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Producing Methane Enriched Biogas using Solvent Absorption Method

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Waste-to-energy (WTE) production is one of the sustainable solutions to fulfill energy demands and minimize the environmental problems associated with waste landfilling. This work investigates the biogas production and methane (CH_4) enrichment for anaerobic digestion (AD) of fruit and vegetable waste (FVW). The effect of pH and temperature were studied using a lab scale batch anaerobic digester. The raw biogas was pebbled through water, NaOH, $Ca(OH)_2$ and triethanolamine (TEA) for biogas purification and CH_4 enrichment. The results showed that mixed fruit waste (MFW) provides 10 % more biogas yield than mixed fruit vegetable waste (MFVW). The maximum biogas yield of 0.030 (g/g volatile solids) was achieved at thermophilic temperature (TT). The optimum pH range under mesophilic temperature (MT) and TT condition was in between 8.3 - 8.8. The use of NaOH, $Ca(OH)_2$ and TEA increased CH4 enrichment upto 5 %, 9 % and 7 %. Biogas having 71 % CH4 contents with 28 % reduced CO_2 and 150 ppm H_2S was produced using $Ca(OH)_2$.

1. Introduction

The energy provision is one of the limiting factor in economic growth of developing or under developed countries (Chaudhry et al., 2009). Pakistan is facing severe energy shortage and its annual import cost of energy in terms of fuel is around 7 billion US$, which is about 40 % of total imports (Heedge and Pandey, 2008). It is anticipated that Pakistan will face 29 % energy deficit in 2021-2022 (Amjid et al., 2011). The energy requirements will increase three times in 2050, while the developments on the supply side are not very inspiring (Asif, 2009). Therefore, there is a significant need of exploring and developing alternative renewable energy resources through research, science and development (Zafar et al., 2014).

Pakistan have immense resources of biomass such as sugarcane bagasse, wood, citrus pulp, slaughterhouse waste, poultry litter, dung and fences, municipal solid waste (MSW) and crop residues (Asif, 2009). However, the sustainable disposal of these waste sources is still at infancy. All of the collected waste is disposed in landfills or open dumpsites. There are several waste management strategies available in the world such as sanitary landfilling, recycling, composting, anaerobic digestion (AD), waste-to-energy (WTE) etc. (Wilson, 2008). The AD technology is one of the promising practices to treat organic solid wastes (Bouallagui et al., 2003).

The raw biogas contains (40 – 75 %) methane (CH_4), (15 - 60 %) of CO_2 as main components while water (5 -10%), H_2S (0.005 - 2 %), Oxygen (0 - 1 %), NH_3 (< 1 %), CO (< 0.6 %) and N_2 (0 – 2 %) are trace components. The composition of raw biogas depends on the feedstock and operational conditions (Lestinsky et al., 2014). The biogas produced from fruit and vegetable waste (FVW) contains about 65 % CH_4. The fractions other than CH_4 are known as contaminants and produces malodourous and toxic compounds, which deteriorate the biogas quality and atmospheric sustainability (Sitorus and Panjaitan, 2013). Therefore, it is necessary to remove CO_2 and other contaminant fractions to obtain biomethane (Gamba, 2013). There are several biogas purification and CH_4 enrichment technologies such as cryogenic separation, polyethylene glycol scrubbing, carbon molecular sieves, membrane separation,

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physical absorption, CO_2 fixation by chemical or biological methods and absorption by chemical solvents (Abatzoglou and Boivin, 2009). The chemical absorption method provides liquid/ gas contact for biogas purification and CH_4 enrichment (Zafar, 2014). This study aims to produce CH_4 enriched biogas from FVW by using chemical absorbents like NaOH, $Ca(OH)_2$ and triethanolamine (TEA).

2. Material and Methods

2.1 Reactor Set-Up

The polyglass reactor with 292 mm height and 152 mm inner diameter was used for AD (Figure 1). An inverted cylinder of 1 L and gas collecting bags of 2 L were used as gas recovery system. The supporting equipments include pipes, valves, thermocouples, heater blanket, water bath and control panel. Each piece of equipment is fabricated on stainless steel frame of 1,143 x 558 mm dimensions to make a lab scale AD system.

