

Mendukung Pengembangan Biofuel Generasi Kedua: Peruraian Anaerob Termofilik Vinasse untuk Berselaras dengan Kapasitas Pabrik Bioetanol Berbahan Dasar Molasse

Supporting Second Generation Biofuel Development: Thermophilic Anaerobic Digestion of Vinasse for Harmonizing with Molasses-Based Bioethanol Plant Capacity

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ABSTRAK: Biofuel generasi pertama merupakan dilema lingkungan karena dampaknya terhadap pembukaan lahan hutan menjadi area perkebunan. Bukan hanya dari sisi lingkungan, biofuel memiliki masalah lain dari sisi sosioekonomi. Produksinya membutuhkan tanaman sebagai bahan bakunya yang akan menimbulkan perseteruan antara sumber makanan dan sumber energi. Perseteruan ini akan berimbas pada masyarakat miskin akibat kenaikan harga makanan. Bioetanol berbahan dasar molase adalah biofuel generasi kedua yang lebih menguntungkan dari aspek lingkungan, sosial, dan ekonomi. Namun, produksinya menghasilkan vinasse sebagai limbah. Vinasse tidak bisa dibuang langsung ke lingkungan karena kandungan material organiknya yang tinggi yang akan berdampak pada air, tanah, dan udara. Di sisi lain, kandungan material organik yang tinggi pada vinasse dapat diubah menjadi biogas dan merupakan potensi yang tinggi bagi pabrik bioetanol berbahan dasar molase. Artikel ini adalah studi pendahuluan untuk mengolah vinasse menggunakan peruraian anaerob termofilik dengan metode menaikkan suhu inokulum mesofilik secara langsung dan *starvation*. Pada OLR tertinggi, yaitu 1.2 g.L-reaktor⁻¹.hari⁻¹, produksi metana mencapai 146 mL/hari. Hasil menunjukkan kinerja mikroba termofilik yang tangguh yang merupakan bukti bahwa metode ini sesuai untuk memperkaya mikroba peruraian anaerob pada inokulum mesofilik.

Kata Kunci: termofilik;peruraian anaerob;vinasse;biogas;metana

ABSTRACT: First-generation biofuel is environmental quandary due to its impact on forest conversion into plantation areas. Not only the environmental sector, but first-generation biofuel also has other issues in the socioeconomic sector. It consumes crops as its feedstock which will be a conflict between food and energy source. This conflict will impact vulnerable people by raising food prices. Molasses-based bioethanol is a second-generation biofuel that is more beneficial from the environmental, economic, and social aspects. Molasses-based bioethanol production process generates waste named vinasse. Vinasse can't be directly discharged into the environment due to its high organic matter concentration which is harmful to the waterbody, soil, and air. On the other hand, the high organic matter contained in vinasse can be converted into biogas and is a huge prospect for molasses-based bioethanol plants. This study was a preliminary study for processing vinasse using thermophilic anaerobic digestion specifically by temperature direct escalation and *starvation* method to the mesophilic originated inoculum. At the highest OLR, which was 1.2 g.L-reaktor⁻¹.day⁻¹, methane production attained 146 mL/day. The result showed robust performance of thermophilic microbia which is an averment of the compatible method for enriching thermophilic anaerobic microbia in mesophilic originated inoculum.

Keywords: thermophilic; anaerobic digestion;vinasse;biogas;methane

1. Introduction

Liquid biofuel is popularly promoted as a substitution for liquid fossil fuel for some reasonable reasons. It has

compatible properties to be blended with liquid fossil fuel so they need no significant changes in handling and distribution. Bioethanol is one of the most popular liquid biofuels for the substitution of petrol and kerosene

(Rahmadi et al., 2013). The main reason for these substitutions is for continuous energy resource sustainability as biofuel feedstock is a renewable source.

Biofuels reduce green house gas (GHG) emissions (Demirbas, 2008)(Rahmadi et al., 2013). Biofuels have some characteristics which promote them as more impactless to the environment. Biodegradable, as its obvious characteristic, is the concrete fact of its contribution to sustainability. It will be less hazardous compared to fossil fuel in case of coastal and inland waters (Vasudevan et al., 2005).

Not only environmental sector, but biofuels also have the same or even brighter opportunities in economic sector. For naturally crop-rich countries, like Indonesia, biofuel industries are easily developed anywhere across the country. This prosperity is a potential for Indonesia to increase employment and improve the developing area to a more advanced economic position. Biofuel development will be a balancer of crops price at the moment when crop production is at its highest peak. This balancer will be a great fortune for the smallholder (Rahmadi et al., 2013).

