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METHANE POTENTIAL OF HOUSEHOLD WASTE; BATCH ASSAYS DETERMINATION
ศักยภาพการผลิตก๊าซมีเทนจากของเสียบ้านเรือน; การทดลองในห้องปฏิบัติการ

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Abstract

An assay for determination of the methane potential of household waste (HHW) was developed. The assay was performed in batch vials with thermophilic inoculum from a biogas plant co-digesting swine manure with industrial waste. Methane potential of 500 mL/gVS was achieved within 10 d. Blending of the HHW household waste was suitable method for homogenization of the material. Although blending altered the physical image of the sample, it did not alter the original composition of the material. Thermal pre-treatments of the waste (70°C for 1 hr) and combined thermal alkaline pre-treatment (70°C for 1 hr and addition of NaOH for achieving pH 10) did not influence to the methane potential of household waste. The absence of effect on the methane potential by the applied pre-treatment indicates that pre-treatment is not required for determination of the methane potential of easily biodegradable substrates. Different amounts of household waste were added to the vials, while the amount of inoculum was the same resulting in different I/S ratios. All the tested I/S ratios in the range of 5 to 15 were found to be appropriate for the methane potential assay from household waste, as no significant volatile fatty acids (VFA) accumulation was observed at any of the tested ratios.

Keywords: anaerobic digestion, household waste, methane, VFA

บทคัดย่อ

การทดลองในห้องปฏิบัติการเพื่อศึกษาหาศักยภาพการผลิตก๊าซมีเทนจากของเสียจากบ้านเรือนได้ถูกพัฒนาขึ้น การทดลองถูกสร้างขึ้นในขวดแก้วขนาดเล็กที่บรรจุหัวเชื้อจุลินทรีย์อุณหภูมิสูงจากสถานีผลิตก๊าซชีวภาพที่ใช้มูลสุกรร่วมกับของเสียอุตสาหกรรม ผลผลิตก๊าซมีเทนปริมาณ 500 มล. ต่อกรัมของแข็ง

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ระเหยง่าย เกิดขึ้นภายในเวลา 10 วัน การผสมของเสียจากบ้านเรือนเป็นวิธีการที่เหมาะสมเพื่อให้ของเสียเป็นเนื้อเดียวกัน แม้ว่าการผสมจะทำให้ลักษณะทางกายภาพของของเสียเปลี่ยนไป แต่ก็ไม่ทำให้ส่วนประกอบดั้งเดิมของของเสียเปลี่ยน การบำบัดของเสียเบื้องต้นโดยใช้ความร้อน (70°C 1 ชม.) และการใช้ความร้อนร่วมกับสภาพความเป็นด่าง (70°C 1 ชม. และเติมโซเดียมไฮดรอกไซด์ ให้ได้พีเอช 10) ไม่มีผลต่อศักยภาพการผลิตก๊าซมีเทนจากของเสียจากบ้านเรือน การที่การบำบัดเบื้องต้นไม่สามารถช่วยให้ศักยภาพการผลิตก๊าซมีเทนเพิ่มขึ้น แสดงให้เห็นว่า การบำบัดเบื้องต้นนี้ไม่จำเป็นสำหรับการศึกษาศักยภาพการผลิตก๊าซมีเทนจากของเสียที่ย่อยสลายทางชีวภาพได้ง่าย ของเสียจากบ้านเรือนในปริมาณที่แตกต่างกันได้ถูกใส่ไว้ในขวดแก้วขนาดเล็ก ในขณะที่ใส่หัวเชื้อจุลินทรีย์ในปริมาณที่เท่าๆ กัน เป็นผลให้มีสัดส่วนของหัวเชื้อจุลินทรีย์ต่อของเสียที่แตกต่างกัน สัดส่วนทุกๆ สัดส่วนของหัวเชื้อจุลินทรีย์ต่อของเสียที่ได้ทำการทดลอง อยู่ในช่วง 5-15 ถูกพบว่ามีความเหมาะสมสำหรับใช้ในการทดลองในห้องปฏิบัติการ เพื่อศึกษาหาศักยภาพการผลิตก๊าซมีเทนจากของเสียจากบ้านเรือน เนื่องจากไม่พบการสะสมของกรดไขมันระเหยง่ายในทุกสัดส่วนที่ทดสอบ

