



Characteristics of the steam degradation of poly(lactic acid) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

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Abstract

The introduction of biodegradable plastics is considered a practical approach to reducing plastic waste accumulation in the environment. Regardless of their biodegradability, plastics should be recycled to effectively utilize and circulate carbon as a resource. Herein, the use of pyrolysis was examined as a method for recycling two common biobased/biodegradable plastics: PLA and PHBH. The pyrolysis of PLA produced lactides (10.7 wt% at 400 °C), but the yield was decreased when the pyrolysis temperature was increased. The presence of steam promoted the hydrolysis of PLA: a steam concentration of 25 vol % increased, the production of lactides at 400 °C to 17.4 wt%. The pyrolysis of PHBH primarily yielded crotonic acid (30.1 wt% at 400 °C), and the yield increased with increasing pyrolysis temperature (71.8 wt% at 800 °C). Steam injection increased the hydrolysis of oligomers, resulting in a 76.1 wt% yield of crotonic acid at 600 °C with a steam concentration of 25 vol %. Thus, we determined that hydrolysis and pyrolysis progress simultaneously under a steam atmosphere, increasing the chemical feedstock recovery from PLA and PHBH. These findings may lead to the proposal of effective degradation methods for treating biobased/biodegradable plastic wastes and ways to maximize the conversion efficiency and target product yields.

Introduction

Petroleum-based plastics became commercially available in the 1950s, meeting needs for lightweight, inexpensive, and durable materials. Approximately 352 million tons of petroleum-based plastics were produced in 2021, approximately 180 times the amount produced in 1950 [1]. However, the entire lifecycle of petroleum-based plastics produces detrimental environmental effects, including environmental accumulation, nonrenewable resource depletion, and carbon emissions. Bioplastics have been recommended as a substitute for petroleum-based materials with promise for solving these problems. Bioplastics are

polymers that are made from renewable resources or are biodegradable. Biobased and biodegradable plastics are notable because of their carbon-neutral characteristics. Moreover, making and using them instead of petroleum-based plastics can simultaneously reduce petroleum consumption and combat the problem of environmental plastic accumulation. Numerous countries have implemented policies to encourage the adoption of bioplastics [2, 3]. As a result, the global production of biodegradable plastics is expected to triple within the next five years [4].

Although biodegradable plastics can be degraded into water and carbon dioxide in nature, their environmental impacts are not entirely benign. For example, poly(lactic acid) (PLA) can be decomposed only by hot composters or digesters and undergoes little decomposition in soil or marine environments [5–8]. Additionally, discarded biodegradable plastics can be fragmented into microplastics [9]. Therefore, biodegradable plastic waste products, similar to petroleum-based plastic waste, should be well managed and sent to recycling systems to minimize their environmental impact [10, 11].

Petroleum and biodegradable plastic mixtures are generated during the recycling stage because of the increased substitution of biodegradable plastic products for

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petroleum-based plastics. To increase their thermal stability and improve their mechanical properties, biodegradable plastics are often blended with other polymers or additives (such as plasticizers and fillers) and laminated with other plastics [12–15]. Therefore, cost-effective recycling methods for handling petroleum-based and biodegradable plastics must be considered.

Pyrolysis is a promising method for recycling plastic waste to obtain chemical feedstocks and fuels. This method is not sensitive to feedstock quality, and the product can be tuned by changing the reactor type, operating conditions, or catalysts [16–18]. The pyrolysis of PLA and poly(hydroxyalkanoate) (PHA), the most prevalent biobased/biodegradable plastics, has been investigated. Acetaldehyde, CO, CO₂, lactide, and oligomers are the primary products of PLA pyrolysis [19, 20]. Among these pyrolyzates, lactide is the most noteworthy because it is a critical material for the synthesis of PLA. Pyrolysis is a unique technology for recovering lactides from PLA waste through thermal depolymerization [21, 22]. However, the low recovery rates of pyrolysis methods have limited their practical application [23, 24]. To increase the recovery efficiency, catalytic pyrolysis and co-pyrolysis have been proposed for recycling PLA. Metallic catalysts, including tin and magnesium, can selectively produce lactides at reduced decomposition temperatures [25, 26]. Wood powder can effectively increase lactide yield owing to its ability to supply free radicals during co-pyrolysis [19, 23, 27]. Unfortunately, catalyst deactivation and product purification are distinct challenges that must be addressed during catalytic pyrolysis and co-pyrolysis. Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) is a member of the PHA family with a broader processing window and good thermal stability [28]. Previous studies have revealed high production of crotonic acid, a monomer of PHBH and poly(3-hydroxybutyrate) (PHB), at temperatures exceeding 600 °C [24, 29]. Therefore, lowering the production temperature of crotonic acid and increasing its yield are highly desirable.

