

## **Optimum Solid Loading Rate for Biogas Production from Agricultural Wastes**

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**Abstract:** Turkey was the fourth and third largest producer of tomato and pepper from greenhouses, respectively, according to FAO in 2012. The huge amount of agricultural wastes generated from the production of tomato and green pepper are served as renewable sources for energy production via anaerobic digestion (AD). For efficiently biogas production, it is essential to determine the operation conditions of AD such as solid loading rate (SLR) for target wastes.

The aim of this study is to optimize SLR for optimum biogas production from tomato and green pepper wastes. For this purpose, biochemical methane potential tests were carried out at 37 °C with 7% and 15% of SLRs. For supplying the nutritional requirements of AD process, cow manure was also added as a 10% of the selected SLR. As the biogas production from tomato wastes was nearly 75% increased with the increase in SLR from 15% to 7%, the optimum SLR was determined as 7% for anaerobic digestion of tomato wastes. On the other hand, decreasing SLR of pepper waste from 15% to 7% is resulted with only 11% decrease in biogas production. When the energy revenue between the 7% and 15% SLRs is compared with disposal cost of nearly two-fold pepper wastes, suitable SLR for pepper wastes can be suggested as 15%. Consequently, the optimum SLR for anaerobic digestion of tomato and pepper was determined as 7% and 15%, respectively.

**Key words:** Agricultural wastes, biochemical methane production, solid loading rate, anaerobic digestion

### **INTRODUCTION**

Tomato and pepper production in Turkey is carried out both open and greenhouse cultivation in many areas. Pepper (*Capsicum annum* L.) and tomato (*Lycopersicon esculentum*) which is located in Solanaceae family, because of their high nutritional value and to rise rapidly production is quite important vegetable crops. According to Turkish Statistics Institute survey, total tomato and pepper production in Turkey were 11,820,000 tons and 2,159,348, respectively, in 2013 (TUIK, 2013).

Anaerobic digestion (AD) is a process which breaks down organic matter in simple chemical components without oxygen. This process can be very useful to treat organic waste such as; sewage sludge, organic farm wastes, municipal solid wastes, green wastes, organic industrial and commercial wastes. Energy generated

through AD can help reducing the demand for fossil fuels. On a financial aspect, the advantage of AD is to convert residues into potentially saleable products: biogas, soil conditioner, liquid fertilizer. It can be also contribute to the economic viability of farms by keeping costs and benefits within the farm if the products are used on-site (Monnet, 2003).

Co-digestion is a anaerobic digestion method for the removal of the different wastes together (Ağdag and Sponza, 2007). Co-digestion is used for improving yields of anaerobic digestion of solid organic wastes due to its benefits. For example, dilution of toxic compounds, increased load of biodegradable organic matter, improved balance of nutrients, synergistic effect of microorganisms and better biogas yield are the potential benefits that are

achieved in a co-digestion process (Khalid et al., 2011). Co-digestion of organic wastes accelerates biodegradation process through biostimulation with providing excess amount of nutrients (Hartmann and Ahring, 2005). The main benefits of co-digestion can be summarized as the facilitation of a stable and reliable digestion performance, the production of a digested rich in nutrients, and an increase in biogas yield (Khalid et al., 2011).

The aim of this study is to optimize solid loading rate (SLR) for optimum biogas production from tomato and green pepper wastes. For this purpose, biochemical methane potential tests were carried out at 37 °C with SLRs of 7% and 15%. For supplying the nutritional requirements of AD process, cow manure was also added as a 10% of the selected SLR. Furthermore, hydrolysis and overall reaction rate constants of anaerobic co-digestion of tomato or pepper wastes with cow manure were evaluated by using first order reaction kinetic model.

## **MATERIALS and METHOD**

### **Agricultural Wastes and Characterization Analysis**

Greenhouse residues, harvested in Jan 2014, were provided from research greenhouses belonging to Akdeniz University. The greenhouse residues primarily consisted of roots, stalks, leaves and fruits from tomato and pepper cultivation were grounded to 4–5 mm particle size, are stored in sealed plastic bags at –20 °C until used for BMP experiments. The cow manure was obtained from the research farm of Agricultural Engineering Department of Akdeniz University. The cow manure is also stored at at –20 °C until used for BMP experiments.