Indonesia is the biggest crude palm oil (CPO) exporter these days and its demand and price does not show deflation yet. There is no guarantee that Indonesia will have the availability of the crop in abundance. Sugarcane, as one of the bioethanol feedstock, is in unfortunate production capacity. Indonesia was once a great exporter of sugarcane in the era of Dutch colonialism but then its production declined in the 20th century (Rahmadi et al., 2013). In 2020, Indonesia produced 2.13 million tons of sugarcane yet the consumption was 2.66 million tons which is an indicator of the limited feedstock of sugarcane for bioethanol (Puspitasari, 2021). Therefore, utilizing sugarcane as a first-generation biofuel feedstock will be a conflict between energy sources and food sources (Boly & Sanou, 2022).

Not stopping on the energy and food source, first-generation biofuel has not only advantage but also threat to the environment. The data from Indonesia Central Bureau of Statistics shows an increase in the land use for crops as presented in Figure 1. We can see the plantation area of crops does not show their retardation unless in 2019-2021 caused by the massive pandemic of COVID-19. This data told us the forest conversion into a plantation which is another environmental quandary of first-generation biofuel.

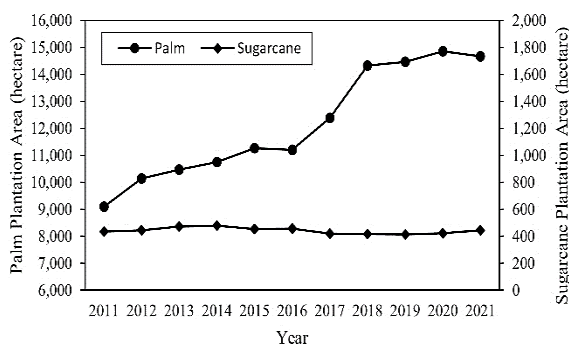


Figure 1. Plantation Area of Palm and Sugarcane (hectare) (Badan Pusat Statistik, 2021)

The first generation of biofuels is the major biofuel utilized in Indonesia. On the other hand, it should be fully supported by second-generation biofuels which are derived from biochemical and thermochemical conversion like bioethanol from molasses. Molasses is a waste that comes from the sugarcane refining process. It is a threat to the environment but by using fermentation, the molasses can be converted into bioethanol. We convert the threat into a potential second-generation biofuel but this process does not totally remove the threat as it still produces waste called vinasse. It contains a high concentration of organic matter and can potentially cause several harm to the water body, soil, and air (Hoarau et al., 2018).

Molasses-based bioethanol plants in Indonesia have an issue with processing vinasse. Coming out as the bottom product of the bioethanol distillation process, vinasse is only accumulated in pools. Shutdown of bioethanol production is a common occasion as a consequence of having no more available pool to contain the vinasse. Discharge of vinasse to the environment occurs only in the wake of vinasse's natural decomposition in the pools. After the discharge of the vinasse, the pools are empty, and starting up of the bioethanol production can be executed. Vinasse is a drawback for bioethanol production so it deserves a proper treatment to harmonize with the bioethanol plant capacity.

Vinasse's characteristic is matched to the feedstock of anaerobic digestion. It is an organic matter with a high water content which is not profitable for conventional technologies such as landfilling, and gasification (Dhamodharan et al., 2015; Zhang et al., 2007). The high organic matter concentration is shown by the Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) which are ranged about 104,000-134,000 mg/L and 46,100-96,000 mg/L (Bergmann et al., 2018; Wardani, N A, Afiqah, N, Azis, M M, Budhijanto, 2020).

The reaction rate of thermophilic anaerobic digestion is 50% higher than mesophilic operation (Deublein, 2011). A study (Dinsdale, R. M., Hawkes, F. R., Hawkes, 1996) compared anaerobic digestion which processed coffee plant waste in mesophilic and thermophilic conditions. The mesophilic anaerobic digestion achieved its highest capacity at 1.3 kg COD.m⁻³.day⁻¹ of OLR and 25 days of HRT while the thermophilic one can operate up to 1.6 kgCOD.m⁻³.day⁻¹ and 20 days of HRT.

