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# ENHANCEMENT OF METHANE PRODUCTION FROM ALKALINE PRETREATED POLY (LACTIC ACID) WASTE BY THE CO-DIGESTION PROCESS

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**ABSTRACT:** The objectives of this research were to evaluate the biomethane production yield from the anaerobic co-digestion process and biodegradation potential of the post-consumer plastic waste made from Polylactic acid (PLA). The PLA waste was pretreated with sodium hydroxide (NaOH) and further utilized as a co-digestion substrate, along with organic waste. The potential of alkaline pre-treatment and co-digestion of PLA with food waste and market waste for methane production was investigated. The continuous stirred-tank reactor (CSTR) feed batch was carried out on the laboratory scale. The results from the CSTR test revealed that the utilization of pre-treated PLA as a single substrate could produce biomethane for 148 L/kgVS$_{added}$. The co-digestion of pre-treated PLA with market waste could enhance biomethane production yield as high as 282.7 L/kgVS$_{added}$. Biomethane production obtained from co-digestion of pre-treated PLA with food waste was 211.6 L/kgVS$_{added}$, which was 1.6 times higher than utilizing the food waste alone.

*Keywords: Polylactic acid (PLA), Thermal-alkaline pre-treatment, Co-digestion, Methane production*

## 1. INTRODUCTION

Bioplastic is an eco-friendly, biodegradable plastic which can be degraded under appropriate environmental conditions. Currently, bioplastics are widely used in many countries to reduce the consumption of petroleum-based plastics [1]. It has been forecasted that the worldwide growth of biopolymer and bioplastic will increase as high as 12% annually. In 2018, the global production capacities of bioplastics are 6.6 million tons. Among various types of plastic, Polylactic acid (PLA) contributed to the second-highest volume consumption for bioplastics overall [2]. PLA derives from renewable resources, such as corn starch, tapioca roots, chips, starch or sugarcane. PLA is commercially available for various applications, ranging from films, bags, packaging, electronic parts and even medical plastics. However, the most common applications for PLA are biodegradable biopolymers in medical and food packaging applications. Despite the various advantages, PLA has associated limitations, such as slow degradation rate and low affinity to the cells; pH and temperature are the main factors that impact the degradation process [3]. As a result, finding the appropriate method for recycling and recovery of PLA can be a challenging task.

In general, landfilling is considered the best available option for PLA waste disposal. Theoretically, PLA is produced from lactic acid, which converts to PLA by a polymerization reaction. This can disrupt the biological and chemical degradation mechanism significantly. As a result, PLA might be unable to be directly broken down and consumed by cells as effectively as by lactic acid itself. Moreover, PLA has a highly crystalline structure, which is also not easy to degrade under aerobic and anaerobic mesophilic conditions [4]. Sin [5] stated that the degradation of PLA is initiated through a hydrolysis process, followed by the enzymatic or microorganism digestion. Such degradation eventually leads to the fragmentation of PLA, which is ultimately transformed into harmless substances. Massardier-Nageotte [4] reported that PLA showed some mass loss when aerobic conditions were applied. However, the mass loss was insignificant for the anaerobic conditions. This can be explained through slow biodegradation of PLA, which suffered from a lack of microorganism colonization on the sample surface. Kale [6] also reported that PLA, under composting plant conditions, showed disappearance within 30 days. This compares to landfill conditions, which required 6 months for major fragmentation to occur and 15 months in order to observe a significant amount of mass loss. For biodigester conditions, the fermentation of PLA under anaerobic biodegradation took 100 days at 37 °C in order to complete the degradation process [7]. Furthermore, thermophilic conditions can increase the efficiency of PLA biodegradation as well. Prior experimentation proved that a 1.5 L reactor at 55 °C resulted in a 91% PLA degradation within 75 days, along with 53.8% of methane production [8]. Much research has reported that pre-treatment can be considered an important process to significantly enhance biodegradation [9]-[10].

Currently, there are few studies focused on anaerobic fermentation, which produce methane as a renewable energy source. Samitthiwetcharong [11] observed that biogas production from pre-treated PLA with 0.5 M NaOH at 60 °C could obtain 215 ml/g$VS_{added}$, 3.7 times higher than non-pretreated PLA films. Vasmara [12] also stated that biogas production from biochemical methane potential (BMP) at 55°C from the PLA could obtain biogas for 282 mL CH4 g-1 VS. When PLA was utilized in the co-digestion process with pig slurry, maximum methane was achieved at 12%, which was higher than theoretical values. The methane ratio during PLA degradation at 35 °C and 55 °C were in the range of 50% - 60% [8]. Regarding the present work, the focus of this study was investigating the utilization of the precursor for PLA in biogas production. The aim of this study was to enhance the biogas yield achieved from the anaerobic co-digestion process between organic food waste/ market waste and the pre-treated alkaline PLA.

