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BIOMETHANE POTENTIAL OF SAFFLOWER HARVEST RESIDUES

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Abstract

Residues from agricultural production are sources of raw material for biomass energy. Biogas technology allows organic waste/residues to be recovered. Safflower harvest residues (SHR) are resulted from safflower production. The purpose of this study is the assessment of the methane volume obtainable from SHR with dairy manure (DM) in the anaerobic fermentation process. Five mixtures of SHR and DM were prepared considering the mixing ratio (miR= SHR/(SHR+DM), dry basis, as 0.06, 0.27, 0.49, 0.74, and 1.0. Batch fermentation test was carried out in bioreactors made of eighteen 2-L flasks located in a temperature controlled water bath with a dimension of 80 x 60 x 20 cm. The mixing of each bioreactor was done by mechanical rotating mixers driven by motor coupled with 10 rpm output gearbox. During the experiment, methane (CH_4), carbon, nitrogen, pH, EC, dry matter, and organic matter were measured. The results were presented in the study.

***Key words**: Biogas process, dairy manure, safflower harvest residues, biomethane potential.*

INTRODUCTION

The main determinants of economic growth, social development and quality of life for communities are energy and energy use. Today, energy needs due to emerging technologies and demographic and economic growth are rapidly increasing not only in the world but also in Turkey (Tuncer et al., 2006; Acaroglu, 2007; Akova, 2008; Yearling et al., 2010; Yilmaz, 2012; Aries and Şenel 2013, Aybek et al., 2015). Much of the energy demand in the world is covered by fossil sources (oil, coal and natural gas) (Onurbaş Avcıoğlu et al., 2011; Yılmaz, 2012).
Vast majority of energy needs are met by fossil fuels. Emissions from these fuels have a large share in global warming due to greenhouse effect leading to the shift of research into renewable energy sources (Koç and Şenel, 2013). Biomass has an important place under renewable energy resources. Biomass is defined as non-fossil organic matter of biological origin (Üçgül and Akgül, 2010; Yılmaz, 2012; Basu, 2010). Biomass energy is transformed into energy sources such as biodiesel, bioethanol, biogas by various technological methods (Akova, 2008; Öğüt, 2007). Organic materials with methanogenic bacteria can be converted to biogas in an anaerobic environment (by anaerobic fermentation). Biogas is formed as a product of anaerobic material degradation and contains 60-75% methane (CH_4), 23-38% carbon dioxide (CO_2), 2% hydrogen (H_2) and 2% hydrogen sulphide (H_2S) depending on the organic substance (Edelmann et al., 2005).
Biogas technology allows both the energy obtained as a result of organic origin waste and the waste to be imparted as an organic fertilizer throughout fermentation progresses.
Assessment of organic matter residues is important for environmental pollution and clean energy production. For this purpose, the most common source for use in developing countries is biomass. Approximately 15% of world energy consumption and about 43% of energy consumption in developing countries are provided with biomass (Başçetinçelik et al., 2007).
Turkey is an important agricultural country with high potential in terms of both crop and animal production. With the biogas technology and production, an economic input in terms of energy will be provided to rural development with the sustainable quality of the environment by reducing harmful wastes.
In 2016, there were also 14 223 million head of cattle in Turkey (TurkStat, 2016). In light of these data, Turkey's cattle manure potential is

approximately 611 589 tons per year. SHR exists after harvest of safflower in the field. This study aimed to determine biogas potential of SHR with DM at five different mixing ratios. The result of this study could help biogas designer/decision maker on the utilization of safflower stalk residues with dairy manure.

MATERIALS AND METHODS

This study was conducted at the Compost and Biogas laboratory Süleyman Demirel University (SDU). Research involves SHR and DM. DM was collected from Dairy Farm at Agricultural Application and Research Center at SDU. SHR was obtained from a farmer in Isparta. The anaerobic digestion test was carried out using a Biomethane Potential Test Unit. Batch fermentation test was carried out in bioreactors made of eighteen 2 L flasks located in a temperature controlled water bath with a dimension of 80 x 60 x 20 cm. It consists of a 1500 W electrical heater, circulation pump and water reservoir. The mixing of each bioreactor was done by mechanical rotating mixers driven by 12 V DC motor coupled with 10 rpm output gearbox.

During the study, the mixers were set to run with a cycle of 1 minute on - 29 minutes off. SHR was dried in the solar tunnel drier at Agricultural Machinery and Technology Engineering Department, Faculty of Agriculture at SDU. Dried SHR was milled with an industrial mill. Inoculum was obtained from previous experiment. The inoculum, a mixture of liquid+solid phase, was prepared in a 50 L tank at 37°C.

