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Research Article

Effects of pretreatments on the production of biogas from cow manure

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ABSTRACT

In this study, some pretreatments were applied to cow manure to determine water solubility and biogas production. Aqueous phases containing 10 % solids by mass were prepared in the study. Chemical substances (NaOH), which were as much as 10, 15, and 20 % of the solids by mass, were added to the aqueous phases, and then they were subjected to microwave and hotplate thermal pretreatments separately (for 15, 30, 60 minutes). Following the pretreatments, the water solubility percentages of the solid materials were determined in the un-pretreated and pretreated aqueous phases. The pH of the aqueous phases, which yielded the highest water solubility, was adjusted to 7 using acid. Afterwards, the aqueous phases were incubated at 35 °C for 32 days in an incubator, and biogas and methane measurements were made in aqueous phases every 4 days. As a result of the study, maximum water solubility was found to be 92.8% (by mass), maximum biogas yield 378 mL/1g, and dry solids and maximum methane content values 41%.

1. Introduction

Biogas is a gas mixture which is produced by the fermentation of organic-based waste/residues in an anaerobic environment. It is colorless - odorless, lighter than air. It burns with a bright blue flame and comprises 40-70% methane, 30-60% carbon dioxide, 0-3% hydrogen sulfide, and very little nitrogen and hydrogen depending on the composition of organic substances in its composition.

The thermal value of the biogas comes from the flammable methane gas in its composition. The amount of heat obtained from 1 m^3 biogas is 4700-5700 kcal/m^3 [1].

The effective heat of 1 m^3 biogas is equivalent to the following energy values:
0,62 liter of kerosene
1,46 kg of charcoal
3,47 kg of wood
0,43 kg of butane gas
12,3 kg chip
4,70 kWh electric energy

Fuel equivalents of 1 m^3 biogas:
0,66 liter diesel
0,75 liters of gasoline
0,25 m^3 propane [1].

Various wastes such as animal waste (feces of cattle, horses, sheep, and poultry animals, wastes from slaughterhouses, and waste from the processing of animal products), vegetal waste (unprocessed parts of plants and waste from the processing of vegetal products such as finely chopped stalks, straw, stubble and corn residues, sugar beet leaves and grass residues), and urban and industrial wastes with organic content (sewage and bottom sludge, waste from paper industry and food industry, dissolved organic matter and highly concentrated industrial and domestic wastewater) are used in biogas production.

Table 1 presents biogas yields and methane quantities in biogas that can be obtained from various sources [1].

Solid animal wastes are regarded as the ideal source for biogas production (65% methane, 35% CO_2) after a

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biological treatment. The resulting biogas is of great significance for both electricity and heat generation [2].

Daily and annual wet manure quantities that can be obtained on the basis of animal weight are as follows:

- 5-6% kg-wet manure/day of live weight of cattle
- 4-5% kg-wet manure/day of live weight of sheep-goat
- 3-4% kg-wet manure/day of live weight of chicken [1].

Table 2 presents the amounts of annual wet manure that can be obtained on the basis of animal weight and Table 3 presents the biogas quantities that can be produced by the type of manure [1].

Table 1. Biogas yields that can be obtained from various sources and methane quantities in biogas [1].

SOURCE	Biogas Yield (liter/kg)	Methane Ratio (% by volume)
Cattle Manure	90-310	65
Poultry Manure	310-620	60
Pig Manure	340-550	65-70
Wheat Straw	200-300	50-60
Rye Straw	200-300	59
Barley Straw	290-310	59
Corn Stems and Residues	380-460	59
Flax, Hemp	360	59
Grass	280-550	70
Vegetable Residues	330-360	Variable
Various Agricultural Residues	310-430	60-70
Peanut Shell	365	-
Fallen Tree Leaves	210-290	58
Algae	420-500	63
Wastewater Mud	310-800	65-80

Table 2. Annual wet manure quantities that can be obtained on the basis of animal weight [1].

Number of Animals	Animal Species	Wet Manure Quantity (ton/year)
1	Cattle	3,6
1	The ovine	0,7
1	Poultry	0,022

Table 3. Biogas yield that can be produced depending on manure type [1].