Steam degradation is a promising technology for improving the efficiency of polyester decomposition. The ester bonds in the polyester chains can be cleaved by pyrolysis and hydrolysis, and long-chain structures can be depolymerized into monomers [30]. In our previous study, we reported that steam degradation can promote the hydrolysis of polycarbonate [31], polyimide [32, 33], poly(butylene terephthalate) [34], poly(ethylene 2,6-naphthalate) [34], and poly(ethylene terephthalate) [34, 35], thereby increasing the production of valuable chemicals. These reports indicate that steam degradation technology can enhance the decomposition of PLA and PHBH. However, to the best of our knowledge, the influence of steam on the thermal degradation of PLA and PHBH has not been investigated. Furthermore, owing to the structural

disparities among various polyesters, the relative dominance of pyrolysis and hydrolysis during steam degradation varies, potentially resulting in distinct steam degradation pathways. Hence, the steam degradation of PLA and PHBH should be extensively investigated. In this study, we investigated the steam degradation of PLA and PHBH in a tube reactor at 400–800 °C and three different steam concentrations. The pyrolysis products were identified and quantified, and the effects of temperature and steam concentration on the pyrolysis products were investigated.

Materials and methods

Materials

PLA was purchased from Standard Test Piece Co., Ltd. (Kanagawa, Japan). PHBH (6 mol.% hydroxyhexanoate unit) was obtained from Kaneka Co., Ltd. (Tokyo, Japan). The plastic pellets were ground to a particle size of <100 mesh. The compositions of these samples were analyzed using an elemental analyzer (JM10, J-Science Lab, Japan), and the results were consistent with the theoretical values (Table 1). Before the experiments, the samples were dried at 40 °C for more than 12 h in a vacuum oven. The chemicals used in the experiments were purchased from Kanto Chemical Co. (Tokyo, Japan).

Steam degradation experiments

Steam degradation experiments were performed in a tube reactor [36] equipped with a syringe pump (Fig. 1). Approximately 0.1 g of a sample was placed near the inlet and fixed with quartz wool. An electric furnace was moved to the inlet to heat the sample until the temperature reached a preset value. The temperature of the sample chamber reached the preset temperature within 1 min. Simultaneously, distilled water was pumped into the tube reactor using a syringe pump to produce a steam concentration of 0, 25, or 50 vol% (total flow rate of helium and steam: 50 mL min⁻¹). After heating for 10 min, the furnace and syringe pump were switched off. The tube was naturally