Before the BMP tests, characterization analysis were carried out with tomato, pepper and manure. The analyses of dry matter (TS), organic matter (VS), chemical oxygen demand (COD) were performed according to standard methods (APHA, 1995). Carbohydrate concentration was determined as glucose by Anthrone method based on quantifying the carbonyl functions (C=O) (Dreywood, 1946). Protein concentration was determined according to Lowry method (Lowry, 1951). The characterization analysis results of tomato and pepper wastes and also cow manure are presented in Table 1.

Batch biochemical methane potential (BMP) tests were carried out at two Solid Loading Rate (SLR), to compare effect of SLR on the methane production

from the tomato or pepper wastes. The SLRs was selected as 7 and 15% as a dry matter basis for BMP tests. For supplying the nutritional requirements of AD process, cow manure was also added as a 10% of the selected SLR.

### **Biochemical Methane Potential Test**

Methane production was measured with batch BMP tests in mesophilic (37°C) conditions following the procedures established by Carrere et al. (2009). Mixture of tomato or pepper wastes and manure were put into 500 mL reactor with anaerobic seed sludge, from anaerobic digester of Hurma municipal wastewater treatment plant (Antalya, Turkey). The food to microorganisms (F/M) ratio was set as 0.5 (gVS waste /gVS anaerobic seed sludge) with the solid concentration of 3-5 gVS/L in BMP bottles. The oligo nutrients and buffer solution were supplied in BMP bottles as follows (the concentrations are presented in mg/L in parenthesis): NaHCO<sub>3</sub> (2600), NH<sub>4</sub>Cl (172), KH<sub>2</sub>PO<sub>4</sub> (65), MgCl<sub>2</sub>. 6H<sub>2</sub>O (39), CaCl<sub>2</sub>.2H<sub>2</sub>O (19), FeCl<sub>2</sub>.4H<sub>2</sub>O (20), CoCl<sub>2</sub>.6H<sub>2</sub>O (5), MnCl<sub>2</sub>.4H<sub>2</sub>O (1), NiCl<sub>2</sub>.6H<sub>2</sub>O (1), ZnCl<sub>2</sub> (0.5), H<sub>3</sub>BO<sub>3</sub> (0.5), Na<sub>2</sub>SeO<sub>3</sub> (0.5), CuCl<sub>2</sub>.2H<sub>2</sub>O (0.4), Na<sub>2</sub>(Mo)O<sub>4</sub>.2H<sub>2</sub>O (0.1). The pH of all batch experiments was set to neutral pH at the beginning of the BMP test. Triplicate bottles for BMP analysis were set for all samples. The BMP tests were also performed with inoculum to take into account the biomethane produced by anaerobic seed sludge. For calculating the normalized cumulative methane potential for each sample, the amount of methane produced by inoculum was subtracted.

The headspace of reactors was flushed with Nitrogen/Carbon dioxide (N<sub>2</sub>/CO<sub>2</sub>, 70/30%) mixture gas to obtain anaerobic condition. BMP reactors were incubated at 37°C and tests lasted until the biomethane production become insignificant. The volume of biogas was measured by water displacement device and its composition was determined using gas chromatography (GC, Varian 4900) equipped with a thermal conductivity detector (TCD) and 10 m PPQ column. The temperature of injector port, detector and column oven were 150, 145 and 150 °C, respectively. Nitrogen was used as the carrier gas at a flow rate of 25 mL/min.

A gas standard consisting of 60% (v/v) CH<sub>4</sub> and 40% of CO<sub>2</sub> was used for calibration.