Manure Type	Manure Quantity	Biogas Quantity that can be Obtained (m^3/year)
Cattle	1 ton	33
The ovine	1 ton	58
Poultry	1 ton	78

When Turkey's energy statistics are examined, it can be seen that animal and vegetal residues make up 9% of the total energy production and 4% of the total energy consumption. The share of animal manure among other items is big. In our country, animal chip is utilized for heating and cooking. The use of animal manure on agricultural lands is more economical than converting it to energy by burning. Animal manure has superior properties in comparison to artificial fertilizers. In addition to providing soil nutrients, it also improves soil structure. Preventing the burning of animal chip and ensuring its use in agricultural lands is only possible by giving an energy substitute to the rural area. This substitute energy is biogas, which can also be obtained from animal manure [3].

Utilization of animal wastes as biogas is also important from an environmental point of view.

The unpleasant smell which is one of the biggest problems arising from animal husbandry facilities will be removed by anaerobic digestion of waste. Raw manure that is kept outdoors in farm raising animals can leak into ground or surface water with rainwater or wind. This causes eutrophication in surface waters and pollution in ground waters. With biogas investment, these negative effects will come to a halt.

During the maturation of the manure in biogas generators, an environment based on a natural decomposition basis is created, and so reproduction of harmful parasites and pathogenic microorganisms become impossible and thus waste environment can not threaten the environment and human health [4].

A review of the related literature in the light of these facts has yielded the following findings:

Kearney et al. found the daily biogas production produced by some bacteria found in cattle manure in an anaerobic medium in the laboratory at 35 °C, for 25 days, and at pH 7.6 conditions as 510-620 ml/day and the methane ratio as 42-50% [5].

Pound et al. conducted a study to compare the amounts of biogas produced from cattle manure mixed with urea and urea-free compressed sugar cane in anaerobic conditions. It was found that when they increased the percentage of compressed sugar cane in the mixture, the pH of the slurry in fermentation decreased, and then biogas production slowed down respectively. It was determined as a result that biogas production was directly proportional to the amounts of pH of the slurries [6].

Sözer and Yaldız determined an optimum biogas production yield by mixing banana greenhouse wastes and cattle dung at various ratios. The study was conducted by adding 15%, 30%, 45%, 60% and 75% banana greenhouse wastes into cattle dung at 37 ºC, in laboratory biogas generators with continuous flow, for

15-day waiting period. As a result, the highest raw material specific methane production rate was determined as 0,149 L g^{-1} organic dry matter/day from 30% banana greenhouse waste and 70% cattle dung mixture [7].

Kobya studied biogas production from cattle dung at different temperatures (20, 25, 30, 35 °C). In the study, T_{Gaz}, T_{CH4}, TOM changes were examined for various temperatures and time periods and related model equations were obtained. It was found that at 35 °C, a total of 8.630 liters of biogas was obtained from 80g dry cattle dung, while 9.670 liters of biogas were obtained from 80g fresh cattle dung. It was found as a result of the study that as the temperature increased, the degradation rate of T_{Gaz}, T_{CH4}, TOM increased by time [8].

By using laboratory scale biolithic reactors, Aslanlı tried to determine the effect of boron compounds on biogas production from animal wastes. Boron compounds were added to the reactors at different doses and at different temperatures. Cattle dung was diluted with tap water at a ratio of 1:1 g/ml and then incubated for 35 days in anaerobic conditions at 25, 37 and 50 °C for biogas production. Ammonium tetraborate, borax, boric acid, lithium tetraborate and potassium tetraborate were added to the reactors at different doses. Effective biogas production was observed in the reactor with maximum level ammonium tetraborate (0,50 g/L) at 25 °C incubation and the reactor with borax (0,86 g/L) at 37 °C. On the other hand, boron compound was observed to have no effect on biogas production [9].

Varinli determined the optimum thermal pretreatment temperature for the maximum biogas production from apple marc and evaluated the methane production potential as a function of the thermal pretreatment temperature. Thermal pretreatment was applied at 11 different temperatures such as 25 °C, 50 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, 150 °C and 170 °C. Measurements were made in reactors operated for 42 days and the biogas content of gas samples taken at periodic intervals was determined by gas chromatography. The highest biogas production was obtained from samples pretreated at 150 °C, while the lowest was obtained from pretreatment samples at 110 °C. More gas production was achieved in samples with thermal pretreatment than the samples without thermal pretreatment. Experimental studies have shown that thermal pretreatment has a positive effect on biogas and methane production from apple marc [10].