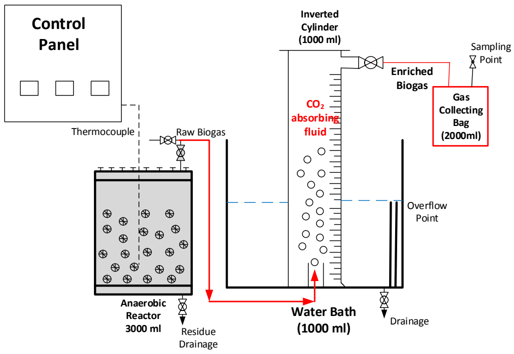


Figure 1: Process Flow Diagram

2.2 Substrate Preparation

The FVW was collected from canteens of University of Gujrat, Pakistan. The feed was prepared by chopping the FVW in meat mincer using disc hole size of 3/16". The mixed fruit waste (MFW) of banana, apple and orange is used in reactor 1 (R1), while mixed fruit vegetable waste (MFVW) of banana, apple, poes peels, potato peels and cabbage was fed in reactor 2 (R2). The first and second experimental schemes (S1 and S2) have 300 g waste and 1,700 g of water, whereas third and fourth schemes (S3 and S4) have 500 g of waste and 1500g of water. For biogas purification and CH_4 enrichment, the experimental schemes (S1-S4) used water, NaOH, $Ca(OH)_2$ and TEA. These chemicals have 1 molar strength and used in inverted gas collecting cylinder.

2.3 Experimental Schemes

Four different experimental schemes S1, S2, S3 and S4 were performed. Each scheme has two reactors R1 and R2. The R1 is batch reactor filled with feed of MFW whereas, the R2 have MFVW as feedstock. The experimental schemes; S1 and S4 were operated under thermophilic temperature (TT) of 55 ^oC, while S2 and S3 were operated under mesophilic temperature (MT) of 35^{o}C with the help of a control panel. The hydraulic retention time (HRT) of 7 d were used in all schemes. The raw biogas from reactor is pebbled through absorbing liquids (AL) and stored in gas collecting bags.

2.4 Analytical Methods

An oven (Electrolux oven) was used for determining the moisture and dry solid (DS) contents of substrate. A furnace (Lenton thermal design EF11/8B) was used to determine the volatile solid (VS) contents of the substrates. A pH meter (Thomas scientific meter TC 325 pH) was used for measuring the pH values from the operational reactors. A digital weighing balance was used for measuring the weight of gas collection bags. A gas chromatography (GC-2010 gas chromatograph with head spacer and RGA arrangement) was used for analyzing the contents of CO_2, CH_4 and H_2S of biogas.

3. Results and Discussion

3.1 pH Variation and Biogas Production

The experimental schemes S1 and S4 were carried out under TT condition and their results of biogas production and pH variation for both R1 and R2 are shown in Figure 2 (a & g) and (b & h). While, the results of S2 and S3 schemes under MT condition are presented in Figure 2 (c & e) for biogas production and Figure 2 (d & f) for pH variation. The optimum pH in the S1 for both reactors (R1 & R2) was 8.4. The optimum pH range in S4 for R1 and R2 was 8.7 - 8.8. During day 2 to 4 of S4 operation, the pH remained in alkaline zone and then decreased to acidic zone for days 5 to 7. The pH variation in S2 for 7 d HRT is shown in Figure 2 (d). The R1 and R2 showed no biogas production during first 3 d at pH 5.7-6.7. The optimum pH zones in S2 for R1 and R2 were 8.4-8.5. The pH values in R1 and R2 at the end of 7^{th} d were 4.9 and 5.2. At this pH, no biogas production was reported in both reactors. It was observed in S2 that the biogas production initiated slowly at MT than TT. The variation in pH for S3 is shown in Figure 2 (f). For the first 3 d, the value of pH was in between 5.9-6.8 for R1 & R2. While, the optimum pH values in R1 and R2 was 8.3.