**Table 1. Characterization of tomato and pepper wastes and cow manure**

| Parameter                      | Tomato | Pepper  | Cow Manure |
|--------------------------------|--------|---------|------------|
| TS (gTS/kgSample)              | 158.77 | 128.43  | 193.70     |
| VS (gVS/kgSample)              | 132.44 | 104.35  | 149.64     |
| COD (mg COD/gVS)               | 561.57 | 1154.14 | 2072.93    |
| sCOD (mg COD/gVS)              | 301.17 | 258.70  | 300.72     |
| Carbohydrate (mg Glucose/gVS)  | 129.76 | 92.54   | 590.14     |
| sCarbohydrate (mg Glucose/gVS) | 43.80  | 69.39   | 56.20      |
| Protein (mgPro/gVS)            | 280.75 | 416.50  | 320.05     |

### Mathematical Modelling

As the hydrolysis is a rate limiting step in anaerobic digestion, the hydrolysis rate constants ( $k_H$ ) were determined for each BMP results by evaluating the hydrolysis period of anaerobic digestion with first-order reaction kinetic model. Additionally, overall reaction rates ( $k_R$ ) constants including hydrolysis, acidogenesis and methanogenesis were determined by first-order kinetic model with the simulation of overall anaerobic digestion period. Model simulations were performed using the AQUASIM 2.0 (Reichert et al., 1998). Aquasim was chosen as a model tool because of its flexibility in allowing the user to specify transformation processes. The parameters  $k_H$  and  $k_R$  were estimated for each model by comparing the simulated results with the measured BMP data, according to the best fit. The parameters were estimated by weighted least squares method. Model parameters were estimated by minimizing the sum of the squares of the weighted deviations between measurements and simulated model results. The optimization process ended when the change in the residual was less than the specified tolerance set on  $1e^{-9}$ .

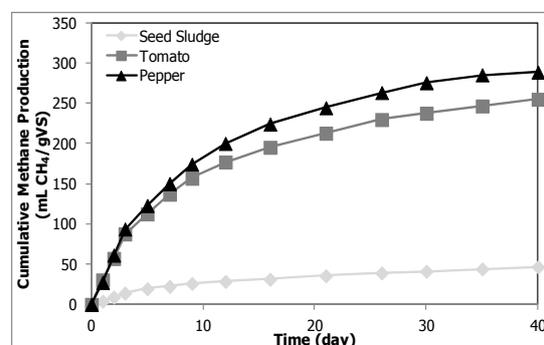
## RESULTS and DISCUSSION

### Effect of SLR on Anaerobic Digestion

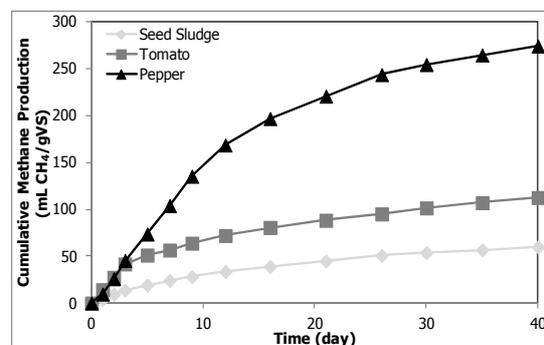
Since the anaerobic digestion of complex lignocellulosic biomass containing cellulose, hemicellulose and lignin is difficult, co-digestion process has gained attention currently. Manure and plant materials are co-digested in an anaerobic digestion process in successful way. By this way, the materials complement each other and the risk of inhibition can be eliminated. The manure fraction provides a wide range of nutrients while the high carbon content of the plant materials results in a balanced carbon/nitrogen ratio of the feedstock being loaded in the digester (Lehtomaki et al., 2007). For

this reason, cow manure was used as co-substrate during the BMP tests carried out with agricultural wastes.

Since processing the more waste with anaerobic digestion is beneficial in terms of the environmental protection and energy production, it is decided to use high Solid Loading Rate (SLR) values in the co-digestion process. To observe the effects of high Solid Loading Rate (SLR) on biogas production, BMP experiments were performed at 7% and 15% SLR. The cumulative biochemical methane productions as mL  $CH_4$ /g VS obtained at the SLR of 7% 15% were illustrated in Figure 1 and Figure 2, respectively.



**Figure 1. The cumulative biochemical methane production at SLR of 7%**



**Figure 2. The cumulative biochemical methane production at SLR of 15%**

As seen from Figure 1 and Figure 2, nearly same amount of biomethane was produced from pepper wastes at 7 and 15% of SLR. This indicates that the optimum process SLR for the anaerobic digestion of pepper wastes should be applied as 15% from the environmental point of view.

The BMP's of the agricultural wastes were normalized with subtracting the biomethane produced by seed sludge. The comparison of the normalized biomethane productions were illustrated in Figure 3.