คำสำคัญ: การย่อยสลายแบบไร้อากาศ, ของเสียจากบ้านเรือน, มีเทน, กรดไขมันระเหยง่าย

Introduction

Anaerobic digestion is an efficient waste treatment technology that harnesses natural anaerobic decomposition to reduce waste volume and generate biogas at the same time[1]. The process involves a consortium of several microbial groups and interrelated biochemical processes such as hydrolysis, acidogenesis, acetogenesis, and finally methanogenesis. The produced biogas typically contains methane 55-75% and carbon dioxide 30-45%, which mostly depending on the pH[2] and digesting temperature[3] of the process.

The use of biogas is increasing rapidly today according to the continuing rising of fossil fuel prices. Biogas is typically used in factory boilers and in engine generator sets to produce electricity and heat[4]. Additionally, upgraded compressed biogas can be used in vehicle transportation, which has become widely used in Sweden, and other countries.

Methane potential is the ultimate specific methane production resulting from a specific feedstock, at conditions permitting the full utilisation of the organic matter. The methane potential is determined by the composition of the raw material, and its biodegradability of it. Typically, carbohydrates and proteins have a theoretical methane potential of 415 and 293-574 Nm^3 CH_4/tons VS while lipids possess a much higher potential (952-1041 Nm^3 CH_4/tons VS)[5]. However, not all organic material can be degraded during anaerobic digestion. Often biofibers and other lignocellulosic material are avoiding digestion as the lignin structure is preventing contact of microorganisms with the cellulosic organic matter.

Anaerobic biodegradability assays are used to establish anaerobic biodegradability, for determination of the ultimate methane potential of wastes. Reliable assays are necessary, as often the determined methane potential is used for estimation of the economic feasibility when designing a biogas plant. A number of different assays have been developed over the last 20 years with a variety of experimental set-ups. In these methods, the experimental set-up, the inocula, the incubation temperature, the pre-treatment of the raw material, are often differences. Especially, for high solids wastes content such as household wastes, in-homogeneity of the raw material constitutes a problem, for assays involving relatively small volumes of samples.

Pre-treatment of the raw material prior to the digestion at thermophilic conditions have been reported for increasing of the methane production[3]. Pre-treatment under alkaline-thermal conditions resulted in the total efficiency for methane production of 0.28 L per g VSS loading[6] and showed selectively destroy unbiodegradable components of the activated sludge in a post-treatment[7]. According to the European regulation (EC) No 1774/2002[8], pre-treatment of the waste at 70°C for 60 min is required in the biogas plants for hygienisation.

The present study was then aiming to investigate whether it could increase the methane potential of household waste. It was also to establish an appropriate method for estimation of the methane potential of household waste.

Materials and Methods

Preparation of the waste and inoculum

The household waste (HHW) was obtained from Vejle City in Denmark. It was blended for homogenization using normal kitchen blender and stored at 4°C prior to use. The inoculum was from a thermophilic (53°C) biogas plant digesting manure with industrial waste (Vegger biogas plant in Denmark). It was taken both directly from the reactor and from the post-storage tank of the plant. This type of inoculum was containing broad trophic microbial composition in order to ensure that the anaerobic conversion of different organic substrates is not limited. In order to deplete the residual biodegradable material in the inoculum for minimizing its methane contribution, the inoculum was degassed by pre-incubated at 55°C for 10 d. The feed stock used as substrate at the Vegger Biogas plant was approximately 60% manure and 40% a wide range of industrial waste such as bentonite bound oil, fish oil, etc. The composition of the waste and inoculum were shown in Table 1.

Table 1 Composition of initial household waste and inoculum

	Household waste*	Inoculum*
TS (% w/w)	30.73	5.58
VS (% w/w)	27.05	3.84
TKN (g/Kg)	10.54	4.92
NH_4-N (g/Kg)	1.03	3.59
Lipids (g/Kg)	58.83	na
Protein (g/Kg)	59.42	na
Carbohydrate (g/Kg)	152.25*	na

* Calculation based on mass balance

Pre-treatment conditions

Thermal pre-treatment

Thermal pre-treatment under thermophilic temperature was carried in a water bath at 70°C for 60 min (follows the EU regulation). Samples were placed in the water bath and heated up for 15 min to reach the setting temperature.

