



Improvement of Methane Yield by Anaerobic Co-Digestion of Sewage and Petrochemical Wastewater: Effect of Temperature

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Anaerobic bio-digestibility of blend municipal sewage sludge (MSS), condensed waste activated sludge (CWAS) and petrochemical wastewater (PWW) has been evaluated utilizing semi-continuous operation, anaerobic reactors worked during mesophilic (37 °C) and thermophilic (55 °C) states. Supplementation of a significant PWW portion (49 % of VS) in an MSS + CWAS combination brought about 2.94 times more methane production, 153 *versus* 450 mL/g volatile solids (VS) under 37 °C furthermore 2.59 times more methane production, 198 *versus* 513 mL/g VS under 55 °C. The supplemented PWW portion might have been not inhibitory for the system. Those effects of this work show the profit from municipal sewage sludge, condensed waste activated sludge and petrochemical wastewater co-digestion.

Keywords: Anaerobic co-digestion, Municipal sewage sludge, Condensed waste activated sludge, Petrochemical wastewater.

INTRODUCTION

Refineries are noteworthy suppliers of petrochemical wastewater which truly made an extreme environmental pollutions [1,2] studied a half expands in methane generation by co-digestion system and minimizing about 0.49 kg VS/m³-d petrochemical wastewater. The possibility of enhanced methane generation by hundred percent through the co-digestion of condensed waste activated sludge (CWAS) and municipal sewage sludge (MSS) was showed over lab investigations [3].

For enhanced biogas generation and to provide sustainable reuse of petrochemical wastewater (PWW) and municipal sewage sludge (MSS), Terengganu province of Malaysia need to run anaerobic co-digestion plants and discharge facility of the effluent. Petrochemical wastewater (PWW) is particularly intriguing as it yields more noteworthy methane creation which can without much of a stretch blend with sewage sludge. Be that as it may, PWW have a few inconveniences: there might be insufficient lipids for gaining admittance to microorganisms and unsaturated fats likewise make them frustrate properties. Kaborious *et al.* [4] thought about the ACoD of primer and profluent slop with fats, oil and grease (FOG) gathered from

wastewater treatment plant (WTP) [4]; foreseen anaerobic co-digestion of glycerol with sewage sludge [5]. Davidsson *et al.* [6] investigated anaerobic co-digestion of sewage sludge with ooze originating from oil trap [7]. In reality, semi- ceaselessly worked anaerobic co-digestion remained is conceivable by including slop of oil trap about 10-30 % or 46 % natural feed, yet unreasonably over the top 71 % volatile solids (VS) and 55 % lipid content in the feed mix realized insufficient absorption and the digester fermentation with a succeeding decrease in creating biogas [8]. The obstacle in the methanogenesis stage by unsaturated fats having long-chain has been incited by over-loading.

To our best of knowledge, the co-digestion of municipal sewage sludge (MSS), condensed waste activated sludge (CWAS) and petrochemical wastewater (PWW) has not been studied till to date. The aim of this work might have been on survey furthermore quantify those anaerobic biodegradations about MSS co-digested with huge amounts for PWW, under totally blended semi-continuously nourished mesophilic alternately thermophilic methane production. Such data will be beneficial to securing that possibility furthermore reduces expense of that co-digestion for MSS and PWW. Benchmark information utilized in this work included extreme degradability for those

sewage and FOG (fats, oil and grease) segments, alongside mesophilic and thermophilic semi-continuous co-digestion for without municipal sewage sludge (MSS) and petrochemical wastewater (PWW) [4].

EXPERIMENTAL

Test accumulation: The petrochemical wastewater (PWW) was collected from petronas penapisan Terengganu, Malaysia and municipal sewage sludge (MSS) was taken from Bukit Losong 1 Water Treatment Plant, Kuala Terengganu, Terengganu, Malaysia. Those MSS and PWW samples were dispatched to laboratory immediately and preserved at 4 °C. As municipal sewage sludge (MSS) samples were diluted (1.3 % TS, 0.8 % VS), therefore, MSS have been preserved at 4 °C to 2 days and the resilient have been thickened.

