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EXPERIMENTAL LAB-SCALE BIOGAS PRODUCTION BY ANAEROBIC CO-DIGESTION OF AGRICULTURAL RESIDUES AND BREWERY WASTEWATER

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ABSTRACT. As a result of environmental and economic concerns, anaerobic co-digestion process has gained increasing interest as a viable technology for both energy production and waste treatment. In this work, anaerobic co-digestion of agricultural residues (animal slurry and corn grains) and wastewater from a local brewery plant was studied using a laboratory-scale experimental installation. Multiple batch experiments (Tst1-Tst7) were carried out in which the influence of the substrate mixture ratio, the temperature and the purging of N_2 of the reactor on the process was analyzed. Batch anaerobic-digestion experiments were performed at initial pH values between 7.5÷7.9 and at two temperature regimes (termophilic and mesophilic) and the substrates involved in the experiments were characterized using solid biofuels European Standard (EN 14774, EN 14775, EN 14918, EN 15297). The biogas was characterized by determining the CH_4, CO_2, and H_2S fraction over time. The best results were obtained when nitrogen purging was used to minimize the exposure of the substrate mixture to oxygen at an operating temperature of 45°C and a volume ratio of animal slurry to wastewater of 3:1 and 150 g of corn grain. Higher operating temperature and N_2 purging had a positive impact by increasing biogas production and decreasing the H_2S fraction of the total produced gas.

Keywords: *biogas production, agricultural residues, lab-scale experiments, N_2 purging*

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INTRODUCTION

Anaerobic digestion (AD) is a versatile process by which various types of organic matter are converted to biogas using technology that may be designed at different scales providing benefits such as energy autonomy, pollution mitigation, and waste valorization. It also sustains economic entities in the agricultural, industrial, and municipal sector due to the fact that it can be adapted to the energy needs and local available renewable resources including waste generated in the aforementioned sectors. The advantages attained by using various types of substrates in the anaerobic digestion have made the anaerobic co-digestion of multiple feedstocks an important research field in improvement of the AD technology [1-3].

In addition to the common types of waste exploited in the anaerobic digestion technology, such as food waste (from industrial and commercial activities, restaurant and household activities), organic fraction of the municipal solid waste, agriculture waste (from harvest activity and animal husbandry and farms), sewage sludge, it has to be mentioned another category of organic waste: wastewaters. The wastewaters with potential use for biogas production are provided mainly from food production and biorefineries (e.g. pulp, paper and biofuels production) sectors and among the wastewaters reported in the scientific literature for the AD process there may be mentioned: brewery wastewater, wastewater from household and personal products, yogurt/ cheese whey wastewater, meat processing wastewater, ethanol wastewater, palm oil mill effluent, biodiesel wastewater, seafood processing wastewater, agro-industrial wastewater [4-6]. The high organic load, high biodegradability, microbial presence, low degree of physical and chemical contamination make the wastewater appealing co-substrates for anaerobic digestion. Therefore, the wastewaters can be mixed together with complementary substrates such as other types of wastewaters, animal manure, food waste, lignocellulosic biomass, algae e.g. to improve the nutrient content, C/N ratio and to overcome the toxicity contained in some of the wastewaters for the AD process [5, 6].

The exploitation of wastewater by anaerobic fermentation serves not only as an approach to improve the AD process for biogas production but also as a treatment method for industrial effluents with high organic strength, for which before discharging a purification step is required. In this way, anaerobic co-digestion of wastewaters represents a viable option to diminish considerable source of pollution for the soil, groundwater and atmosphere which contribute to the energy savings of the waste provider industry and to reduce the sludge excess accumulation. Furthermore, AD for wastewater treatment shows economic benefits over aerobic treatment technologies (such as sequencing batch reactor, activated sludge and aerobic filter) because the demand for some operations such as aeration, sludge disposal, and maintenance of the mechanical device contribute to their operating costs [5, 7-10].