In the study, the grinded SHR samples were placed in 2 L glass bottles with 3 replicates at different mixing ratios and then placed in a water bath (37°C). The bottles prepared at different mixing ratios were connected to 5 L biogas bags.

The mixing ratio (dry weight basis) was defined as miR = SHR/(SHR+DM). The selected miR values was 0.06, 0.27, 0.49, 0.74, and 1.0. Initial physical and chemical properties of feedstocks are given in Table 1. The amount of SHR, DM, and inoculum used in mixes (dry weight basis) and the resultant miR and C/N ratio are given in Table 2. Prepared samples were analyzed for dry matter content (DMC) (AOAC, 1990) and organic matter (OM) (AOAC, 1990). pH and EC of the fresh samples were extracted by shaking at 180 rpm for 20 min at a solid: water ratio of 1:10 (w/v), and measured using pH and EC meters (Models WTW pH 720 and WTW Multi 340i), respectively.

Total carbon (C) and nitrogen (N) of samples were analyzed using CN analyzer (Vario MACRO CN Elemental analyzer). The biogas volume was determined using a gas meter (Ritter, Bochum, Germany). Methane (CH_4) concentration was measured using a sensor (PIR 7200 Draeger).

After the measurements were made on 3, 5, 7, 11, 17, 25, 35, and 47 days, the experiment was terminated.

Table 1. Initial physical and chemical properties of feedstock's

Parameters	SHR	DM	Inoculum
DMC, %	90.83±0.10[c]	18.17±0.60	6.99±0.52
OM, %	92.45±0.15	85.07±0.19	73.26±0.11
EC, µS/cm	3.18±0.01	7.43±0.03	11.60±0.21
pH	6.96±0.12	6.80±0.09	7.88±0.13
C, %	51.36±0.53	43.47±0.10	23.13±0.12
N, %	1.27±0.13	1.46±0.03	1.98±0.15

Table 2. Compositions of feedstock's used to formulate mixes

Mix	SHR kg/kg	DM kg/kg	Inoculum kg/kg	miR -	C/N ratio
Mix-1	0.561	0.000	0.439	1.00	24.66
Mix-2	0.433	0.154	0.413	0.74	22.75
Mix-3	0.303	0.310	0.387	0.49	20.83
Mix-4	0.171	0.469	0.360	0.27	18.92
Mix-5	0.006	0.629	0.333	0.06	17.00

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RESULTS AND DISCUSSIONS

Initial and final values of DMC, OM, pH, and EC values were given in Table 3. In the starting mixtures; DMC was the highest in Mix-2 (8.97%) and Mix-5 (7.36%) was the lowest, OM was the highest in Mix-2 (87.02%), lowest in Mix-5 (83.97%), the pH value was the highest in Mix-2 (7.89) and the lowest in Mix-1 (6.97), and EC values were the lowest in Mix-4 (10.61 µS/cm). At the end of the experiment, DMC was the highest in Mix-5 (5.79%) and Mix-1 (5.24%) was the lowest, OM were the highest in Mix-2 (77.47%) and the lowest in Mix-1 (67.40%), the pH values were the highest in Mix-4 (7.73%) and the lowest in Mix-1 (6.97%), and EC values were the highest in Mix-4 (13.39 µS/cm) and the lowest in Mix-1 (10.57 µS/cm). The result showed that DMC, OM, and EC values of mixes increased at the end of the experiment. However, there was no clear trend in terms of pH (Table 3).

Table 3. Initial and final DMC, OM, pH and EC values of mixes

Mix	Initial DMC %	Final DMC %	Initial OM %	Final OM %	Initial pH	Final pH	Initial EC µS/cm	Final EC µS/cm
Mix-1	8.84	5.24	85.25	67.40	7.85	6.97	9.14	10.57
Mix-2	8.97	5.74	87.02	77.47	7.89	7.69	9.60	11.09
Mix-3	8.12	5.52	86.30	75.86	7.61	7.51	10.24	12.32
Mix-4	7.58	5.47	85.24	75.87	7.31	7.73	10.61	13.39
Mix-5	7.36	5.79	83.97	75.78	7.25	7.58	10.53	12.49

Methane measurement

CH_4 content (%) as a function of time could be divided into two phases (Figure 1). The first phase (day 0-3) was characterized by a rapid hydrolysis stage where low concentrations of CH_4 were detected since the phase was designed to decompose the principal constituents of the SHR and DM. Then, CH_4 content of biogas sharply increased to > 54% for all mixes.