## 2. MATERIALS AND METHODS

### 2.1 Substrate and Raw Materials

A commercial PLA film with 80 μm thickness was used in this experiment. The PLA was cut into 1-2 mm by a grinder. The alkaline pre-treatment conditions were created by soaking the ground PLA film in 0.5 M sodium hydroxide solution (w/v) in the ratio of 1 g of PLA per 10 ml of NaOH for 2.5 days at ambient temperature. BMP experiments were used to determine the optimum conditions for the pre-treatment of PLA [11].

The food and market waste were collected from a university cafeteria in Chulalongkorn and a fresh market in Bangkok. The major component of food waste was rice and vegetables while most of the organic waste contained various kinds of vegetables, such as Chinese cabbage, cauliflower, leaves, Chinese kale and lettuce. The vegetable waste was ground before the experiment.

Inoculum used in the continuous stirred-tank reactor (CSTR) was obtained from the mesophilic anaerobic digester from the biogas production plant of a soft drink company. The inoculum was analyzed using standard methods to determine the total solids (TS) and volatile solids (VS), as shown in Table 1.

Table 1 Characteristics of substrates and inoculum

| Substrate | TS (%) | VS (%) | COD (mg/L) | pH | C/N |
|---|---|---|---|---|---|
| Food waste | 35.29 | 33.83 | 148,732 | 4.95 | 31.15 |
| Market waste | 49.38 | 45.85 | 41,239 | 5.68 | 11.01 |
| PLA | 99.78 | 99.78 | - | - | - |
| Inoculum | - | 2.5 | - | - | 8.51 |

### 2.2 Experimental Procedure

A total number of four reactors was used in this study. Each reactor contained 2% of VS, with a variation of conditions, as shown in Table 2. Different mixtures of biomass type and fractions were prepared in order to investigate the biogas production and performance for the co-digestion process. For each reactor, the ratio of substrate to inoculum was maintained at 3 L: 2 L, in which the 2% VS substrate was prepared for 3 L and the 2.5% inocula was prepared for 2 L. A flowchart of biomethane production experiment is shown in Figure 1.

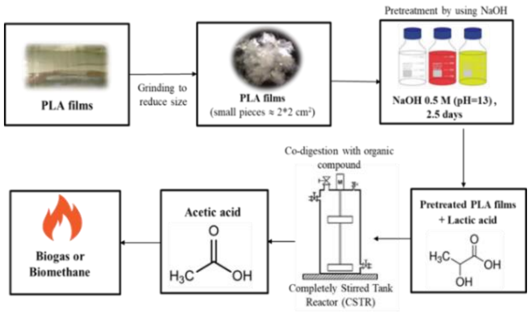



Fig.1 Flowchart of biomethane production from alkali pre-treatment PLA with food waste

### 2.3 Operation Scheme

The number of substrate fractions with an initial 2% of VS for 3 L was added to the CSTR. $NaHCO_3$ 3 g/L was added to the reactor to provide buffer capacity. The ratio of substrates in each reactor and its chemical characteristics are shown in Table 2. The biogas production volume was recorded daily. The batch experiments were incubated until no further gas was produced (60 days). Samples of 50 ml were taken from each reactor to analyze TS, VS, soluble COD (sCOD); this occurred three times per week. A methane gas composition analyzer was used to measure the methane content by gas chromatography with a thermal conductivity detector (TCD).