Batch tests: A batch test has been performed with those municipal sewage sludge (MSS), condensed waste activated sludge (CWAS) and petrochemical wastewater (PWW) separately, and additionally in mixture (MSS + CWAS; MSS + CWAS + PWW) utilizing 150 mL serum flasks. Seeds have been cultivated from Losong 1 water treatment plant, Kuala Terengganu, Terengganu, Malaysia mesophilic anaerobic digesters, which have been pre-digested for 90 days [9]. Incubation have been carried out in the dim In 37 °C and the bottles were shaken manually one time per day.

Fermentation framework: The whole assimilation framework incorporated two automatically blended 5 L and 1.5 L glass digesters. Each reactor required a water coat furthermore their heats have been maintained by a water recirculation system utilizing two warmed water baths. The 5 L digester has been set on 37 °C and the different 5 L reactor has been set on 57 °C. The 1.5 L digester used as the feeding tank, have been set to room temperature (22-24 °C), also have been cleaned once a day. Both digesters were squandered manually one time per day using syringe, 5 min prior to running. Feeding of both digesters have been attained manually once a day by a 50 mL syringe (operation 1), alternately with a peristaltic pump for 6 min each 4 h (operation 2). Gas specimens were collected from those digesters by syringe and examined.

Digester start-up: The mesophilic digester has been operated with a processed sewage example acquired from Bukit Losong 1 water treatment plant, Kuala Terengganu, Terengganu, Malaysia. The thermophilic digester might have been off taking after the same system. Both digesters were equilibrated to the required temperature of 5 days before operation. The primary pH for both digesters was 7.5 and 7.7.

Fermentation: Non-stop testing for municipal sewage sludge (MSS), condensed waste activated sludge (CWAS) and petrochemical wastewater (PWW) under both mesophilic and thermophilic states has been directed in two runs. Operation 1 involved a regulate examination about mesophilic *versus* thermophilic fermentation and the feed have been a blend for MSS and CWAS. For operation 2, the feed has been a blend of MSS, CWAS and PWW and has been operated on two side-by-side methane stage reactors running individually, during mesophilic and thermophilic states.

Analysis: All the water quality parameters were measured according to standard procedures of APHA, 2005. Biogas

generation sum was measured by section moving strategy where at 10 g/L of NaCl and pH 2, the liquid getting to be water. The accuracy of this estimate was ± 10 mL for semi-persistent reactors and ± 1 mL for bunch tests. The biogas fraction was analyzed by a gas chromatography device (Shimadzu GC-8A) outfitted with an integrator C-R8A and a connected CTRI segment, which was included two fragments: 3.18 mm separate over the inside section, stacked by silica gel, permitted separation of carbon dioxide from different gasses. A 6.4 mm estimation outside segment, stacked with a sub-nuclear strainer, detached option gasses. Argon gas was utilized as the transporter gas at 2.7 bar. The stove and injector and indicator temperature were 30 and 105 °C individually. The vaporous material identification was completed by a warmth sensor and the electric flow thickness was kept 75 mA. The volume of infused biogas was 1.5 mL (Fig. 1). The institutionalization was performed with a standard gas made of 24 % carbon dioxide, 6 % hydrogen, 2.5 % oxygen, 9.5 % nitrogen and 58 % methane.

The volatile fatty acids (VFA) was estimated by a gas chromatography gadget (Fisons Instruments, GC-8000) which was outfitted by a flame ionization marker and a modified analyzer (Fisons Instruments, AS 800). The segment portion had a length of 14 m, the width of 0.52 cm and Phase ECTM 1000 film was 1.3 μ m named as semi-fine Econocap FFAP (Alltech). The temperature for splitless injector temperature (245 °C) and the indicator (270 °C) were adjusted separately. Within 3 min, the reactor temperature was increased from 85 °C to 125 °C. At 24 kPa, nitrogen was utilized as the transporter gas. The infused test volume was 1 μ L. Hardware institutionalization was set up by a legitimate blending of six kinds of acids: acetic acid, butyric acid, valeric acid, propionic acid, isovaleric acid and isobutyric acid at 1.0 g/L exclusively. Scope of institutionalization was kept 0.25-1.0 g/L by standard blend weakening. All out VFA level was estimated by center standard procedure (aging of 50 mL H₃PO₄, 1.0 g of ethyl-2-butyric acid was destructive in water of 1.0 L) by a blend of equivalent volume of the example and the inner standard arrangement.