Other research was focusing on the comparison between mesophilic and thermophilic anaerobic digestion (Shi et al., 2018). Using wheat straw and food waste as their substrate, the biogas production of thermophilic reactor was 4.9-14.8% higher than the mesophilic one. Previous research on anaerobic digestion of vinasse was comparing these two operation temperature ranges (Wardani, N A, Afiqah, N, Azis, M M, Budhijanto, 2020). At the same 60 days of HRT, the mesophilic and thermophilic gas production were 39 and 192mL/day respectively. These are obvious evidences of the thermophilic anaerobic digestion superiority over mesophilic anaerobic digestion.

According to Speece (2008), mesophilic inoculum conceives also thermophilic bacteria so it is usable for

starting up a thermophilic anaerobic digester. In several thermophilic anaerobic digestion researches, the mesophilic-originated inoculum was suddenly operated in 55°C (Tatara et al., 2005, 2008; Ueno & Tatara, 2008). The most common method is gradually increased temperature but it is not more profitable than a sudden temperature escalation (Speece, 2008). Stabilizing temperature is more time-consuming than a sudden temperature escalation (Schmidt & Ahring, 1994; Speece, 2008).

Using anaerobic digestion, vinasse will be processed to minimize its organic matter concentration before a proper release to the environment. In addition, it will assess the biogas potency of anaerobic digestion with vinasse as the feedstock. This study will give evidence of how compatible the thermophilic anaerobic digestion is, especially with the sudden temperature escalation and starvation method, to be applied as waste treatment in molasses-based bioethanol plants.

2. Material and Method

2.1 Inoculum

This experiment used digested POME as inoculum. The digested POME was taken from a mesophilic biogas reactor in the Bioprocess Laboratory, Gadjah Mada University, Special Region of Yogyakarta, Indonesia. The inoculum was ensured to not have any large debris by being filtered. The COD was then set to 19,000 mg/L and the pH was adjusted to be neutral.

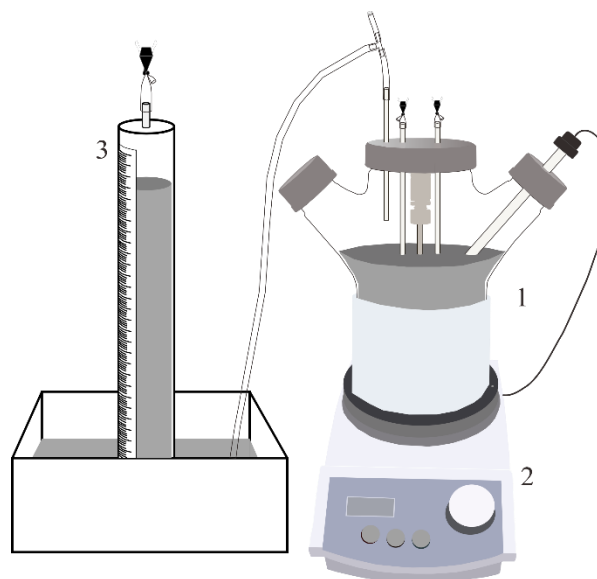
2.2 Feedstock

Vinasse was the feedstock used in this anaerobic digestion experiment. It was attained from PT. Madubaru, Special Region of Yogyakarta, Indonesia. Ensuring no large debris went into the experiment reactor, the vinasse had been first filtered. The vinasse was kept on the refrigerator at 4 °C. Prior to the reactor feeding, the COD concentration, temperature, and pH of the vinasse were adjusted to 12,000 mg/L, 50-55°C and 7 respectively.

2.3 Anaerobic Digestion Experiment

The experimental equipment used in this study is shown in Figure 1. Inoculum with a volume of 1,500 mL was first added to the reactor. It was then flushed with nitrogen to drive the oxygen away and adjusted to be at neutral acidity. The operation temperature was then set to 50-55 °C. The reactor was connected to a gasometer for measuring gas production. The gasometer consisted of a basin and a scaled tube filled with a 75%-saturation salt solution with pH 2. The scale on the gasometer was in centimeter. It needs some calculation to be converted into biogas volume with (Walker et al., 2009) as the reference. The reactor was operated in batch operation during the starvation period. When there was gas production deflation, the vinasse was then fed into the reactor with 60 days of HRT for about 7-14 days waiting for stable gas production. The HRT was then gradually decreased from 60 days to 42, 30, 21, 15, and 10 days of

HRT. This HRT gradual decreasing meant a gradual increasing of OLR from 0.2, 0.286, 0.4, 0.57, 0.8, to 1.2 g.L-reactor⁻¹.day⁻¹.