Table 2 Experimental setup: number of substrates in each batch reactor and chemical characteristics

| Reactor | Substrate | TVS(%) | TVS (%) | %C | %N | C/N ratio |
|---|---|---|---|---|---|---|
| 1 | PLA | 2 | 2.00 | 33.56 | - | - |
| 2 | PLA pre-treated with 5 M NaOH for 48 h (pretreated PLA) | 2 | 2.56 | 39.98 | - | - |
| 3 | Co-digestion of pre-treated PLA and food waste with ratio 1:1 (pretreated PLA: FW = 1:1) | 2 | 2.65 | 36.77 | 1.08 | 34.13 |
| 4 | Co-digestion of pre-treated PLA and market waste with ratio 1:1 (pretreated PLA: MW= 1:1) | 2 | 2.54 | 30.01 | 1.43 | 21.02 |

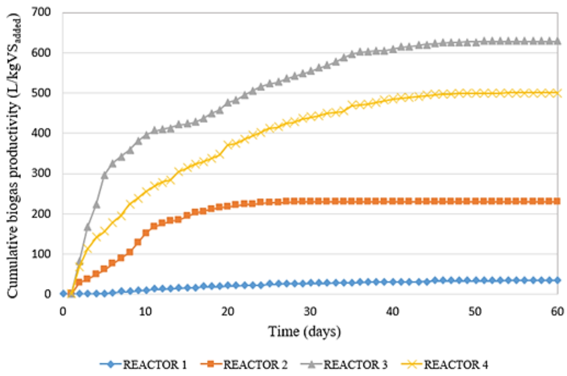
## 3. RESULTS AND DISCUSSION

### 3.1 Effect of NaOH Pre-treatment on PLA

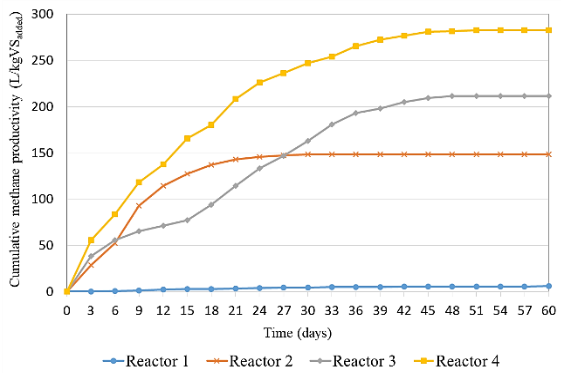
PLA was pre-treated by soaking with a 0.5 M NaOH solution (w/v) for 60 hours prior to use as feedstock for anaerobic digestion in CSTR. The NaOH solution, was used for the PLA pre-treatment, was analyzed for lactic acid concentration. The results revealed that the concentration of Lactic acid was 18,200 mg/l. Gorrasi [13] reported that the hydroxide ion ($OH^-$) from NaOH could increase the reaction rate of the hydrolysis by minimizing the structure of the PLA and degrading it to the lactic acid form. The detection of lactic acid could confirm that the hydrolyzed PLA was transformed into lactic acid, which would then convert into acetic acid, the methanogens enabler for the biogas production [3], [14]-[15]. As a result, pre-treatment of the alkaline solution proved to be effective for PLA in the anaerobic or co-digestion process, along with the organic food waste or other biomass, for biomethane recovery.

### 3.2 Bio-methane Production

Co-digestion between alkaline pre-treated PLA and organic waste could increase the methane content in the obtained biogas. The biogas and methane yield from the pre-treated PLA film substrate were 230 and 148.3 $L/kgVS_{added}$, respectively (Fig. 2). It was observed that the percentage of methane in biogas was as high as 64.5%. This resulted from the hydrolysis and defragmentation of the PLA into the lactic acid, according to the pre-treatment process. Consequently, the microorganism that produced acid could directly transform the lactic acid into the acetic acid. Similarly, the methanogen could transform the acetic acid into methane. However, it took 27 days following the commencement of the system operation until the biological reaction of the methane generation was complete.




(a) Biogas yield




(b) Methane yield

Fig.2 Cumulative biogas and methane productivity of pre-treated PLA and co-digestion of pre-treated PLA with organic waste.

The results from the co-digestion experiment revealed a higher amount of biogas and methane as compared to the reactor which utilized the pre-treated PLA alone. For the co-digestion process, it was observed that pre-treated PLA and food waste using a 1:1 ratio achieved the highest biogas production at 627.4 $L/kgVS_{added}$. The reactor that utilized pre-treated PLA and market waste at a 1:1 ratio was the second highest biogas producer at approximately 500.4 $L/kgVS_{added}$. However, the methane content in biogas obtained from pre-treated PLA and market waste was significantly higher than that obtained from pre-treated PLA and food waste. As a result, co-digestion between pre-treated PLA and food waste achieved the highest methane yield at 282.7 L/kgVS$_{added}$, while the methane yield achieved from the co-digestion of pre-treated PLA and food waste was 211.6 L/kgVS$_{added}$. Theoretically, the lactic acid is the primary reactant for the biogas production process. This phenomenon could explain why biogas production was increased. Furthermore, the co-digestion between the bioplastic and organic waste could also increase the biomethane production. Wang [14] reported that organic waste could increase the degradation rate of the PLA in anaerobic conditions with the proper temperature, pressure and ammonia content to degrade the protein in the food waste.