RESULTS AND DISCUSSION

Those outcomes of the analysis of municipal sewage sludge (MSS), condensed waste activated sludge (CWAS) and petrochemical wastewater (PWW) shown that all wastewater samples were acidic with the CWAS had the maximum pH of 6.7, those PWW example Hosting the least pH of 4.1, and the recreated MSS blend had a pH of 5.7. Those COD/VS proportion might have been 2.28, 1.95 and 2.97 to that MSS, CWAS and PWW sample. A huge level of dissolvable COD and VFAs might have been found in the samples, demonstrating that a remarkable level of solubilization and pre-acidification took place during shipping. All specimens had higher ammonia concentration over 200 mg/L. The TKN-to-VS proportion to PWW (0.013) might have been lower compared with MSS (0.07-0.08). Further subtle elements for characterization are described elsewhere [10].

Biodigestibility: These biodigestibility tests have been done after 120 days and points were stated by Siddique *et al.* [11]. The measurement of methane generated normalized to the COD removed ranged between 339 to 344 mL/g COD,

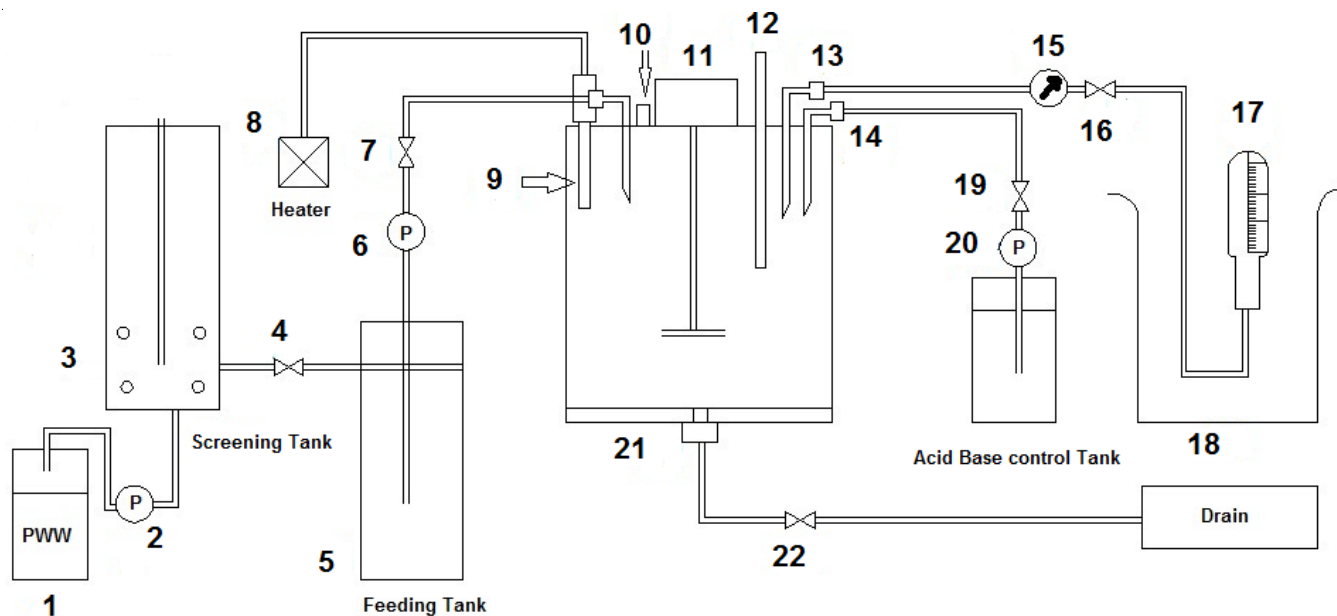


Fig. 1. Experimental setup of CSTR. 1 = Raw PWW dosing zone; 4,7,16,19,22 = Control valve; 3 = Screening tank, 5 = Feeding tank; 2,6,20 = Peristaltic pump; 8 = Heater; 9 = Temperature sensor; 10 = Pressure controller; 11 = Stirrer motor with stirrer; 12 = pH sensor; 13 = Gas collection wire; 14 = Acid base control wire; 15 = Biogas flow meter; 17 = Biogas collection tank; 21 = Process reactor (capacity 5 L); 18 = Water displacement system