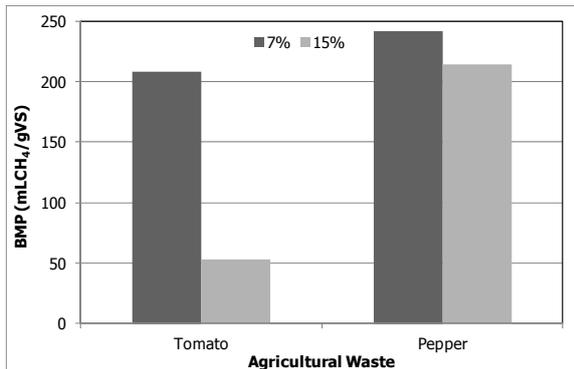


Figure 3. The normalized BMP of agricultural wastes

As seen from Figure 3, more biogas produced from the tomato wastes when BMP test were performed with SLR of 7% instead of 15%. This revealed that increase in SLR created negative effect on the anaerobic co-digestion of tomato wastes. The accumulation of inhibiting substances such as fatty acids in the digester at high SLR was reported by Vandevivere (1999). Therefore, the optimum SLR was determined as 7% for anaerobic digestion of tomato wastes.

The maximum biometan productions were measured as  $255.13 \pm 12.37$  mL CH<sub>4</sub>/gVS and  $288.74 \pm 6.98$  mL CH<sub>4</sub>/gVS at the SLR of %7 for tomato and pepper. Generally, the anaerobic digestion were implemented on the mixture of these agricultural wastes with other agricultural residues and therefore, the operational parameters was not investigated for anaerobic digestion of tomato or pepper wastes alone.

Only one report on the individual biogas production from tomato and pepper wastes was able to be compared with results of this study. In this recent study, the biogas productions were measured as  $279.8 \pm 42.26$  mL CH<sub>4</sub>/g VS for pepper and  $276.9 \pm 37.74$  mL CH<sub>4</sub>/g VS for tomato (Ferrer et al., 2014). This methane potentials are very similar with the methane productions measured in this study.

### Effect of SLR on the Anaerobic Digestion Kinetic

For evaluating the effect of SLR on the kinetic of anaerobic digestion, the BMP results of co-digested tomato or pepper wastes with cow manure were analyzed by first order reaction kinetic model (Equation 1) (Llabres-Luengo and Mata-Alvarez, 1987).

$$M_p = P_M (1 - \exp[-k_h \times t]) \quad (1)$$

The hydrolysis rate constants ( $k_H$ ) were determined by simulating the BMP data of first 3 days, as the hydrolysis period completed in first three days according to Figure 1 and Figure 2. The accuracy of simulation results were ascertained by regression coefficients obtained between the measured data and model results as shown in Figure 4 (a) and (b).

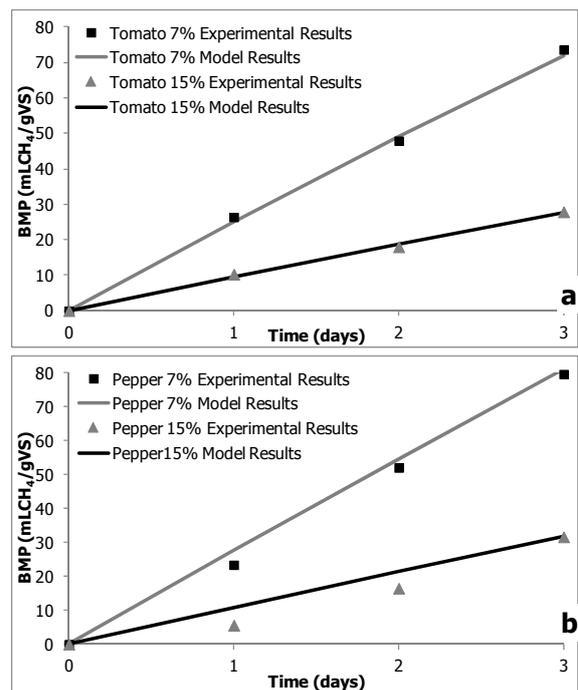
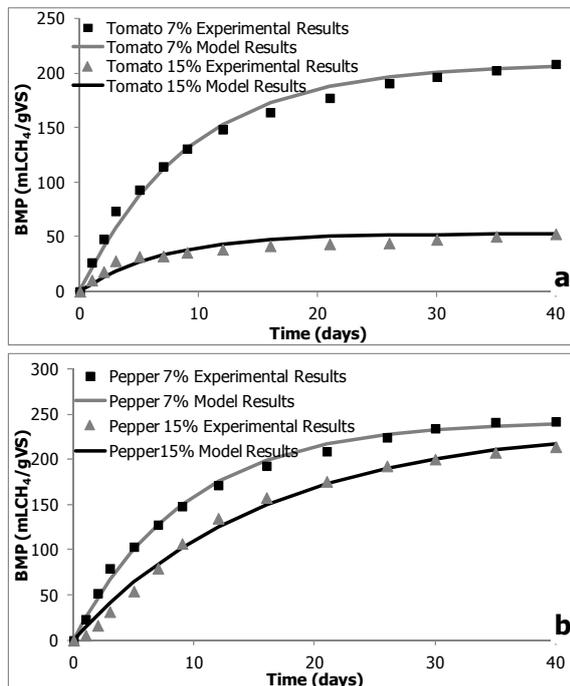