Combinations of wastewaters with solids or semi-solids waste and utilization of slurries are suitable for wet fermentation (low solids anaerobic digestion) in low rate systems: batch, fed-batch and continuous. The most common reactor type for wet fermentation is Continuously Stirred Tank Reactor (CSTR), wherein the retention can be ranged between 2 and 4 weeks [8, 11]. Another type of waste generated in large quantities with serious environmental implication, as in the case of industrial wastewater, is animal manure which contains both bacteria and nutrients, for which improper management can lead to ground water contamination and public health threat. As an alternative to disposal in landfill sites, anaerobic digestion of animal manure is used to maximize the benefits while overcoming the pollution problems. However, due to the low carbon to nitrogen (C/N) ratio, the animal manure is commonly used in mixtures with carbon rich co-substrates such as lignocellulosic biomass to satisfy the anaerobic digestion requirements [12, 13].

In this study, different mixtures of wastewater from brewery with animal slurry and corn grains were used for anaerobic co-digestion lab scale batch experiments to investigate the influence of operating parameters on the process behavior. Hence, variation of the temperature domain, mixture ratios and the exposure to oxygen of the substrates inside the reactor were conducted with an emphasis on studying the modification of the pH in time, the amount of produced biogas and the biogas composition, respectively.

RESULTS AND DISCUSSION

Increased pH values of the mixture are given by the animal manure contained in the mixture which usually contains high concentration of NH_4-N. In figure 1, it is represented the variation of pH over time for anaerobic co-digestion batch experiments Tst1-Tst7, as presented in Table 2. It can be noticed that the values of the initial pH of the Tst3-Tst7 are between 7.5 and 7.7, wherein the animal slurry to wastewater volume ratio is 3:1 and higher initial pH value (7.9) were recorded for Tst1 and Tst2 where the animal manure to wastewater volume ratio is higher. The optimal pH range for maximal biogas production by anaerobic digestion is 6.5÷7.5, but the pH can be extended to wider ranges such as 6.5÷8.5 depending on the substrate and digestion technology [14, 15]. Still, based on other scientific studies, biogas production decreases at pH values above [16-20]. In figure2 are represented the total amount of biogas, methane and carbon dioxide for each batch experiment presented above in table 1. In the first set of experiments, low concentrations of methane and carbon dioxide of the total gas are obtained and it can be concluded that the variation of substrate mixture ratio has little impact on the process performances and that the selected operating conditions and the pH control were not favorable for the process. Furthermore, the variation of CO_2 and CH_4 low concentration over time are illustrated in figure 3.

Therefore in the second set of experiment enhanced biogas, methane and CO_2 production were obtained. The best results are attributed to batch experiment Tst7, with a total production of biogas of around 15 liters of which 51% is CH_4 and 31.6% is CO_2.

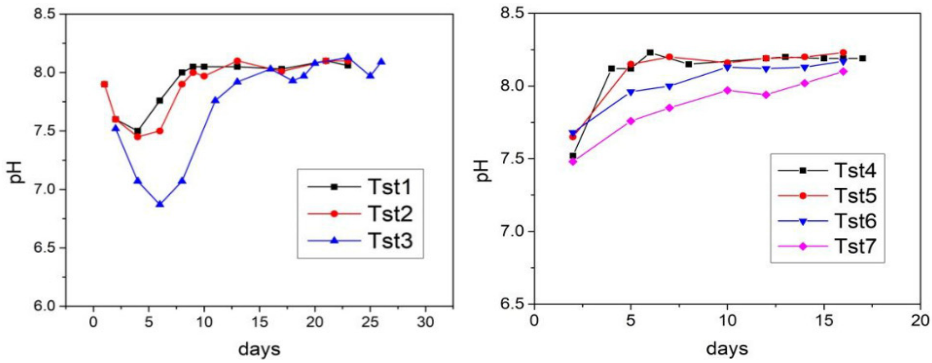

Figure 1. The pH profile in the anaerobic co-digestion batch experiments (Tst1-Tst7)

Comparing the Tst7 with Tst4, it can be noticed that the total amount of biogas, CH_4 and CO_2 for Tst4 was 49.7%, 49.9% and respectively 47.7% lower than in the case of Tst7. These results showed that the use of N_2 purging in order to diminish the suspension mixture exposure to oxygen led to enhanced biogas production.