Thermal-alkaline pre-treatment

Alkaline condition was provided using potassium hydroxide (2 M KOH). The alkaline solution was added to the samples in order to reach pH 10 and then heated in the water bath at 70°C for 60 min.

Batch set-up and monitoring

Anaerobic digestion was conducted in batch experiments using 1.120 L glass bottles. HHW sample was roughly blended for ensuring homogenous sampling but still kept the original composition. It was then mixed with water into slurry of 1, 2, and 3 gVS/100 mL. In all bottles, 400 mL of inoculum was added with 100 mL of HHW slurry[9]. Inoculum was continuously stirred and kept under anaerobic conditions during transferring. After the HHW slurry and inoculum was added into the bottles, the bottles were flushed with N_2 for 2 min to provide anaerobic conditions. The bottles were then placed in the incubator at 55°C. For methane potential determination, the different HHW contents of 1, 2, and 3 gVS were tested, while for the effect of pre-treatment observation, the HHW content was fixed at 2 gVS. The 2gVS HHW household waste with 400 mL inoculum was chosen as this ratio was previously reported as the optimum substrate/ inoculum composition for methane potential assays[9]. Batch test was carried out in tetraplicate. One bottle for each substrate concentration was used for volatile fatty acids sampling, while the three others were

used for detection of the accumulated methane production in the head space of the bottles. Three blanks with only water (100 mL) and inoculum (400 mL), in order to determine the methane production from the inoculum were included. Additionally, controls with 2 g avicel (cellulose) were used as a reference substrate.

Methane content in the headspace of the test bottles was measured throughout the experiment. The effect of pre-treatment conditions was evaluated by comparison of methane yields from untreated and treated samples. During the first week, the measurement was conducted daily. Later, it was observed twice a week. Volatile fatty acids evolution in each substrate concentration was monitored during the experiment to investigate the relation or inhibition effect on methane potential.

Evaluation of data

The headspace of each batch was calculated by subtracting the added amount of inoculum and substrate (assuming the density of substrate and inoculum was 1 g mL^{-1}) from the volume of the bottle. Gas sampling of 0.2 mL of headspace was measured directly on the GC and the produced amount of methane was determined followed the method of Hansen et al.[9]. The actual methane potential of the HHW household waste was calculated by subtracting the ultimate methane production accumulated in the headspace of the bottles with the samples from the methane accumulated in the headspace of the blanks containing only inoculum and water and divided by the VS content of the waste (Eq.1 and Eq.2). The ultimate methane production was assumed to be reached, when the methane production had reached a plateau and was stable for approximately 7 d. The theoretical methane potential of the household waste was calculated based on equation (1) and (2) and used to compare to the actual value obtained from the batch experiment.

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 \quad (1)$$

$$B_{0.th} = \frac{\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)22.4}{12n + a + 16b}\left(STP \Big/ \frac{CH_4}{g - VS}\right) \quad (2)$$

when $B_{0,th}$ = theoretical biological methane at 0° C, 1 atm

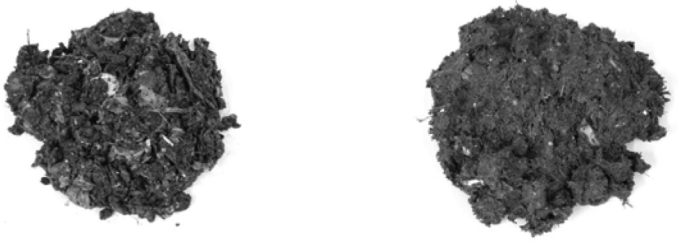
Analytical methods

Determination of the total solids (TS), volatile solids (VS), Total Kjeldahl nitrogen (TKN), ammonium (NH_4-N), and lipids was carried out according to the Standard Methods for the Examination of Water and Wastewater (10). TS and VS were measured by drying the sample at 105°C for 24 hr and then igniting it at 550°C for 2 hr, respectively. TKN and ammonium were measured by the titrimetric method. Lipids were analysed by Soxhlet method. Protein was estimated by multiplying the organic N content with 6.25 which corresponds to the molecular weight/N-weight ratio of a typical amino acid. Biogas composition in methane was quantified with a gas chromatograph (Shimadzu GC-14A) equipped with a thermal FID detector and working range of methane content ~ 5-100% (ENV-lab, DTU, Denmark). Volatile fatty acids (VFA) was analysed by GC-2010 SHIMADZU (ENV-lab, DTU, Denmark).