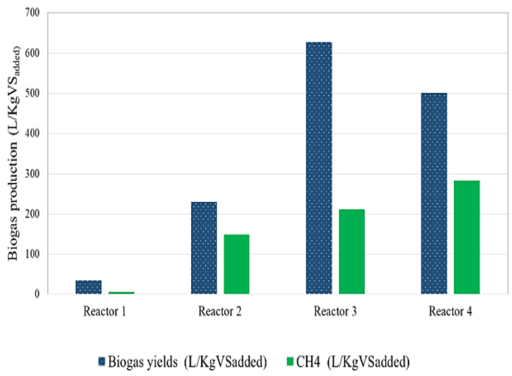


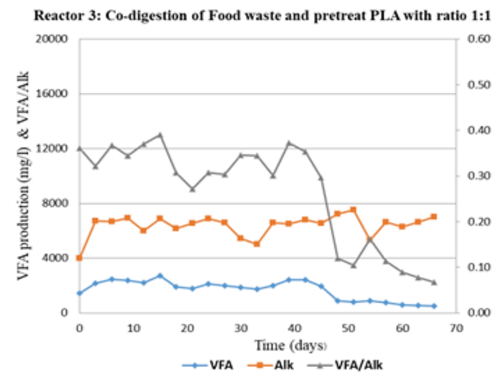

Fig.3 Biogas and methane productivity of pretreated PLA and co-digestion of pretreated PLA with organic waste.

In addition, the co-digestion between pre-treated PLA and market waste obtained 1.9 times higher amount of methane than obtained from the use of pretreated PLA as a single substrate, as shown in Figure 3. The co-digestion experiment of pre-treated PLA with food waste could increase the methane production capacity for 1.43 times higher than the reactor, which utilized only the pre-treated PLA alone. The obtained results could indicate that co-digestion of pre-treated PLA and organic waste could enhance the methane production in the co-digestion anaerobic process.

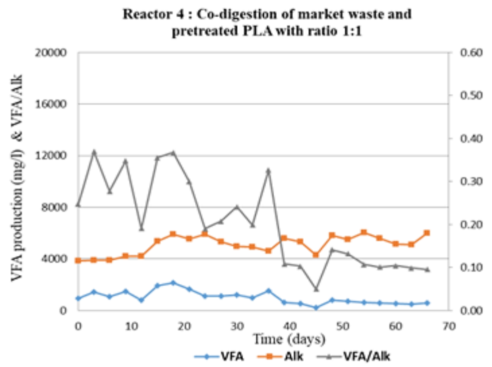
### 3.3 Digester Performance

Table 3 reports the pH and alkalinity ratios (VFA/ALK) of the effluents of various substrates during a 60-day incubation period. The results showed that all CSTR batch experiments had a VFA/ALK ratio in the range of 0.05 - 0.39 (Figure 4). The alkalinity results for each batch also contributed to higher than 2,500 mg as $CaCO_3$/l, which revealed the notable buffer capacity of the overall system. These results indicate the high stability of a system in which the VFA/ALK was below 0.4.

The result from sCOD removal efficiency (Table 3) showed that normal PLA could not biologically degrade within 65 days in an anaerobic condition. However, the alkaline pre-treated PLA could be biologically degraded by the anaerobic bacteria. Consequently, the alkaline pre-treatment could help promote the degradation of PLA and transition it into lactic acid by increasing the rate of hydrolysis. Lactic acid can be subsequently transformed into the biogas [15]. The results also revealed that COD removal efficiency of the pre-treated PLA comparable to the market waste.




(a) pretreated PLA: FW = 1:1




(b) pretreated PLA: MW =1:1

Fig.4 The performance of an anaerobic digester of co-digestion.