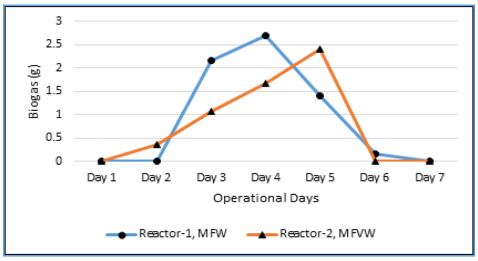
The methanogens and acetogens microbes show optimal efficiency in the pH ranges of 6.5 - 8.0 and 5.0 - 8.5 (Rao et al., 2010). Moreover, according to Boe and Angelidaki (2006) and Korres and Nizami (2013), the optimum pH range for anaerobic digester should be in between 7.0 - 8.5. The optimum observed pH in this study was 8.3 - 8.8, which is also in line with the above mentioned recommended range. The FVW have high biodegradability in AD system and can produce the volatile fatty acids (VFAs) in the reactor (Björnsson et al., 2001). The accumulation of VFA can function as a process indicator to assess the performance of the AD system (Nizami et al., 2009). The VFAs can lower the pH of the reactor, inhibit the microbial attack of methanogens bacteria and reduce the overall biogas yield (Nizami et al., 2012). These findings are in line with the results of this study that overall biogas yield was low for MFVW than MFW due to the VFA attack and consequently, the pH was decreased in the reactors down to 4 during 6^{th} and 7^{th} days (Figure 2).

3.2 Temperature Variation and Biogas Production

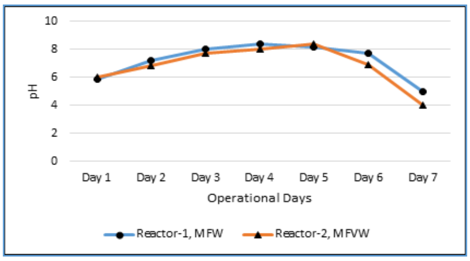
The biogas yield in g biogas/g volatile solids (VS) for all experimental schemes is shown in Figure 3(a). The experimental results showed that the S1 produced biogas upto 0.024 g/g VS from R1 and 0.02 g/g VS from R2. While, the S2 produced higher biogas yield (0.025 g/g VS from R1 was and 0.023 g.g VS from R2) than S1. The biogas yield in S3 was higher in comparison to S1 and S2; 0.028 and 0.024 g/g VS from R1 and R2. At TT in S4, the R1 had biogas yield upto 0.030 g/g VS, while R2 had biogas yield upto 0.028 g/g VS. Therefore, it is evident that S4 with higher feed waste (500 g) under TT produced highest biogas. Literature review shows that the microorganisms are sensitive to different toxic compounds and to disturbances at TT (Duran and Speece, 1997). While, the reaction rate at MT is slow but more robust (Schnürer and Jarvis, 2009). This study showed higher biogas production at TT, but the process of MT seems more stable, which is also according to the scientific literature (Suleman and Mahmood, 2014).

3.3 Biogas Purification and CH_4 Enrichment

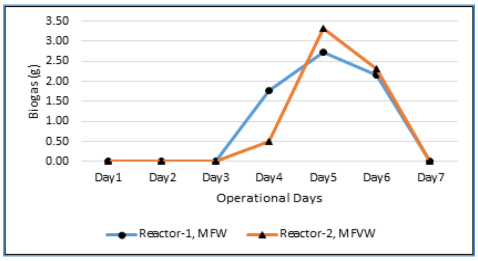
The gas samples of all experimental schemes were analyzed and characterized for the percentages of CO_2, CH_4 and H_2S (Figure 3b-d). The outcomes of S1 illustrated that the gas produced from R1 had 37.5 % CO_2, 62 % CH_4 and 200 ppm H_2S contents. On the contrary, the gas collected from R2 constituted 36.2 % CO_2, 63.4 % CH_4 and 250 ppm H_2S. The S2 produced 32 % CO_2, 67 % CH_4 and 100 ppm H_2S from R1, while the R2 produced the biogas which has 30 % of CO_2, 68 % of CH_4 and 150 ppm of H_2S. The results of S3 shows that the biogas produced from R1 had 28 % of CO_2, 71% of CH_4 and 150 ppm of H_2S. On the other hand, R2 produced the biogas which had 29 % CO_2, 70.2 % CH_4 and 155 ppm H_2S. The S4 indicates that the gas collected from R1 had 30 % of CO_2, 69 % of CH_4 and 120 ppm of CO_2, while from R2 these fractions were 31.5 % CO_2, 68.5 % CH_4 and 130 ppm of H_2S.