Figure 4. The simulation results to obtain  $k_H$  for anaerobic digestion of (a) tomato (b) pepper

After the determination of the  $k_H$  value for each BMP result, overall reaction rate constants were determined by first order reaction kinetic model by minimizing the sum of the squares of the weighted deviations between all measured BMP data and simulated model results. The simulation results were given in Figure 5 (a) and (b).



**Figure 5. The simulation results to obtain  $k_R$  for anaerobic digestion of (a) tomato (b) pepper**

As seen from Figure 5, the BMP results were adequately fit by first order reaction kinetic. The hydrolysis and overall reaction rate constants and their regression coefficients determined from the modeling studies were presented in Table 2.

**Table 2.  $k_R$  and  $k_H$  values for co-digested tomato or pepper wastes with cow manure**

| Agricultural Waste | $k_R$ (d <sup>-1</sup> ) | $R^2$   | $k_H$ (d <sup>-1</sup> ) | $R^2$   |
|--------------------|--------------------------|---------|--------------------------|---------|
| Tomato (SLR: 7%)   | 0.10994                  | 0.99447 | 0.04852                  | 0.9984  |
| Tomato (SLR: 15%)  | 0.14270                  | 0.94732 | 0.03616                  | 0.99738 |
| Pepper (SLR: 7%)   | 0.10683                  | 0.99648 | 0.02251                  | 0.99741 |
| Pepper (SLR: 15%)  | 0.06301                  | 0.99486 | 0.02910                  | 0.95939 |

The hydrolysis rate constant of co-digested tomato and cow manure was decreased from 0.05 to 0.04 while SLR was increased from 7% to 15 %. On the contrary, overall reaction constant was increased

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parallel to increase in SLR. Furthermore, biogas production from tomato wastes was nearly 75% decreased when SLR was increased from 7% to 15%. The reason of this result should be related to possible substrate inhibition.

## CONCLUSIONS

The study aimed to the evaluation of the optimum SLR for energy generation from the agricultural wastes via anaerobic co-digestion. According to the experimental result, the anaerobic co-digestion at a high SLR like 15% is reasonably good solution for disposal of wastes derived from the cultivation of pepper.

On the other hand, the high SLR negatively affected the biomethane production from the tomato wastes. Therefore, the co-digestion process should be operated at a moderate SLR for energy production from tomato wastes. According to experimental results, the optimum SLRs for the anaerobic digestion of tomato and pepper were suggested as 7% and 15%, respectively. The results obtained in this study should be regarded as as starting point for the studies on the biogas production from agricultural waste came out from local agricultural applications in Turkey.

The experimental results were analyzed by first order reaction kinetic model for evaluating the effect of SLR on the overall reaction kinetic constant and hydrolysis rate constant. The kinetic evaluation was indicated that although the overall rate constant was rise in direct proportion to SLR, the hydrolysis rate of tomato was adversely affected from increase in SLR. This observation may be explained with the substrate inhibition when the tomato was subjected to anaerobic digestion at the high SLRs.

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