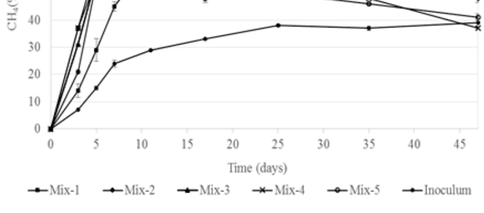

Figure1. Time - dependent methane ratios of mixtures

The level of CH_4 content for all mixes fluctuated between 37% and 60%. It could be said that the level of CH_4 measured for Mix-4 was always higher than the other mixes during the experiment.

Biogas and methane production

The time - dependent daily biogas and CH_4 production of the inoculum and the mixtures are given in Figure 2. The daily biogas and CH_4 production of the mixtures reached maximum values within 3-7 days, starting from day 1. The highest daily biogas and CH_4 production in mixtures were in Mix-5 between 4-6 days and Mix-4 between 4-5 days. The lowest daily biogas and CH_4 production in mixtures were in Mix-1 (Figure 2).

Cumulative biogas and CH_4 production of the mixture and inoculum over time are shown in Figure 3.

Cumulative biogas production was the average of 3 samples measured for each mixture. The gas production in the mixtures started on the first day and reached the maximum biogas and CH_4 production towards 47th day.

The highest cumulative biogas production value was in Mix-2, and the lowest cumulative biogas production value was in Mix-1.

The highest cumulative methane production value was in Mix-2, and the lowest cumulative methane production value was in Mix-1 (Figure 3).

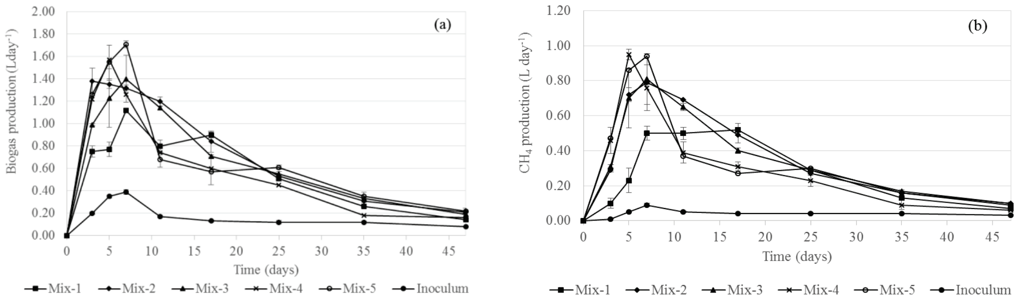

Figure 2. Daily biogas and CH_4 production as a function of time

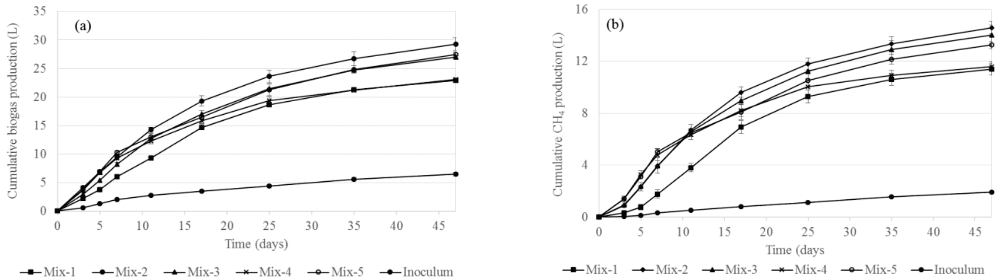

Figure 3. Cumulative biogas and CH_4 production as a function of time

The cumulative specific CH_4 production rates of mixtures after subtracting the contribution of inoculum is given in Figure 4.

The specific CH_4 productions were determined for Mix-1 through 5 as 205.31, 249.39, 218.22, 159.59, and 167.73 NmLg^{-1} OM, respectively.

The reported range of specific CH_4 productions in this study are in agreement with those 167 mL/g OM (Amon et al., 2006), 125-166 mL/gOM (Amon et al., 2006), 317 mL/g OM (Zhang et al., 2013) and 271 mL/g OM (Frauke et al., 2015).

It should be noted that no pre-treatment were applied to initial material (substrates and digested dairy manure) for CH_4 production.

As a result of this study, the specific methane production values of SHR and DM mixtures are between 159.6-249.4 NmL/g OM.