### 3.4 Scanning Electron Microscopy (SEM) Study

A topology study of pre-treated PLA films was done using scanning electron microscopy (SEM) with a magnification of 2000 times (as shown in Figures 5-8). Four sets of PLA film and pre-treated PLA were used for the topology study, including 1) the PLA film obtained from the non-pre-treated

PLA digestion alone, 2) the pre-treated PLA digestion alone, 3) Co-digestion of pre-treated PLA: FW and 4) Co-digestion of pre-treated PLA:MW. For the pre-treated PLA film, a high density of pores was observed in only 15 days of operation. The porosity density was further increased after 60 days of operation. This result indicated that NaOH could enhance the porosity of the PLA film, which increased the biodegradation process and promoted the bioavailability of the microorganism or enzyme for effective functioning. The result from Figures 6 and 7 emphasized the enhancement of biogas production due to co-digestion of pre-treatment PLA. It was shown that using pre-treated PLA with organic waste from single substrate digestion promoted biogas production, resulting in a high porosity PLA surface.

Table 3 pH, temperature and VFA/ALK ratio from co-digestion of pre-treated PLA and organic waste

| Reactor | Substrate | pH | Temp (°C) | VFA/ALK ratio | % SCOD removed |
|---|---|---|---|---|---|
| 1 | PLA | 6.50 – 7.95 | 29.9 – 34.9 | - | - |
| 2 | Pre-treated PLA | 6.65 – 7.94 | 30.7 – 34.6 | 0.07-0.33 | 88.37 |
| 3 | Pre-treated PLA: FW = 1:1 | 6.78 – 7.82 | 29.7 – 34.7 | 0.07-0.39 | 94.32 |
| 4 | Pre-treated PLA: MW =1:1 | 6.90 – 7.96 | 30.7 – 34.9 | 0.05-0.37 | 90.51 |

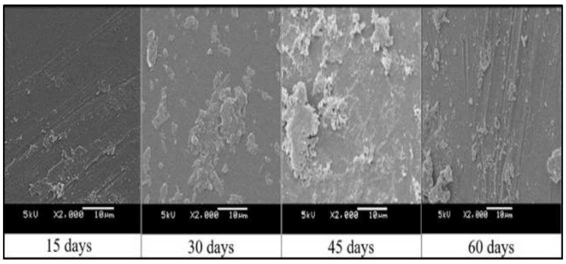



Fig.5 Surface of non-pre-treated PLA films from single substrate digestion

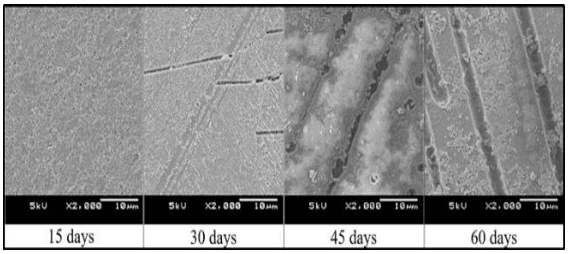



Fig.6 Surface of alkaline pre-treated PLA films

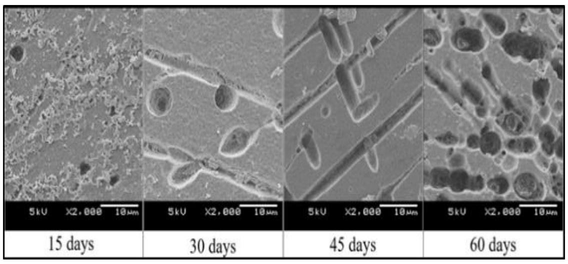



Fig.7 Surface of pre-treated PLA films from co-digestion with food waste.

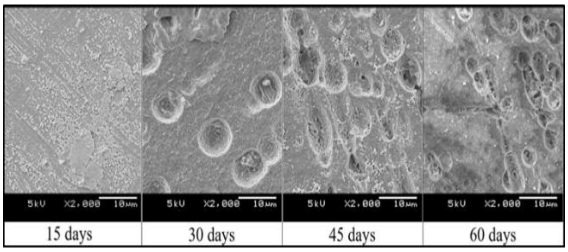



Fig.8 Surface of pretreated PLA films from co-digestion with market waste.

## 4. CONCLUSION

Pre-treatment of the PLA film by NaOH at pH 13 (NaOH 0.5 M) for 60 hours promoted PLA degradation. This, in turn, developed into lactic acid, which further converted into acetic acid, which is the primary substrate of the biogas production for the methanogen after the anaerobic operation. Furthermore, co-digestion of alkaline pre-treated PLA with the market and food waste achieved a greater biomethane yield as compared to PLA alone. As a result, PLA waste could be used as a substrate for the anaerobic co-digestion process. In addition, alkaline pre-treatment of PLA could also aid in promoting biomethane yield.

## 5. ACKNOWLEDGMENTS

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