- 1: reactor
- 2: heater and magnetic stirrer
- 3: gasometer

Figure 1. Experimental Equipment

2.4 Analytical Methods

Gas production was read on the scale of the gasometer. Two times a week, methane concentration was analyzed using Gas Chromatography Shimadzu GC 8A Japan. At the same time as the methane concentration analysis, the liquid composition of chemical oxygen demand (COD), soluble chemical oxygen demand (sCOD), and volatile fatty acid (VFA) were also analyzed. The concentration of COD and sCOD were analyzed using colorimetry procedure (APHA, 2017a). VFA concentration was analyzed using titration method (APHA, 2017b).

3. Results and Discussion

3.1. Gas Production

As shown in Figure 2(a), the starvation period was run in a batch phase for 15 days in purpose to minimize the amount of innate substrate in the inoculum. When the gas production went down, it indicated that the amount of innate substrate was low already and the continuous phase was ready to be started.

Gas production is proportionally inclined with the inclination of the OLR. The OLR was step by step raised every 7-15 days by decreasing the HRT. The first three OLR phases, 0.2, 0.286, and 0.4 g.L-reactor⁻¹.day⁻¹ were seven days period as the performance showed gas production stability. In 0.571 g.L-reactor⁻¹.day⁻¹ of OLR, gas production showed instability, which would be the consideration of

turning back the OLR to 0.4 g.L-reactor⁻¹.day⁻¹. After 15 days in 0.4 g.L-reactor⁻¹.day⁻¹ of OLR, the gas production climbed its valley and even soared to 167.56 mL/day on the seventh day. This was an indicator of an occurrence of rapid rate microbial growth. On the tenth day of 0.4 g.L-reactor⁻¹.day⁻¹ of OLR, the gas production slightly weakened which alerted the lack of food for the abundant microbes that grew on the seventh day. The OLR then stepped up to 0.571 g.L-reactor⁻¹.day⁻¹.

The OLR then gradually raised from 0.571, 0.8, to 1.2 g.L-reactor⁻¹.day⁻¹ every 15 days. This phase was quite smooth and showed no instability represented by the gas production. The highest gas production was achieved in the 1.2 g.L-reactor⁻¹.day⁻¹ of OLR which was 470 mL/day.

The same pattern occurred in each step of the OLR. Gas production would soar with the inclined OLR then followed by declining gas production 1-3 days later. Higher OLR constructed abundant food milieu for the microbes which provoked rapid microbial growth. In consequence of these

abundant microbes, food competition was a natural occasion. This phenomenon occurred several times in the same OLR like a microbial growth cycle preserving its balance.

Methane production, contained in the biogas, is shown in Figure 2(b). Proportional with the gas production, in 0.571 g.L-reactor⁻¹.day⁻¹ of OLR, methane production was at its lowest level. This hinted at the occurrence of washout. OLR was then brought back to 0.4 g.L-reactor⁻¹.day⁻¹ then the methane production went back to its track. Overall, the methane production was higher with the higher OLR. The highest methane concentration as shown in Figure 2(c) in the 0.2, 0.286, 0.4, 0.57, 0.8, and 1.2 g.L-reactor⁻¹.day⁻¹ of OLR were 13%, 16.9%, 21.9%, 26%, 29.7%, and 28.5% respectively. Whilst the average methane concentration in the 0.2, 0.286, 0.4, 0.57, 0.8, and 1.2 g.L-reactor⁻¹.day⁻¹ of OLR were 8.64%, 14.4%, 24.94%, 21.66%, 26.6%, and 28.56% respectively.