Results and Discussion

Effect of blending process to the physical structure and composition of the HHW

For determination of methane potential of solid wastes such as household waste, both homogeneity and also accuracy in transferring waste into the vials are very important. In this batch assay, the HHW household waste as well as the inoculum was weighed in a two digital accuracy balance scale. The standard deviation of the samples weight was in the range of 0.01-1.62. Homogeneity of the HHW by blending process was important as often HHW in consisting of large inhomogeneous particles, which are difficult to distribute equally in relatively small samples. Representative sampling is important for establishing the methane potential of HHW. Blending of a larger amount of sample could ensure representative sampling of a smaller amount to be applied in the methane potential assay (MPA). However, the blending should be conducted to a minor degree that is not altering the original composition of the samples. The limitation of the blending process is then depends on the original physical structure and composition of the waste. In this experiment, blending of the HHW was done using a normal kitchen blender for a few minutes. The results showed significant difference in a physical image resulting in a more homogeneous structure (Figure 1) but still kept the original composition expressed as TS, VS, TKN, NH_4^+, and lipids (Table 2).



(a) (b)

Figure 1 Physical image of the waste before (a) and after blending stage (b)

Table 2 Effect of blending stage on the composition of household waste

	Household waste	
	Before blending*	After blending*
TS (% w/w)	30.73	29.96
VS (% w/w)	27.05	26.43
TKN (g/Kg)	10.54	9.56
NH4-N (g/Kg)	1.03	1.06
Lipids (g/Kg)	58.83	61.60
Protein (g/Kg)	59.42	53.14
Carbohydrate (g/Kg)	152.25*	149.56*

* Calculation based on mass balance

Residual methane from inoculum

The residual biodegradable organic material in both inocula taken directly from the reactor and the post-storage tank of the biogas plant, resulted in methane production during the pre-incubation (Figure 2). The residual methane production from the inocula was similar, although a slightly higher methane production was register from the digested material directly retrieved from the reactor. This was probably due to the non-ideal mixing and not continuous feeding pattern of the full scale reactors. Typically, pre-incubated period may take between 2 to 5 d [11]. The longer digestion time, 9 d, registered in the present study was from the relatively high content of lignocellulosic fibers contained in manure, which was the main feed of the biogas reactor in Vegger biogas plant. The methane production recorded at the Vegger biogas plant was approximately 50 L methane/L-

feedstock, which indicated that approximately 7% of methane potential of the feedstock was not utilised. It has previously been reported that the full scale biogas plants with one step fully mixed reactor configuration are often loosing (not utilising) 5-20% of the methane potential in the fed feedstocks (12). The relatively low residual methane potential obtained in this study indicated that the Vegger biogas plant, from where the inoculum originated, was very effective in utilising the methane potential in the fed feedstock.

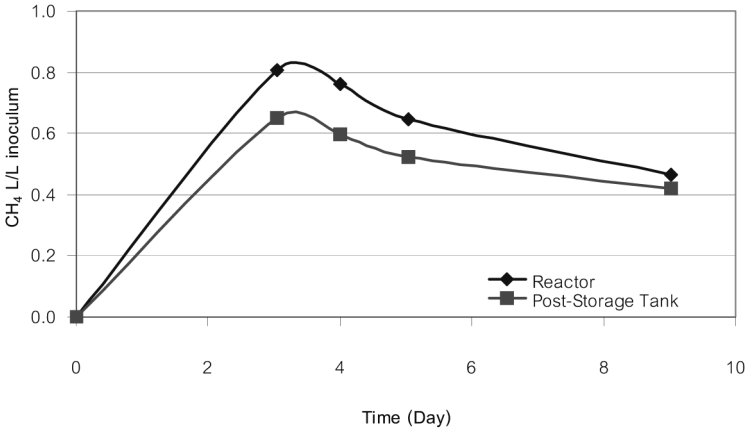


Figure 2 Residual methane of digested material retrieved from the reactor and the post-storage tank of the biogas plant