Ardıç studied increasing the biogas production yield from cow dung. To do this, he separately added H_2SO_4, H_3PO_4, HNO_3, NaOH and KOH as much as 5%, 10%, 15% and 20% of the solid matter in the mixture to aqueous mixtures containing solids as much as 10% of cow dung, and then thermal and thermochemical pretreatments were applied at one, two and three hour-intervals at room temperature and water boiling temperature. The aqueous phases which yielded the maximum water solubility were applied anaerobic treatment at pH=7 and 30 °C for 30 days, and then their biogas and methane volumes were determined by time. At the end of the study, the maximum water solubility of the solid material in the cow dung was found to be 29,7% and the maximum methane production yield was 352,37 $mLCH_4$/gKM. This value was obtained from a three-hour thermochemical pretreatment using NaOH, it was observed that pretreatments conducted using NaOH were found to improve the water solubility of the solid material in cow dung and the biogas, methane production efficiency from cow dung [11].

In this study, cow manure was pretreated so that water solubility and biogas production could be determined. The slurry with 10% solid content added no chemical substance and the slurry with 10% solid content added a chemical substance were subjected to microwave and hotplate thermal treatment at room temperature.

2. Material and Method

2.1. The Pretreatments

Cow manure used as raw material in the study was prepared by drying, grinding and subjecting it to sieve analysis to ensure homogeneity. In the experiments, aqueous phases containing 10% solids by mass were used. An alkaline pretreatment was carried out by adding NaOH solution of 50% as much as 10%, 15%, and 20% of the solids to the aqueous slurry containing 10% solids by mass.

The thermal pretreatments, on the other hand, were carried out by keeping the slurry with 10% solid content by mass in a 700 W microwave oven under a reflux or on a hotplate under a reflux for 15, 30 and 60 minutes.

2.2. Determining Water Solubility and Biogas Yield

The pretreated aqueous cow manure samples were filtered through glass cotton whose fixed weight was measured. The filtration process in the aqueous mixtures continued until the filtered water was transparent. The solid collected in the glass cotton after the filtration process was dried at 70°C - 80°C in the incubator until it was possible to get the weight and their weights were recorded to find the percentage of water solubility. The transactions were made in triplicate.

Samples with the highest water solubility were selected for analysis after dissolution experiments in water. To adjust the pH of the selected aqueous phases to 7, H_2SO_4 solution was added to the aqueous phases which had been subjected to basic pretreatment. The bottles to be filled in 10% aqueous phases obtained from the pretreatment conditions were wrapped with foil to prevent light transmission so that anaerobic disintegration could take place. All aqueous phases were grafted to achieve methane formation. The bottles in which the samples and the vaccine solution were filled in were capped. Certain amounts of nitrogen gas were filled into the capped bottles in which certain amounts of samples were placed so that the oxygen in the bottles can be removed completely. Bottles were left to anaerobic biodegradation in an incubator set at 35 °C to ensure optimum conditions. The volume of biogas and methane emerging in the bottles placed in the incubator was measured with Orsat Gas Analyzer.

First of all, the biogas volume was determined at this device. The entire biogas was then taken up in the absorption column on the device with a CO_2 absorber 33% KOH solution through a level bottle, and then the gas was flushed several times with this solution to assure the absorption of all CO_2.

The reaction of CO_2 with KOH is given in the following equation.

$$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O \quad (1)$$

The remaining gas was then passed to the burette where the other gas level on the instrument was measured, and the methane volume was read here.

3. Results and Discussion

Figure 1 shows the change in the water solubility percentages by mass based on the applied pretreatments.

PRETREATMENTS (Water Solubility):

1. Un-pretreated raw manure
2. 30 minutes MD
3. 15 minutes HP
4. 10% NaOH addition
5. 20% NaOH addition + 15 minute HP
6. 10% NaOH addition + 15 minute MD
7. 15% NaOH addition + 15 minute HP
8. 15% NaOH addition + 30 minute MD

As is shown in Figure 1, the best pretreatment condition in which cow manure dissolved was 20% NaOH addition for 15 minutes HP pretreatment with 92.8% value. All pretreatments increased the water solubility of solid material.