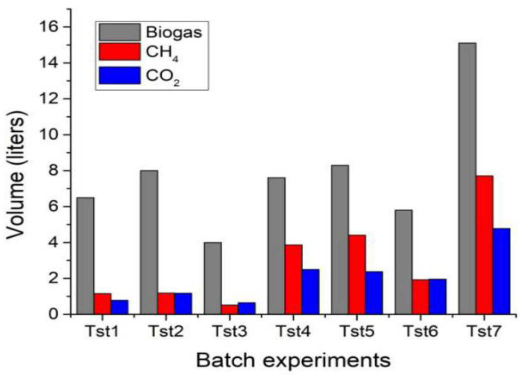

Figure 2. The total amount of produced biogas, methane and carbon dioxide for anaerobic co-digestion batch experiments from Tst1 to Tst7

This can be explained by the oxygen effect on the overall anaerobic digestion process. Based on the scientific literature, hydrolysis (the first stage occurring in the anaerobic fermentation) is carried out in both aerobic and anaerobic condition, whereas the microorganism involved in the following stages (acidogenesis, acetogenesis and methanogenesis) are strictly anaerobic [21, 22]. Higher yields of organic matter conversion were reported in the aerobic hydrolysis, while exposure to surpassing oxygen content lead to oxidation of available soluble carbon into carbon dioxide, reducing the potential conversion into methane. This suggests that too high levels of oxygen have a negative impact on the biogas yields in the anaerobic digestion process [21, 22]. Furthermore, lower pH values were obtained for Tst7 when compared with Tst4, which may imply that higher conversion of the organic substrate into acidic compounds was obtained concomitantly with faster and higher rates methane formation as it is illustrated in figure 3 and figure 5.

Lower operating temperature in Tst6 (37°C) and Tst5 (30°C) led to decreased biogas production, but surprisingly higher in Tst5 than in Tst6. Moreover, lower yield of gaseous mixture consisting of CH_4 and CO_2 of the total produced biogas (around 67%) was attributed to Tst6, while CH_4 and CO_2 gaseous mixture yields in the Tst4, Tst5 and Tst7 were around 83%. Generally, the typical minimum retention time in the anaerobic digestion for mesophilic temperatures is about 30 to 40 days and for thermophilic temperatures it ranges between 15 to 20 days. This fact, corroborated with methane production over the operation time (figure 3 and figure 4), indicates that Tst4 and Tst7 batch experiment correspond to thermophilic behavior, as it is expected. Herein, the maximum methane production was reached between day 4 and day 10 with the methane content of the total biogas in the 55-70% range for Tst7 and between day 7 and day 15 in the 50-65% range for Tst4.

By analogy, evaluating the CH_4 production over time in Tst 6, wherein a different thermal regime was applied, indicates a similar trend of gas production with Tst 4 and Tst 7, with the maximum methane production reached between day 4 and day 9, in the range 42-52%. Otherwise, in the Tst5 batch experiment, methane production reached a maximum plateau for a prolonged period, starting from day 8 to day 17 in the range 60-70%, indicating a slower production rate of biogas in the first 8 days. This trend corresponds to a mesophilic behavior and explains the increased biogas production for Tst5 when compared with Tst6. Figure 4 presents, the evolution of methane, biogas and carbon dioxide production over time as accumulated gases produced for batch experiments Tst4-Tst7, revealing the production ratio of methane and carbon dioxide in relation to biogas.