In this study, methane production from DM (Mix-5) was found to be 167.7 NmL/g OM

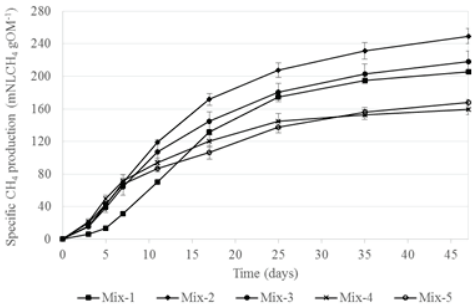

Figure 4. Cumulative specific methane production as function time for all mixes

Specific methane production ($CH_{4,cum}$) as a function of miR

In the study, a Gaussian model was used to determine the best mix of specific methane production ($CH_{4,cum}$) (Figure 5). Gaussian curve was applied to $CH_{4,cum}$ at different miRs. $CH_{4,cum}$ as a function of miR was correlated and the resultant equation with R^2=0.96 (Eq.1) showed that the highest $CH_{4,cum}$ occurred at the miR of 0.73 corresponding to Mix-2. $CH_{4,cum}$ as a function of miR is given in figure 5.

$$CH_{4,cum} = 160.28 + 92.04\ e^{-0.5\left[\frac{miR-0.73}{0.22}\right]^2} \qquad (1)$$

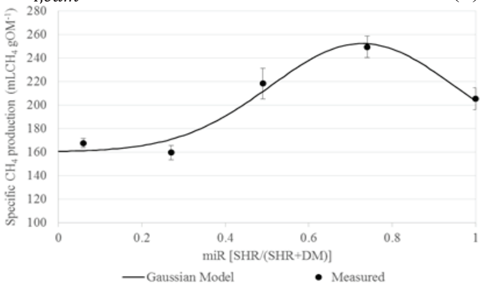

Figure 5. Gaussian model of specific methane production in mixtures

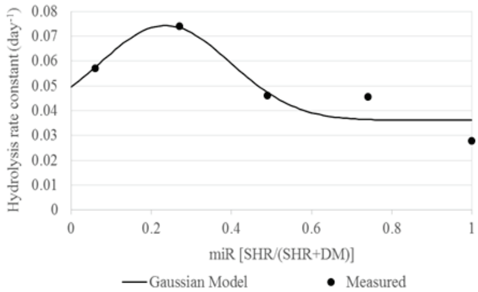

Figure 6. Hydrolysis rate constants of mixtures as a function of miR

Hydrolysis rate constant as a function of miR

The hydrolysis rate constant (K_h) of each mixes was determined using the first-order kinetic model of Eq. (2).

$$CH_{4,cum}(t) = M_{max}[(1 - \exp(-Kh.t)] \qquad (2)$$

Where $CH_{4,cum}$ (t) is the specific methane production at digestion time t days (NmL g^{-1}OM), M_{max} is the potential maximum methane production at the end of digestion (NmL g^{-1}OM). Sigmaplot™ program was used to predict K_h and M_{max}.

The predicted K_h value for Mix-1 through 5 was 0.0279, 0.0455, 0.0461, 0.074, and 0.0571 day^{-1}, respectively. Gaussian curve was applied to K_h at different miR. K_h as functions of miR was correlated and the resultant equation with R_2=0.87 (Eq.3) showed that the highest K_h occurred when miR=0.24. K_h as functions of miR is given in Figure 6.

$$K_h = 0.036 + 0.038\ e^{-0.5\left[\frac{miR-0.24}{0.16}\right]^2} \qquad (3)$$

The Gaussian model was used to determine the change in hydrolysis rate constant of the mixtures (Figure 6).

The modeling result shows that the mixture with the highest hydrolysis rate constant was in Mix-4 and the lowest hydrolysis rate constant was in Mix-1 (Figure 6).

CONCLUSIONS

The results obtained from this research for the experimental determination of the biogas production potential of dairy manure and safflower harvest residue can be summarized as follows:

1. At the end of the experiment; DMC, OM, decreased, EC increased;
2. Cumulative maximum biogas and methane production was in Mix-2, and minimal biogas and methane production was in Mix-1;
3. Specific maximum methane production was found in Mix-2 (249.4 NmL/g OM);
4. Daily biogas and methane productions of different types of dairy manure and safflower harvest residue prepared at different mixing ratios are different;
5. Methane ratios increased with time and then decreased;
6. In the study, it was found that the best mix ratio of the Gaussian model was Mix-2.

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