According to pretreatments, the change in the volumetric cumulative biogas amounts per gram of dry solids in standard conditions is given in Figure 2.

PRETREATMENTS (Biogas Production):

1. 10% NaOH addition
2. 15% NaOH addition + 30 minute MD
3. 20% NaOH addition + 15 minute HP
4. 10% NaOH addition + 15 minute MD
5. 15% NaOH addition + 15 minute HP
6. 30 minutes MD
7. 15 minutes HP
8. Un-pretreated raw manure

When the cumulative biogas amounts obtained at the end of the anaerobic treatment was examined, it was observed that the highest amount of biogas was obtained from 15% NaOH addition + 30 min MD pretreatment condition with 378 mL value. The methane content of the biogas obtained in this pretreatment condition was 41%. Under all conditions, there was an increase in the amount of biogas production compared to that of the unprocessed raw cow manure.

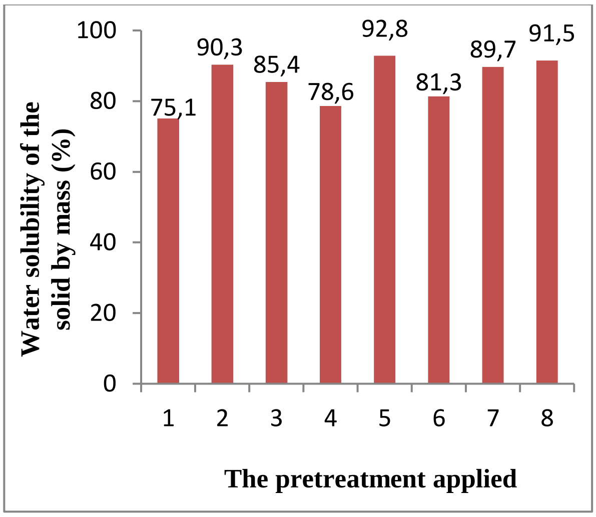

Figure 1. The change in water solubility percentage of solid material as a result of pretreatments

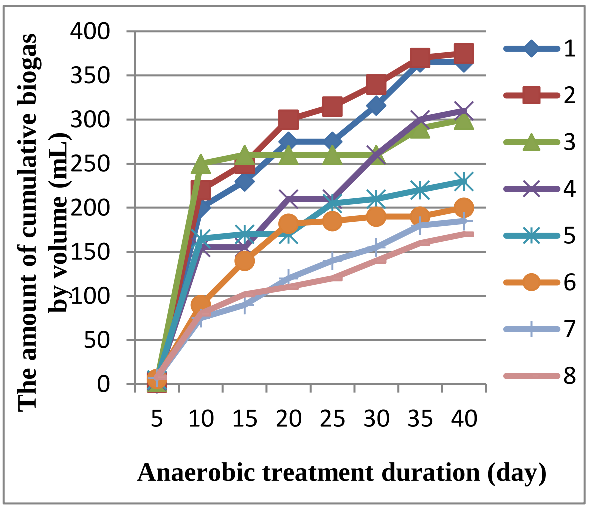

Figure 2. The change in cumulative biogas quantities

4. Conclusion

As a result of the study, it was found that the best water solubility was achieved with 20 % NaOH addition + 15 minutes HP pretreatment which yielded 92.8% achievement. All the pretreatments were shown to increase water dissolution.

The highest amount of cumulative biogas was obtained from 15% NaOH addition + 30 min MD pretreatment condition with 378 mL value. The biogas production yields obtained from all pretreatments were higher than that of the un-pretreated sample. All pretreatments increased biogas production efficiency as well as increasing water dissolution. Thus, the positive effects of pretreatments on the biogas production efficiency were revealed.

When compared to similar studies, the results of this study indicated that pretreatments increased water dissolution and biogas production. Given the positive effects of both chemical and thermal pretreatments on biogas production, applying these pretreatment conditions in biogas production plants will make a great contribution to production and provide economic benefits.

In conclusion, biogas production from animal wastes provides both electricity and heat production, as well as providing many positive social, economic and environmental results.

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