

# Characterization of methane production in a thermophilic anaerobic digestion process treating poly(L-lactic acid) that enhances chemical hydrolysis efficiency

Takeshi Yamada<sup>1</sup>, Masako Hamada<sup>1</sup>, Hideto Tsuji<sup>1</sup>, Akira Hiraishi<sup>1</sup>

<sup>1</sup>Department of Environmental and Life Sciences, Toyohashi University of Technology, Toyohashi, Japan  
(tyamada@ens.tut.ac.jp; mh016@edu.tut.ac.jp; tsuji@ens.tut.ac.jp; hiraishi@ens.tut.ac.jp)

**Keywords:** anaerobic digestion; methane; thermophilic; poly(L-lactic acid); chemical hydrolysis

## INTRODUCTION

Poly(L-lactic acid) (PLLA) is superior to other biodegradable plastics owing to its mechanical, chemical and physical properties; thus, it has attracted substantial attention as a biodegradable plastic material for general use as an alternative to petrochemical plastics. Various types of PLLA products such as packing materials and agricultural materials have expanded to date into further generic use. However, the disposal and re-use of this material is a serious problem because of the large amount of PLLA waste generated. Although “clean” PLLA wastes can be chemically recycled to lactic acid by thermal decomposition and hydrolysis, disposal of PLLA wastes that are unsuitable for such recycling has been handled by methods such as landfill deposition, incineration, and composting. Although no increase in global carbon emission has been reported even with these methods, a more effective system of PLLA waste management should be considered to establish a new earth-friendly resource circulation system. One of the effective uses of such PLLA wastes is to produce methane along with the garbage in anaerobic digestion reactors. However, because biological hydrolysis of PLLA cannot be expected in the anaerobic digestion reactors, hydrolysis of the PLLA to lactic acid is the rate-determining step. Therefore, it is necessary to establish a new method for promoting the chemical hydrolysis of PLLA in anaerobic digestion reactors. Several attempts have been made to develop technologies that would help to recover methane from PLLA wastes<sup>1),2)</sup>. This study focuses on the weight-average molecular weight ( $M_w$ ) and crystallinity ( $X_c$ ) that acts on the chemical hydrolysis because the adjustment of these variables is relatively simple. To recover methane from organic waste, including PLLA waste, we have devised a new process consisting of a high-temperature and high-pressure processing and an anaerobic digestion process. The aims of this study are to identify the  $M_w$  and  $X_c$  of PLLA that are suitable for good methane production and to investigate the characteristics of continuous methane production in a thermophilic anaerobic digestion reactor by using PLLA as the sole substrate.

## MATERIAL AND METHODS

The  $M_w$  of PLLA used in this study was adjusted to a range of 5,400–219,000 in the treatment by high-temperature and high-pressure steam. The  $X_c$  of the PLLA ( $M_w = 16,000$  and  $38,000$ ) was adjusted to 0%–40% by the annealing process. Lactic acid release tests were conducted by adding 1% (w/v) PLLA to the base medium at pH 7.0. Methanogenic activity tests were conducted by adding anaerobic digested sludge with a mixed liquor volatile suspended solids concentration of  $5,000 \text{ mg} \cdot \text{L}^{-1}$  and 1% (w/v) PLLA to the base medium at pH 7.0. Both tests were conducted by shaking at 55 °C. Continuous methane production was evaluated by using a 7 L thermophilic anaerobic digestion reactor at 55 °C. The volumetric organic loading rate (VOLR) was controlled by the PLLA amount and the hydraulic retention time (HRT). The methane concentrations in the reactor and the vial were measured by using a gas chromatograph with a thermal conductivity detector.

## RESULTS AND DISCUSSION

Lactate release tests using PLLA with different  $M_w$  values were performed at 55 °C; successful release by chemical hydrolysis from PLLA occurred at  $M_w$  of 38,000 or less. The lactate release rate from PLLA increased with an increase in  $X_c$ . These facts indicate that adjustment of the low molecular weight and high crystallinity of PLLA promotes its chemical hydrolysis. Next, we investigated the possibility of producing methane from PLLA adjusted for  $M_w$  and  $X_c$  by using the actual anaerobic digestion sludge. Methanogenic activity under thermophilic conditions was detected with PLLAs having  $M_w$  of 16,000–38,000. Of these values, the maximum methanogenic activity was observed when using PLLA with an  $M_w$  of approximately 16,000. In addition, PLLAs with high  $X_c$  enhanced the methanogenic activity under thermophilic conditions owing to the increase in hydrolysates from the

PLLA. These results are in agreement with the behavior of the chemical hydrolysis of PLLA, suggesting that an increase in lactate release has a direct impact on the methanogenic activity of anaerobic digestion sludge.