Methane potential of the household waste

The net methane potential of HHW and the specific yield achieved in the batch digestion are illustrated in Figure 3. The net methane potential of approximately 0.5, 1, and 1.5 L was recorded for the tested 1 gVS, 2 gVS, and 3 gVS HHW, respectively (Figure 3a). The obtained specific final methane yield obtained was approximately 500 mL/gVS (Figure 3b). It agrees well with the methane yield of 495 mL/gVS achieved for the solid organic waste from the study of Hansen et al.[9]. The remaining waste after batch experiment is lignocellulosic containing compound, which can be further used for agricultural utilisation. Practical amount of substrate for batch assays was found at 2 gVS. The amount of substrate higher than 2 gVS showed no significant different on the specific methane yield (Figure 3b). However, it did not clearly show any inhibition effect on the methane production. The slightly lower methane yield was observed from 1 gVS substrate. It

could be from the uncertainty in sampling during batch assays.

The biodegradability of the HHW was almost complete, as the achieved methane potential reached the calculated theoretical methane potential based on stoichiometric conversion of the organic matter to methane and carbon dioxide (Table 3). Calculation of the theoretical methane potential was based on the content of lipids, ($CH_3(CH_2)_{10}COOH$), carbohydrates (($C_6H_{10}O_5$)n), and proteins ($C_4H_{10}N_2O_3$) in HHW, as determined by the chemical characterisation of the waste (Table 1).

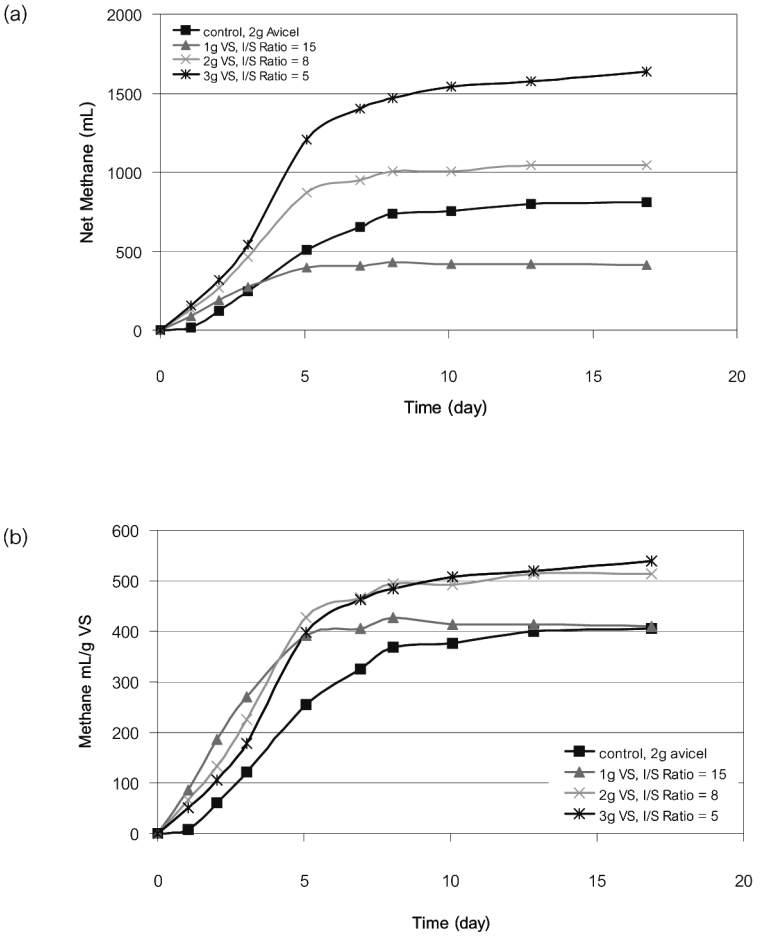


Figure 3 Batch results of methane potential from household waste
(a) Net methane production and (b) Methane yield