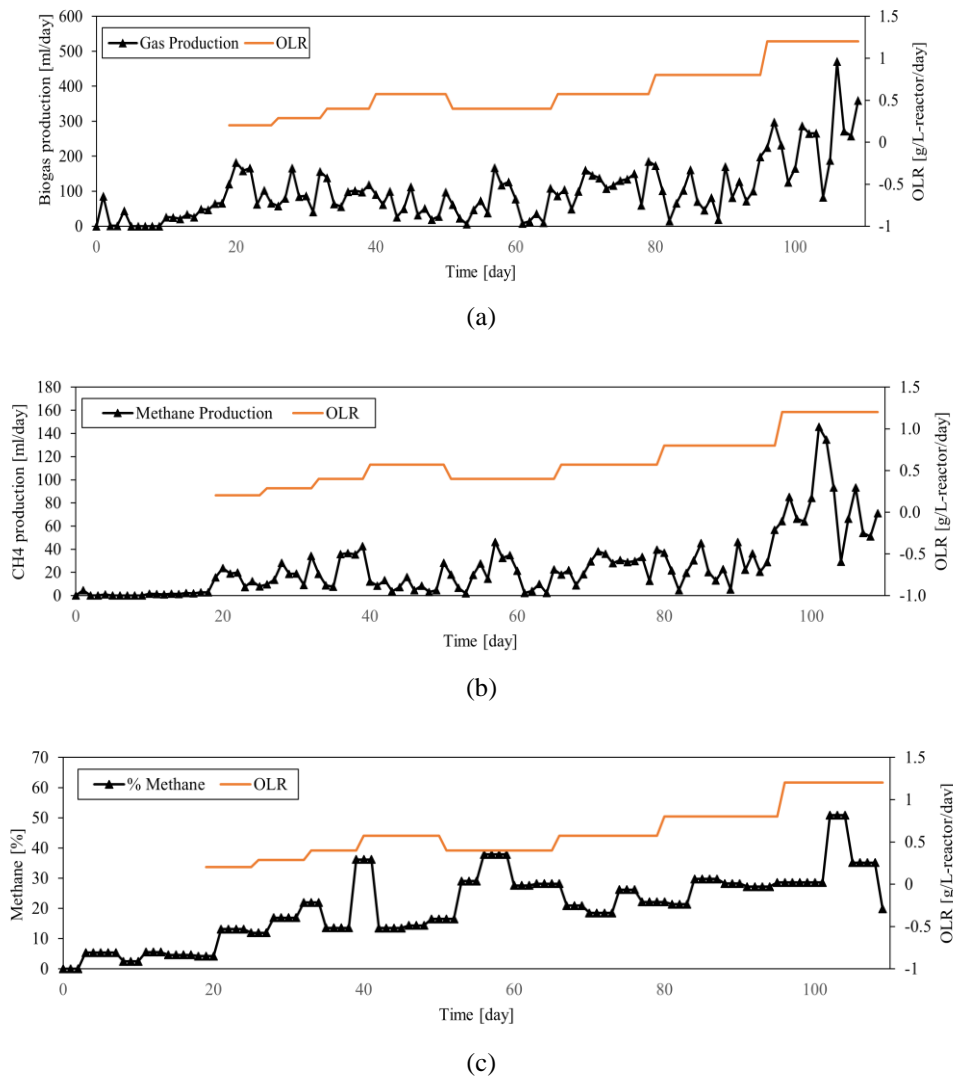


Figure 2. Profile of (a) biogas production; (b) methane production; (c) methane concentration of the thermophilic anaerobic digestion from starvation period to gradually increased OLR from 0.2 to 1.2 g.L-reactor⁻¹.day⁻¹ of OLR

3.2. Liquid Composition

Chemical oxygen demand (COD) concentration shown in Figure 3 is a particulate COD which is the subtraction of total chemical oxygen demand (tCOD) by soluble chemical oxygen demand (sCOD) and volatile fatty acid (VFA). COD concentration decreased as time goes by as most of the initial inoculum washed out from the reactor. Besides, the decomposition of COD into sCOD contributed to the declining concentration of COD and the raising of the concentration of sCOD as shown in Figure 3. This statement was supported by the data of gas production which kept on raising and the stable concentration of VFA which indicated the healthy microbial activity to keep converting sCOD into VFA and next into biogas. Starting from day 84, COD concentration slumped below sCOD concentration which shows well decomposition of COD by the microbes into sCOD. Accompanied with stable VFA concentration and high gas production, this phenomenon was an indication of decent methanogenic performance.

We can see the harmonic fluctuation between sCOD concentration, VFA concentration, and methane production. When the concentration of both sCOD and VFA were dropped, the methane production soared as shown on day 95. On day 95, the methane production soared to 56.7 mL/day at the same time with the lower level of sCOD and VFA concentration, which were 3421 mg sCOD/L and 415.7 mg VFA/L respectively. The stable VFA concentration indicates great methanogen activity. All along the way, VFA concentrations was low unless at day 88 and 98 when VFA concentrations were 1,111 and 1169 mg/L respectively. This phenomenon commonly occurred in a thermophilic anaerobic digestion operated at high OLR according to some research (Aitken et al., 2005; Moen et al., 2001). Soon after these raising, the VFA came lower to 507 and 273 mg/L at day 91 and 102 respectively. This shows a great methanogen activity so that the VFA consumed to its lower level.