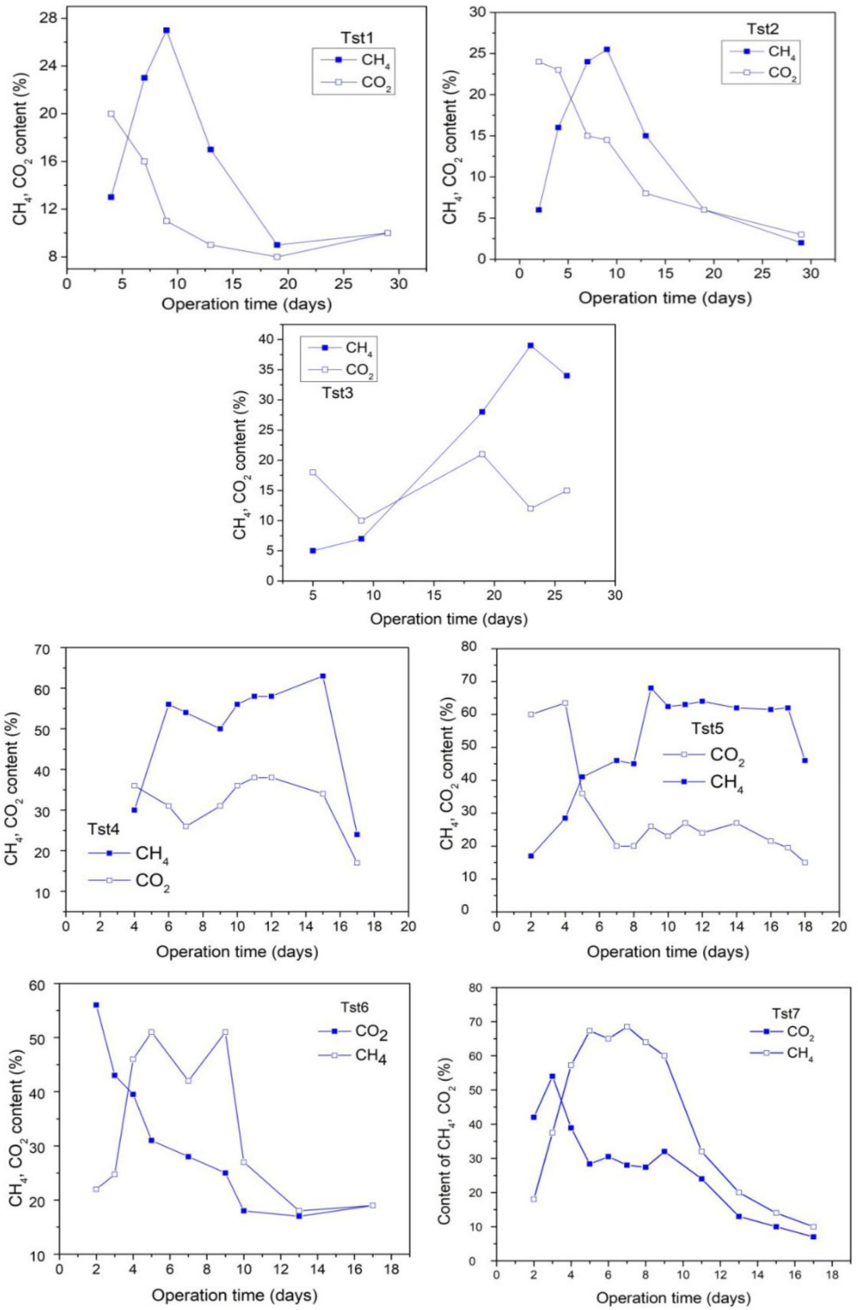

Figure 3. The variation of CH_4 and CO_2 percent of biogas obtained over the operation time of anaerobic co-digestion batch experiments: Tst1-Tst7