Next, this study investigated continuous methane production in a thermophilic anaerobic digestion reactor using PLLA adjusted with optimized values of  $M_w$  and  $X_c$  of approximately 16,000 and 40%, respectively (Fig.1). During the 42 days, the anaerobic digestion sludge in the thermophilic digestion reactor was acclimatized at a VOLR of  $0.5 \text{ kg-COD} \cdot \text{m}^3 \cdot \text{d}^{-1}$  and an HRT of 100 days (Fig.1). Then, the VOLR was controlled in a range of  $0.5\text{--}2.0 \text{ kg-COD} \cdot \text{m}^3 \cdot \text{d}^{-1}$  by changing the HRT. In the acclimatization period, the maximum biogas production rate reached  $0.23 \text{ m}^3 \cdot \text{kg-PLLA}^{-1} \cdot \text{d}^{-1}$ , and the methane concentration gradually stabilized at approximately 50%–55% (Fig.1). The biogas production and methane concentration during the operation period of 43–153 days were almost the same as those detected in the acclimatization phase (Fig.1). The methane conversion rate to the input PLLA was between 23% and 32% under the steady-state condition.

In contrast, after 154 days of the operation, an HRT shorter than 30 days and a VOLR higher than  $1.0 \text{ kg-COD} \cdot \text{m}^3 \cdot \text{d}^{-1}$  caused a decrease in biogas generation and low methane concentration (Fig.1). The amount of withdrawn sludge exceeded the microbial growth because lactate-oxidizing bacteria and methanogenic archaea with properties of low doubling time slowly predominated. The allowable VOLR of the process treating PLLA as the sole substrate was found to be smaller than those treating organic waste such as garbage.

## CONCLUSIONS

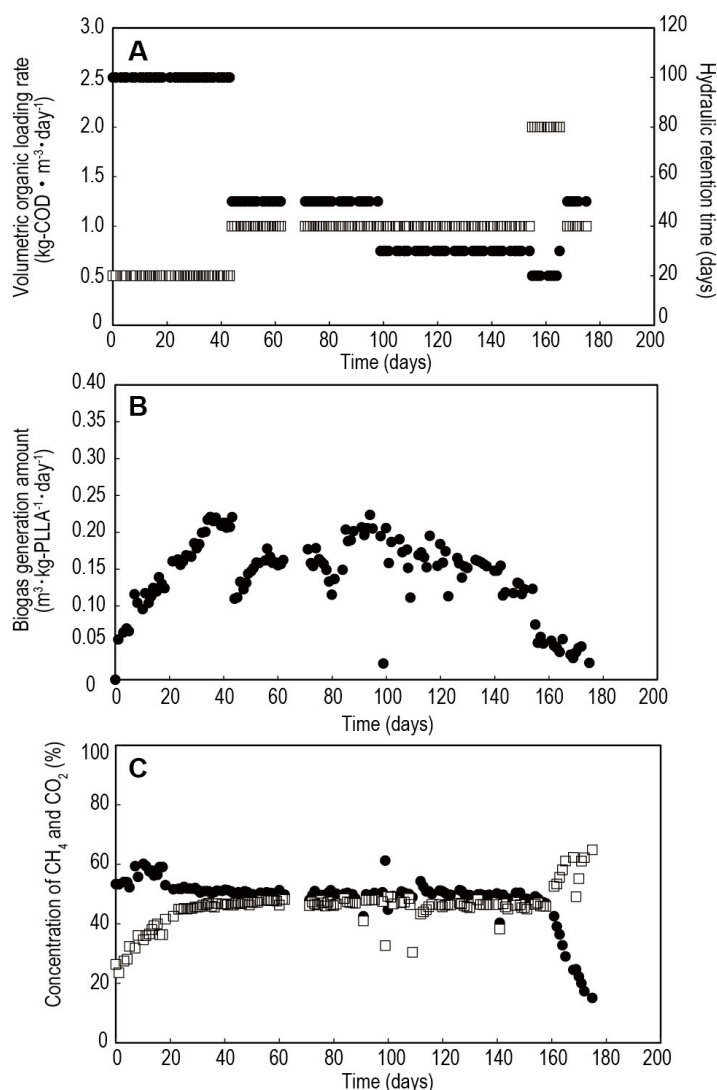
These results suggest that adjustment of PLLA to enhance chemical hydrolysis on the basis of  $M_w$  and  $X_c$  is an effective method for producing methane in thermophilic anaerobic digestion processes.

## ACKNOWLEDGEMENTS

This study was part of a project entrusted to the Adaptable and Seamless Technology Transfer Program (A-STEP) (AS242Z01149N), Iwatani Naoji Foundation, and Research Foundation for the Electrotechnology of Chubu. We also thank Masaya Shimoda and Xiangqin Wu for offering technical help.

## REFERENCES

- 1) Wang, F., Tsuno, H., Hidaka, T., Tsubota, J. (2011) Promotion of polylactide degradation by ammonia under hyperthermophilic anaerobic conditions. *Bioresour. Technol.*, 102 : 9933-9941
- 2) Yagi, H., Ninomiya, F., Funabashi, M., Kunioka, M., (2010) Bioplastic biodegradation activity of anaerobic sludge prepared by preincubation at 55 °C for new anaerobic biodegradation test. *Polym. Degrad. Stab.* 95 ; 1349-1355



**Fig. 1. Operation results of thermophilic anaerobic digester reactor treating PLLA. A: operation conditions (● : HRT and □ : VOLR ; B: changes in biogas generation; C: changes in CH<sub>4</sub> and CO<sub>2</sub> concentration (● : CH<sub>4</sub> and □ : CO<sub>2</sub>).**