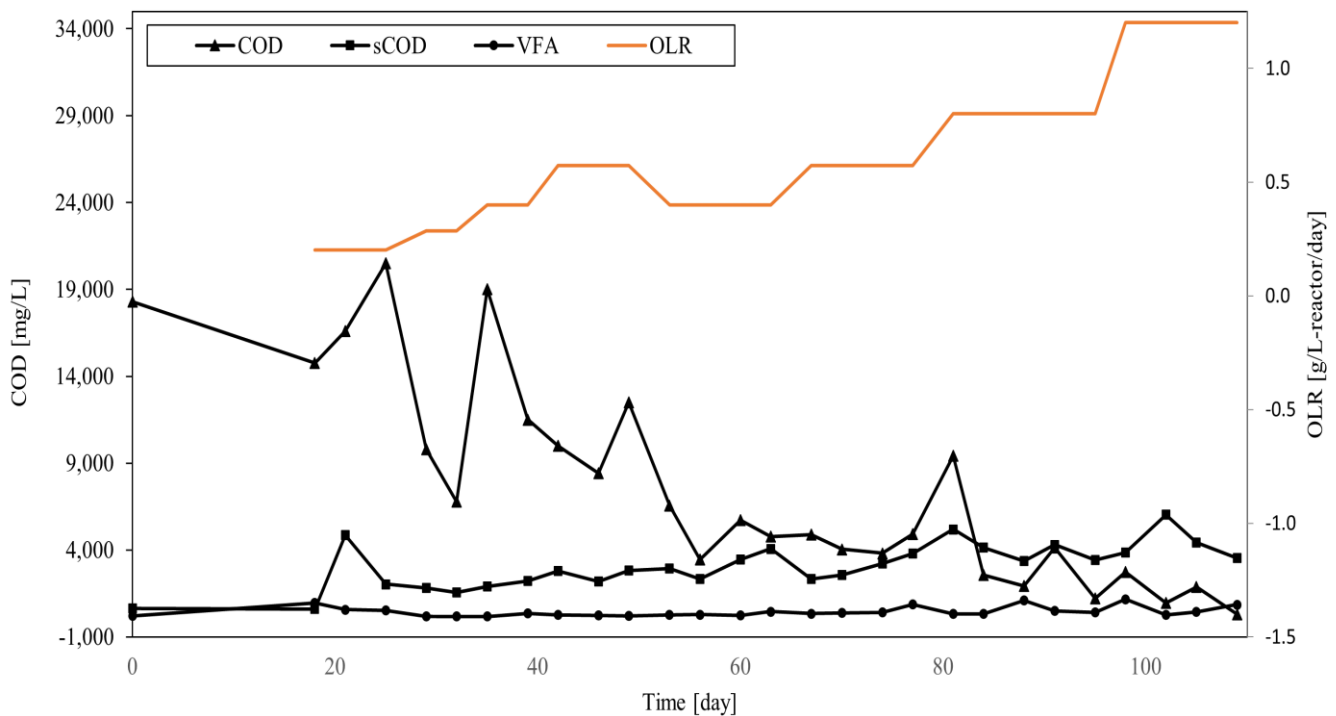


Figure 3. Profile of COD concentration, sCOD concentration, and VFA concentration of the thermophilic anaerobic digestion from starvation period to gradually increased OLR from 0.2 to 1.2 g.L-reactor⁻¹.day⁻¹ of OLR

4. Conclusion

Sudden temperature escalation and starvation method prior to gradual increased OLR is suitable for enriching the thermophilic anaerobic microbes in mesophilic-originated inoculum. Using this method, inoculum will be tolerant to the new substrate as the aftermath of their famine. This anaerobic digestion was still at excellent performance

considering its stable VFA concentration at 1.2 g.L-reactor⁻¹.day⁻¹ of OLR and 10 days of HRT which produced 146 mL/day of methane. It will be a great breakthrough to solve the problem of vinasse waste by using thermophilic anaerobic digestion. Thermophilic anaerobic digestion both removes the vinasse waste and converts it to potential renewable energy.

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