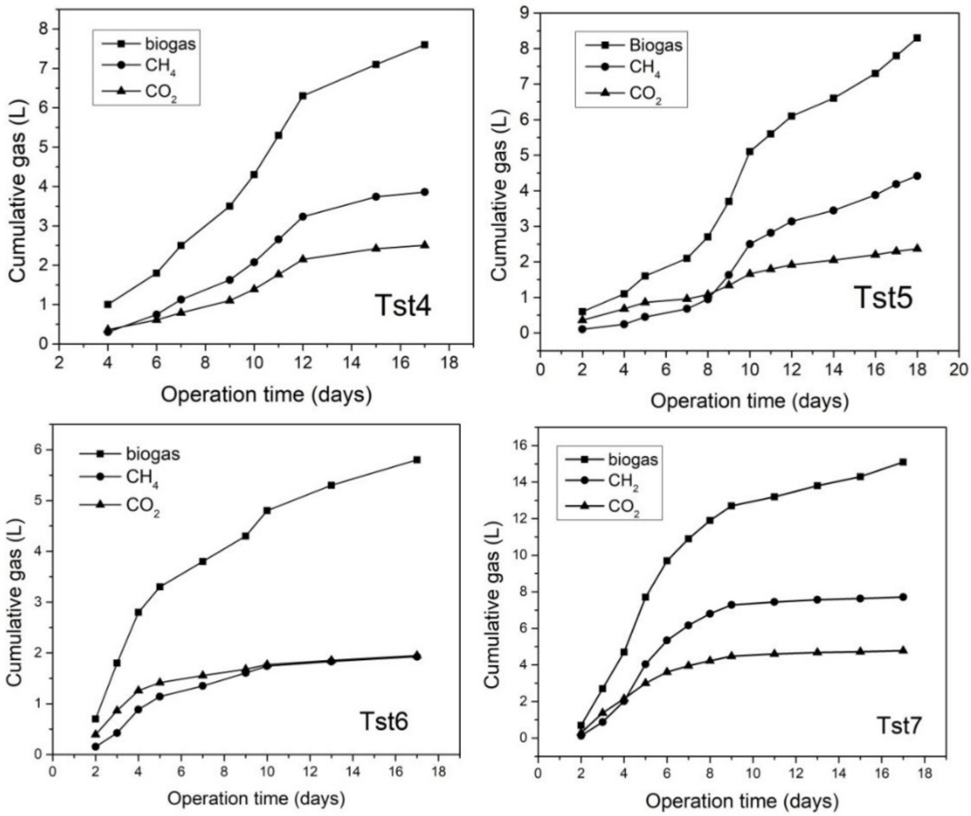

Figure 4. The accumulated gas (biogas, CH_4 and CO_2) obtained in the anaerobic co-digestion batch experiments: Tst4-Tst7

An important aspect in appreciating the anaerobic co-digestion process for biogas production is represented by the content of H_2S of the total biogas. Due to its corrosive action in further biogas utilization technologies, it is desirable to obtain low concentration of H_2S. In table 1, the H_2S content in biogas for batch experiments Tst4-Tst7 are presented.

By assessing the above, it can be noticed that lower H_2S content is obtained during the Tst7 experiment due to the fact that anaerobic co-digestion in case of diminished exposure to oxygen resulted after N_2 purging of the reactor lead to lower activity in sulfur producing microorganisms.

Table 1. Production of H_2S of the total biogas obtained in the second set of batch anaerobic co-digestion experiments

Batch experiment	H_2S content (ppm)
Tst4	680
Tst5	300
Tst6	32
Tst7	417

By comparing the Tst5, Tst6 and Tst7, where different temperatures regimes were operated, the H_2S concentration decreases in the following order: Tst7, Tst5 and Tst6 similarly with the biogas, CH_4 and CO_2 concentration which suggests that lower biogas production is correlated with lower CH_4, CO_2 and H_2S production.

CONCLUSIONS

Based on the results obtained in the first set of experiments (Tst1-Tst3), it can be concluded that the animal slurry to brewery wastewater volume ratio of 4:0 and the addition of acid for the pH control contributed to low methane and carbon dioxide yields of the total biogas when compared to the second set of experiments.

The variation of operating temperature in the experiments Tst5-Tst7, while the substrate mixture was the same (the animal slurry to brewery wastewater volume ratio was 3:1 and the mass of corn grain was 150 g), led to different behavior regarding the biogas and methane production. Hence, the best results were obtained for Tst7 batch experiment, wherein the operating temperature is thermophilic (45°C), followed by Tst5 (operated at 30°C) and by Tst6 (operated at 37°C). Also, by analyzing the Tst4 and Tst7 experiments, it was pointed out that the N_2 purging significantly improved the anaerobic co-digestion process by increasing the biogas and methane production by 100%.