Table 3 Theoretical biogas yield for blended household waste scenario

Component	Theoretical biogas potential (Nm^3 CH_4/tons VS)	Weight of blended 2 gVS household waste (g)	Expected CH_4 Yields (mL)
Lipids	952	0.4662	443.8
Carbohydrates	415	1.1320	469.8
Proteins	293	0.4020	117.8
	Total mL CH_4 per gVS		515.7

Effect of thermal and thermal-alkaline pre-treatment

No beneficial effect of thermal and thermal-alkaline pre-treatments, 70°C and 70°C under pH 10, operated at the same amount of substrate (2 gVS) was observed in this study (Figure 4). As the achieved methane potential was almost 100%, it would not be possible to achieve any additional improvement by pre-treatment. According to the EU regulations, low risk material (catering residues, meat, precooked foods etc.) approved for food consumption, must be treated to at least 70°C for 1 hr in a closed system[8]. Therefore, it has been speculated in many biogas plants that the pasteurisation procedure, would benefit the methane potential of HHW. Our study has however shown that no additional methane production could be achieved from the pasteurized process. This would be probably from the difference in feedstocks with more recalcitrant organic matter composition, such as biofibers or sludge. It has been previously shown that thermal/chemical pre-treatment methods are both affecting the chemical composition but also the physical appearance of structural material at the microscopic level[13, 14]. Beneficial effect from pretreatment under high temperature has been reported in previous studies using more recalcitrant feedstock such as sewage sludge[3] or manure[15].

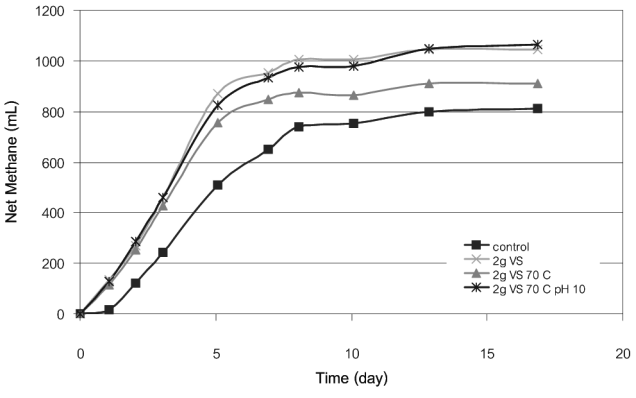


Figure 4 Effect of pre-treatments on the net methane production

Volatile fatty acids monitoring during batch assays of methane potential determination

The main volatile fatty acids (VFA) measurement was acetate and propionate. Their concentration accumulated during the first 2-3 d to the maximum concentration of 18 1092 and 3232 mg/LmM was observed for acetate and propionate, respectively (Figure 5). The observed VFA accumulation was not at any time too high to risk to bring the process in stress. Afterwards the VFA were completely degraded within 10 d, showing that the biogas process proceeded balanced, without any risk of overloading (Figure 5). This indicates that all the tested HHW concentrations were below the overloading level.