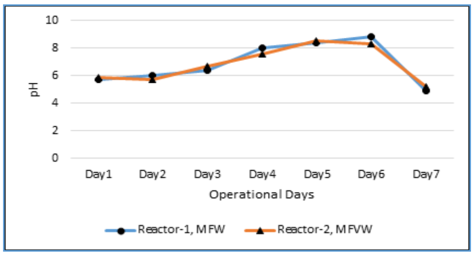
***(a)**. Biogas production for S1 @ 55°C with 300g of feed*



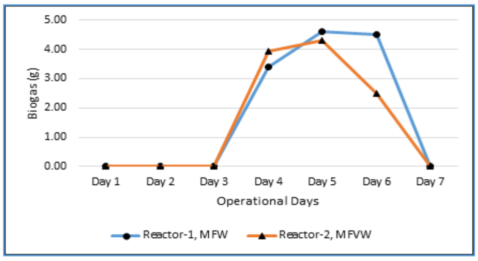
***(b)**. Average pH variation in S1 @ 55°C with 300g of feed*



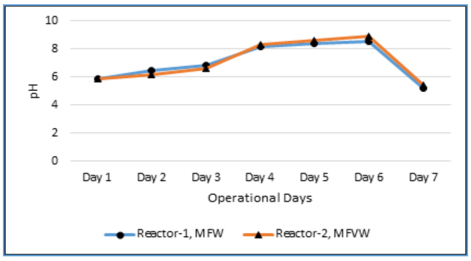
***(c)**. Biogas production for S2 @ 35°C with 300g of feed*



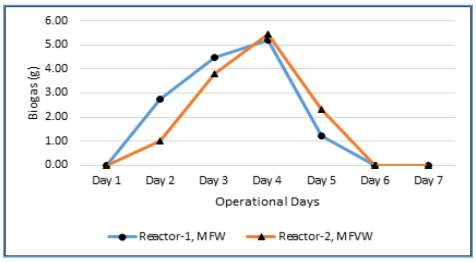
***(d)**. Average pH variation in S2 @ 35°C with 300g of feed*



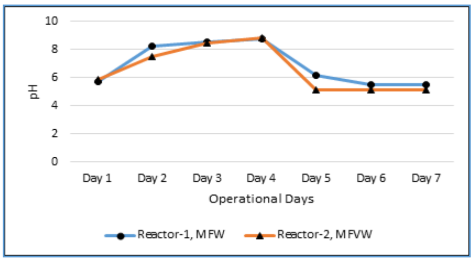
***(e)**. Biogas production for S3 @ 35°C with 500g of feed*



***(f)**. Average pH variation in S3 @ 35°C with 500g of feed*



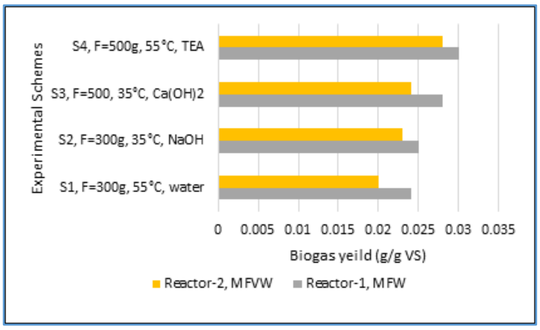
***(g)**. Biogas production for S4 @ 55°C with 500g of feed*