which will be near to hypothetical value of 349 mL mL/g COD. That experimental methane yield for every unit volatile solid (VS) impostor supplemented to these specimens might have been 471, 180, 994 and 292 mL/g VS added, individually. Siddique *et al.* [12] studied that those outcomes of a blend of the wastes might a chance to be sensibly estimated by accepting that every individual wastewater potential to volatile solid and COD removals were consistent. Dependent upon those extreme biodegradability outcomes for every part (MSS, CWAS and PWW) and bringing under consideration those volatile solid portion from claiming each part in the MSS21 + CWAS31 + PWW48 combination, which speaks to the encourage blend for operation 2, those anticipated for the blend volatile solid and COD removals were 53 % and 55 %, respectively, and the methane yield might have been estimated to be 631 mL/g VS.

Operation 1: The operation 1 has been directed to straight-forward analyze mesophilic *versus* thermophilic fermentation of a blend of MSS and CWAS. Points to this operation are reported by Siddique *et al.* [9,11,12]. Both digesters were operated under precisely similar states, but to their temperature (37 *versus* 55 °C). Digestion performance of operation 1 is shown in Table-1. The operational loadings for operation 1 were: 42.4 ± 0.3 g TS/L; 30.3 ± 0.2 g VS/L; 54 ± 3.8 g COD/L; 4.9 ± 0.15 g COD/L; 3.5 ± 0.30 g VFA-COD/L; 6.50 ± 0.03 pH; and 0.3 ± 0.02 g ammonia-N/L. Acidification of feed substrates took place which made pH and VFA levels consistent for the full-scale digesters [13]. The volatile solid removal has been 26.3 % and 31.6 % in the mesophilic and thermophilic digesters, respectively, Furthermore might have been roughly equivalent to the connected cod decimation about 26.4 % and 30.5 %. Acknowledging that extreme degradability from volatile solid and COD deposition for 121-day, the thermophilic digester attained volatile solid and COD removal about 84 % and 75 %, separately. The corresponding degradable volatile

TABLE-1
DIGESTER PROPERTIES OF OPERATION 1 AND 2

Parameters	Operation 1	Operation 2
Volume (L)	1.99	1.99
HRT (day)	13	13
Flow rate (mL/day)	167	167
MSS loading g VS/L-day (%)	0.98	0.91
CWAS loading g VS/L-day (%)	1.44	1.34
PWW loading g VS/L-day (%)	–	2.1
Total loading g VS/L-day	2.43	4.33

MSS = Municipal sewage sludge, CWAS = Condensed waste activated sludge, PWW = Petrochemical wastewater.

solid and COD removal values for that mesophilic reactor were just 69 % and 64 %, separately. Methane yield has been 160 and 198 mL/g VS to the mesophilic and thermophilic digester, individually. Final ammonia levels of mesophilic and thermophilic digester were 496 and 720 mg/L, respectively, which relate with a net ammonia generation about 197 and 421 mg/L, respectively, during the feed ammonia had been deducted. This demonstrates that more proteinaceous material might have been digested at thermophilic states.

Operation 2: This operation might have been operated specifically for the comparison of mesophilic *versus* thermophilic co-digestion of a blend of MSS, CWAS and PWW also to show the enhancement of methane yield because of PWW addition. The digesters aspects throughout operation 2 are recorded in Table-1, while the feeding details of operation 2 are listed in Table-2. Those dissolvable COD were 5 % of the total COD and over 80 % of the dissolvable COD might have been comprised of VFAs, which were 5 g/L. The influent acidification had been occurred that consolidated with the PWW's low pH quality of around 5.0 brought about a low influent pH for 5.6.

