower soluble COD removal rate of 80.7% in Treatment D.

CONCLUSION

This study investigated the effectiveness of cow manure and rice straw for biogas production and presented the performance characteristics of the anaerobic digestion in batch operations. Despite variations in pollutants concentrations, an improved performance of anaerobic digestion of the biodegradable fraction of cow manure and rice straw was achieved. The highest biogas volume recorded in the experiment was 15.6L. The atmospheric temperature varied from 25°C to 41°C. The co-digestion systems were stable in operation at CM to RS ratios of 1:1, 2:1, 3:1, and 4:1, 5:1 while the digestion systems digesting pure RS failed. The highest SMYs were achieved at CM to RS ratios of 4:1 and 5:1. The efficient methane production period lasted 13.0, 18.0, 16, 14 and 15 days at CM to RS ratios of 1:1, 2:1, 3:1, 4:1 and 5:1 respectively. The hydrolysis rate constants were 0.56, 0.46, 0.44 and 0.34 d⁻¹ at CM to RS ratios of 1:1, 2:1, 3:1 and 4:1, respectively. The CM/RS VS ratio of 5:1 is recommended for commercial application.

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