EXPERIMENTAL SECTION

Anaerobic co-digestion batch experiments were carried out using lab scale reactors of 5L capacity with automatic stirring and temperature control, as described in a previous study [23]. Multiple batch experiments were conducted wherein different operating parameters including substrates mixture ratios, temperature domain and the working atmosphere were selected in order to investigate the behavior of the process by analyzing the amount of obtained biogas, biogas composition and pH modification. In table 2, there are presented the operating parameters for each batch experiment. The working volume of the reactor was 4 L and the remaining part was left for gas accumulation. For batch experiments Tst3 - Tst7, the headspace of the reactor was purged with N_2 to remove the air containing the oxygen which is considered a toxic agent for the anaerobic digestion due to the inhibiting effect on the anaerobic microorganism (acetogens and methanogens) [24].

Table 2. The operating parameters for the anaerobic co-digestion batch experiments

Batch	Substrate mixture		Temperature [°C]	N_2 purge	operation time (days)
Experiments code	Animal slurry to brewery wastewater volume ratio	Corn grain [g]			
First set of experiments					
Tst1	4:0	150	35°C	no	26
Tst2	4:0	200	35°C	no	26
Tst3	3:1	150	35°C	yes	26
Second set of experiments					
Tst4	3:1	150	45°C	no	18
Tst5	3:1	150	30°C	yes	18
Tst6	3:1	150	37°C	yes	18
Tst7	3:1	150	45°C	yes	18

Three types of substrates were involved in the experimental investigations: wastewater from brewery factory, animal (cow and chicken) slurry and corn grain (figure 5). The animal slurry was obtained from a local biogas industrial plant (Timişoara, Romania). Therefore, the experimental studies involved in the current work are classified in two sets of experiments. The first set of experiments comprising Tst1-Tst3 were conducted at the same operating temperature and operation time in order to investigate the effect of substrate mixtures and oxygen on the process and the second sets of experiments (Tst4-Tst7), wherein the operation time and substrate mixture were selected to be the same, with the aim of investigating the influence of oxygen and temperature regime. As well, small amounts of acetic acid were added in the reactor for the Tst1-Tst3, whereas no pH adjustments were performed for the Tst4-Tst7. The obtained biogas was collected in sample gas bags and subjected to composition analysis using a portable biogas analyzer (Biogas 5000 Gas Analyzer provided by Geotech). For the first set of experiments, the biogas composition was assessed in terms of CH_4 and CO_2 fraction determination and for the second set of experiments, the analyzed components were CH_4, CO_2 and H_2S.

Figure 5. The anaerobic co-digestion suspension consisted of animal slurry, wastewater and corn grain mixture

As it is presented in table 2, the anaerobic digestion process was carried out at thermophilic (45°C) and mesophilic (30-37°C) temperatures and different operation time were selected (18 and 26 days).

The substrates were subjected to characterization in order to determine the moisture, ash and minor elements content and calorific value (table 3) using solid biofuels European Standard (EN 14774, EN 14775, EN 14918, EN 15297), for the brewery wastewater and animal slurry additional properties (chemical oxygen demand - T_{COD}, orthophosphate - P_T and ammonia - N_T concentration) are presented in table 4.

Table 3. The properties of the substrates based on the European Standards characterization techniques - EN 14774, EN 14775, EN 14918, EN 15297

Substrate	Moisture content (dry basis) [%]	Ash content (dry basis) [%]	Superior calorific power (dry basis) [J/g]	Lower calorific power (dry basis) [J/g]	Minor elements [ppm]				
					Cr	Mn	Ni	Cu	Pb
Corn grain	10.2	1.58	18460	16887	<5	10.0	<5	<5	450
Wastewater from brewery factory	5.1	26.7	17412	16125	<5	102	<5	8.5	<5
Animal (cow and chicken) slurry	8.46	18.7	16699	15444	7.8	-	14	390	<5

Table 4. Additional properties (chemical oxygen demand, orthophosphate, ammonia) of the substrates of high water content

Substrate	T_{COD} (mg/L)	N_T (mg/L)	P_T (mg/L)	source
Wastewater from brewery factory	4679- 5118	59.8 – 79.3	21 – 80.2	Local brewery plant
Animal (cow and chicken) slurry	11200÷24000	>1800÷500	>500÷200	[25,26]

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