TABLE-2
DIGESTER OUTPUT FOR AFTER OPERATION (Average \pm SD)

Parameters	Influent	Effluent (Mesophilic)	Effluent (Thermophilic)
Total solids (g/L)	63 \pm 0.5	42 \pm 0.3	38 \pm 0.3
Volatile solids (g/L)	52 \pm 0.4	28 \pm 0.3	25 \pm 0.3
Total COD (g/L)	130 \pm 9	68 \pm 3	58 \pm 2
Soluble COD (g/L)	6.3 \pm 0.5	0.7 \pm 0.01	1.3 \pm 0.02
Volatile fatty acids (g/L)	5 \pm 0.5	0.07 \pm 0.002	0.09 \pm 0.002
pH	5.6 \pm 0.03	7 \pm 0.04	7.31 \pm 0.03s
NH ₄ (g/L)	0.27 \pm 0.02	0.5 \pm 0.03	0.6 \pm 0.03
Volatile solid (VS) removal (%)	–	47	52
Degradable VS removal (%)	–	86	97
Total COD removal (%)	–	48	56
Degradable COD removal (%)	–	83	95
COD balance (%)	–	-3.9	-4.5
Biogas (mL/g VS added)	–	683	747
Methane (mL/g VS added)	–	450	513
Methane (mL/g VS removed)	–	997	1002

The influent pH and VFA values were well-matched with the individuals studied previously [14]. Operation 2 continued for 30 days that indicates four maintenance periods for both digesters. The methane generation of both digesters throughout operation 2 is presented in Fig. 2. After 11 days, the methane generation was enhanced in both digesters. After 16th day methane generation turned into more consistent. The pH trained maintained nearly similar nature as the methane generation. At the end of 24th days, the pH might have been around 7 to 7.31 in both digesters, respectively whereas the feed pH was seen to be 5.6. The digester output has been listed in Table-2. The thermophilic digester attained 52 % volatile solid removal, contrasted with just 47 % of that of mesophilic digester. The improved volatile solid and COD removal of thermophilic digester brought about a higher methane generation by over 13 % than that of mesophilic digester. As the influent ammonia concentration of 279 mg/L was reduced higher protein degradation was obtained from thermophilic digester.

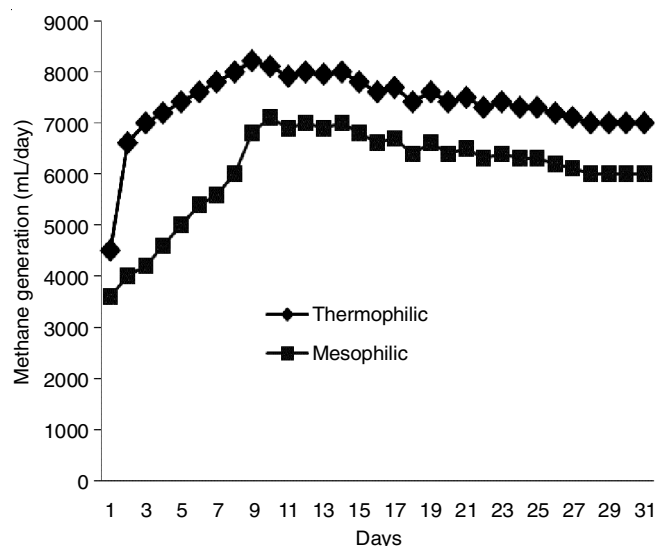


Fig. 2. Gas production during the semi-continuous digestion of MSS + CWAS + PWW (operation 2)

Corelation between operation 1, operation 2 and batch mesophilic co-digestion:

The removal of degradable COD under mesophilic state for MSS, CWAS, PWW and MSS39 + CWAS61 is shown in Table-3. Simulation of the removal of the degradable COD, furthermore its change in to methane, from MSS, CWAS and PWW specimens in light of first-order kinetics produced rate constants as: MSS 0.21 per day; CWAS starting with 0.11 and ended with 0.04-0.06 per day and PWW from 0.11 to 0.16 per day. In addition, first-order kinetics rate constants for the MSS38 + CWAS62 were 0.16 per day initially and subsequently 0.03-0.07 per day [10] likewise accounted that for a MSS32 + CWAS52 + PWW13 sample, those rate constants were: starting 0.07-0.09 per day. It indicated that the supplementation of PWW made the digestion process faster in the carbonaceous environment.