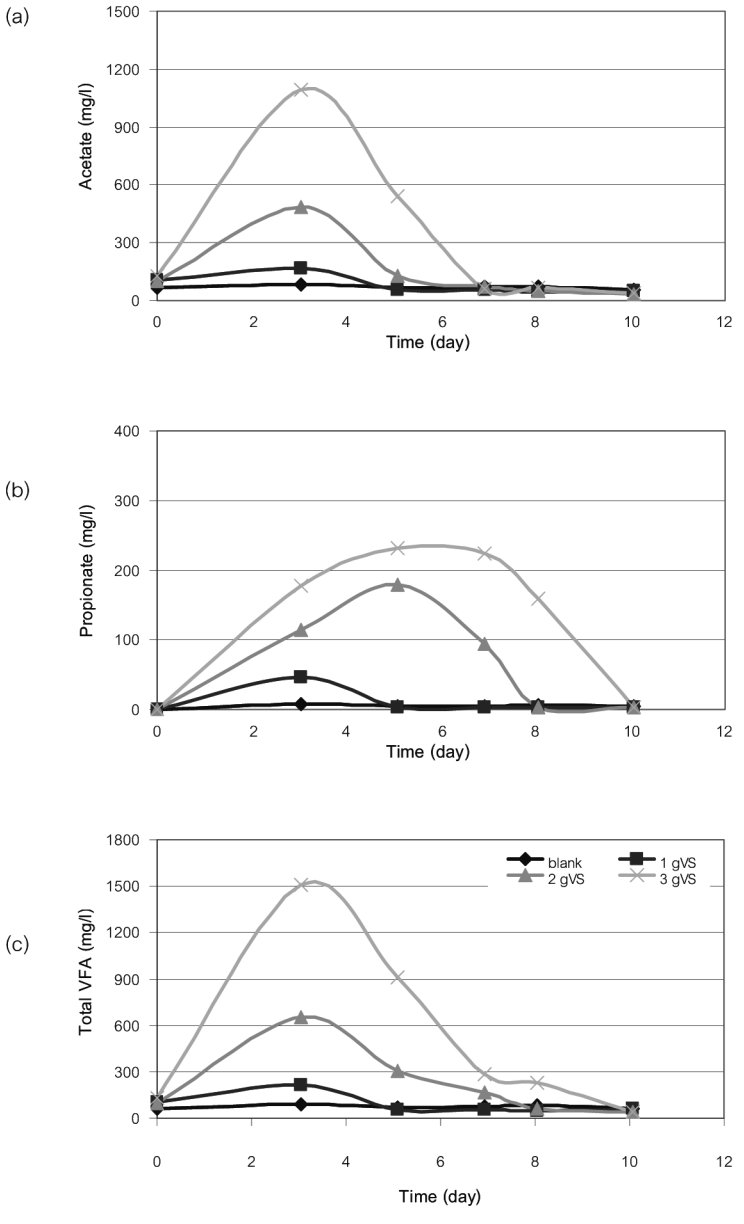


Figure 5 Concentration profiles of volatile fatty acids during batch experiment (a) Acetate, (b) Propionate, and (c) Total VFA.

Inoculum to substrate ratio

The inoculum to substrate, I/S ratio, was in the range of 5-15. The substrate concentration expressed in gram of VS was varied as 1, 2, and 3, whereas the inoculum was fixed at 15.4 gVS for all experiments. Figure 3 shows the I/S ratio and the methane yields for HHW incubated with inoculum at different substrate contents. It can be seen from the graph that the increase in methane production occurred very fast due to the degradation of accumulated intermediate VFA. Finally, all ratios showed almost similar in the methane potential.

The maximum methane yields of 500 mL CH4/gVS was obtained at both 2 and 3 gVS substrate, while 85% of the maximum value was achieved at 1 gVS substrate as well the 2 gVS control, which indicated the applicable range of substrate content to perform the methane potential assay (MPA) in batch experiment. Uncertainty in sampling from the small amount of substrate of 1 gVS batch may cause the lower methane yields obtained in the study. The increase of substrate content higher than 2 gVS did not improve the methane production and may stimulate an occurrence of inhibition phenomenon due to VFA accumulation reaching inhibiting levels. As recently study of Angelidaki et al. [11], inhibition effect was found at high substrate content. However, the present results did not show any inhibition effect at the substrate content of 1 to 3 gVS. It suggested the applicable initial amount of organic material to inoculum amount use for start-up of anaerobic digestion using HHW at the substrate content of 1 to 3 gVS, which expressed in I/S ratio of 5 to 15, respectively.

Conclusion

A methane potential assay from household waste was tested. It was found that the blending of HHW could ensure representative sampling for performing the MPA in batch experiment. Thermophilic anaerobic inoculum from a manure based biogas plant was active and could provide a balanced digestion process of HHW at an I/S ratio in the range of 5 to 15.

Pre-treatments by thermal (70°C) and thermal-alkaline (70°C with pH 10) have no considerable influence on the methane production from HHW. The obtained methane potential of HHW was 500 mL CH_4/gVS, which corresponds to the theoretical calculated methane potential, indicating that HHW is easily degradable feedstock with high methane potential.

The suggested procedure in the present study is simple and useful for methane potential assays of high solids content substrates.

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