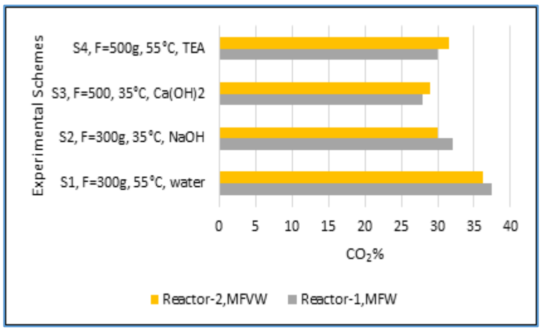
***(h)**. Average pH variation in S4 @ 55°C with 500g of feed*

Figure 2: Biogas production and pH variation under MT and TT conditions

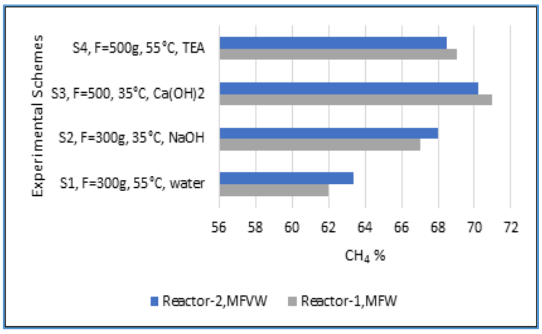
The CO_2 absorbing behavior of S1-S4 is very distinctive from each other. The method of water scrubbing for biogas purification is commonly used because of its availability and low cost (Björnsson et al., 2001). In S1, water was used as biogas purification liquid and its results were used as reference to compare with other experimental schemes (S2-S4). It was observed from the results of S2 that NaOH can provide 5 % more CH_4 enrichment than water. The results of S3 indicates that by using $Ca(OH)_2$, 9 % more CH_4 enrichment was possible compare to water. Moreover, the removal of additional 10% CO_2 and 95 ppm H_2S were also possible. The results of S4 demonstrates that it was possible to achieve additional 7 % CH_4 enrichment, 6 % CO_2 removal and 130 ppm reduction H_2S by using TEA than water. The CH_4 contents in biogas was achieved upto 65 % when using FVW (Sitorus and Panjaitan, 2013)**.** While this study achieved 71 % CH_4 contents (Figure 3c) with 28 % CO_2 and 150 ppm H_2S reduction using $Ca(OH)_2$. This reduction range is nearby with Rattanapan et al. (2009) observations that H_2S can be reduced upto 250 ppm.



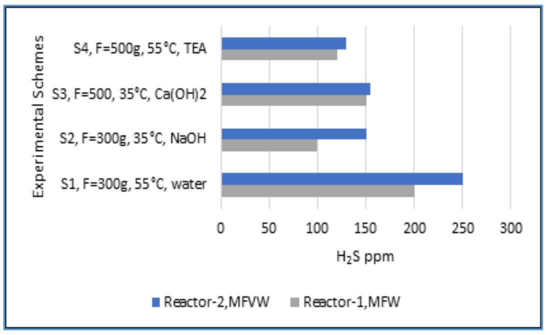
(a). Biogas Yield in all experimental schemes



(b). The contents of CO_2 in biogas from all systems



(c). The contents of CH_4 in biogas from all systems



(d). The contents of H_2S in biogas from all systems

Figure 3: Biogas yield and concentration of CH_4, CO_2 and H_2S in biogas

4. Conclusions

The fruit and vegetable waste were digested anaerobically for biogas production at MT and TT conditions. The CH_4 enrichment by removal of H_2S and CO_2 was also investigated. It was found that TT is more time saving factor with higher biogas yield (upto 0.030 g/g VS) than MT. The optimum pH for biogas production was in between 8.3 to 8.8. The highest level of CH_4 enrichment with 71 % CH_4 contents with 28 % CO_2 and 150 ppm H_2S removal was achieved with $Ca(OH)_2$. The maximum CH_4 enrichment was 5 %, 9 % and 7 % using NaOH, $Ca(OH)_2$ and TEA correspondingly. The overall results indicate that CH_4 enriched biogas can be generated from fruit and vegetable waste at larger scale to fulfill the Pakistan's energy demands with sustainable management of organic fraction of municipal solid waste (OFMSW).

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