TABLE-3
COMPARISON OF FRACTION OF COD REMOVED IN 13 DAYS

Parameters	Influent	Effluent (Mesophilic)	Effluent (Thermophilic)
MSS ^a	Batch	0.84	–
CWAS ^a	Batch	0.43	–
FOG ^a	Batch	0.74	–
MSS + CWAS (39/61 VS) ^a	Batch	0.67	–
MSS + CWAS (39/61 VS) ^b	Semi-continuous	0.65	0.75
MSS + CWAS + PWW (21/31/48 VS) ^c	Semi-continuous	0.84	0.96

MSS = Municipal sewage sludge, CWAS = Condensed waste activated sludge, PWW = Petrochemical wastewater, FOG = Fats, oil and grease

The fraction of degradable COD that might have been digested in operations 1 and 2 at mesophilic and thermophilic states is demonstrated in Table-3. Hypothetically, dependent upon first-order kinetics, batch co-digestion was 19-26 % more COD removal in Table-1 for 11-21 days continuous co-digestion [10]. The thermophilic states throughout operation 1 produced a higher fragmentary digestion of degradable COD that was over 0.73.

A significant higher COD removal has been detected for operation 2. The fragmentary degradable COD removal of 0.84 at mesophilic a state complies with that of MSS and surpasses that of CWAS and FOG in 13 days co-digestion. This improvement may be due to increased loading and bacteriological activity in the semi-continuous system and in addition of the impact of operation 2 acidification. Subsequent improvement of the fractional COD degradation at thermophilic state throughout operation 2 brought about the near-complete fragmentary degradable COD removal of 0.96.

Profit of PWW co-digestion: Volatile solid digestibility of PWW co-digestion with MSS (71 %) might have been two times more over individual digestion of cattle manure (CM) and PWW [10]. The petrochemical wastewater (PWV) has a higher VS/TS ratio, 2 times more volatile solid based methane yield. These features showed that addition of PWV with digestion of MSS can remarkably increase the methane production. A theoretical and practical PWV-derived methane generation has been shown in Table-4. Based on the degradability criteria, PWV methane generation form 0.994 m³/kg VS added, estim-

TABLE-4
THEORETICAL AND PRACTICAL
PWW-DERIVED METHANE GENERATION

Parameters	Value
PWW VS (kg/d)	908
PWW VS (kg/d)	876
Ultimate methane yield from PWW (L @ STP/Kg) VS added ^a	994
Assumed extent of ultimate methane yield (%)	84
Methane produced (m ³ /year) ^b	289000
Value of produced methane (US dollars/year) ^c	122999
Methane value of PWW (US dollars/m ³) ^d	7

^aReported by Siddique and Wahid [10]; ^bAt 20 C and 1 atm; ^cAt \$ 11.85/GJ (\$ 1.25/therm); ^dAs as received by haulers PWW concentration of 2 % solids by weight.

ating that 84% of methane generation will make US \$ 122999 per year in full scale anaerobic co-digestion.

Conclusion

Under semi-continuous feeding supplementation of petrochemical wastewater (PWW) portion (49 % of VS load) in an MSS + CWAS blend brought about 2.94 times higher methane yield, 153 *versus* 450 mL methane/g VS at mesophilic state and 2.59 times bigger methane yield, 198-513 L methane /kg VS at thermophilic state. These effects demonstrate that those co-digestion of PWW with MSS could fundamentally increase methane generation. The enhancement in methane generation might be huge for MSS with generally low biodegradability (for instance for long SRT values) and for high PWW loading, as might have been those the event in this consider. In Malaysia, PWW is presently just something like 6 % of the VS load and may be worth around \$ 144,000/year reduction in gas consumption, a worth that could be expanded to approximately three-fold. However, economical and treatment system considerations should be studied as the effluent nutrients are more under 55 °C than that of 37 °C.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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