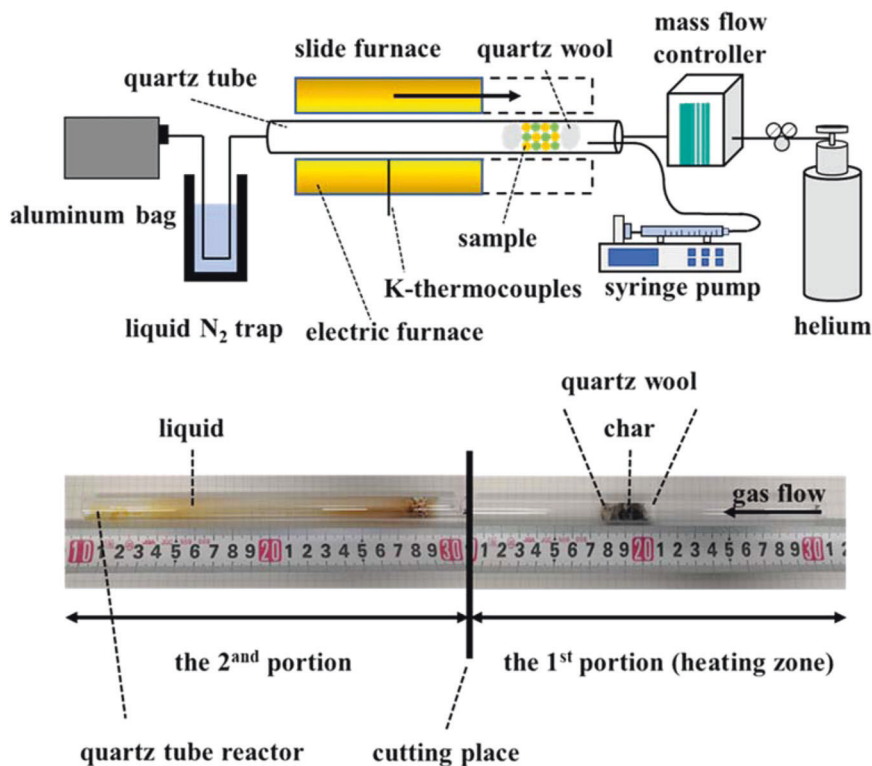
Table 1 Composition of carbon, hydrogen, and nitrogen in PLA and PHBH

Polymer type	Weight composition [wt%]		
	C	H	N
PLA	49.90 ± 0.10	5.64 ± 0.02	— ^a
PHBH	56.58 ± 0.08	7.39 ± 0.00 ^b	— ^a

^aNot detected

^bLess than 0.01%

Fig. 1 Diagram of the pyrolysis equipment and cutting point of the tube reactor after the experiments



cooled to 50 °C, and then the liquid nitrogen was removed, and the volatile products were transferred to an aluminum bag under continuous helium flow. The char remained in the quartz wool and the other pyrolysis products were condensed in a quartz tube outside the heating zone. After the trap temperature reached 25 °C, the reactor was disassembled, and the quartz tube was cut into two parts for weighing. After weighing, tetrahydrofuran (THF) was used to dissolve the pyrolysis products in the quartz tube. To ensure the accuracy of the results, pyrolysis experiments were conducted at least twice.

Analytical methods for determining degradation products

In this study, the degradation products were categorized as gas and liquid. The products collected in the aluminum bag were defined as gases. THF-soluble products were defined as liquids. In this study, THF-insoluble compounds and carbonaceous char were not produced under any of the investigated conditions. The boiling points and melting points of each compound were not considered in product categorization.

The gases were analyzed using a GC-TCD/FID system (Agilent GC8860) with a Gas-pro column (60 m × 0.32 mm × 0.25 μm, Agilent) and two ShinCarbonST columns (2 m, 1/8", 50/80, Agilent). Liquids were identified and quantified using GC-MS/FID (Agilent 7890 A/5975 C)

with an HP-5ms column (60 m × 0.25 mm × 0.25 μm, Agilent). The details of the GC analytical procedure and conditions are presented in Tables S1, S2.

Results and discussion

Effects of pyrolysis temperature on product distribution

PLA

Figure 2a shows the mass balance of PLA degradation at different temperatures and steam concentrations. The total recovery rate was approximately 90%, and the remaining 10% comprised mainly highly volatile compounds, such as acetaldehyde, which were partially evaporated as the product was collected. The pyrolysis gas comprised CO, CO₂, and acetaldehyde, and the liquid products included meso-lactide, D-, L-lactide and cyclic lactide oligomers. In addition, these oligomers exhibited a series of MS signals with $m/z = 56 + (n \times 72)$, where n was assumed to be 2 (dimer), 3 (trimer), 4 (tetramer), or 5 (pentamer), and the main fragment ions are shown in Table 2. These products were consistent with those reported previously [19, 20]. The gas and liquid yields increased and decreased, respectively, with increasing temperature. This result is consistent with the behavior of PLA pyrolysis reported in the literature [37].

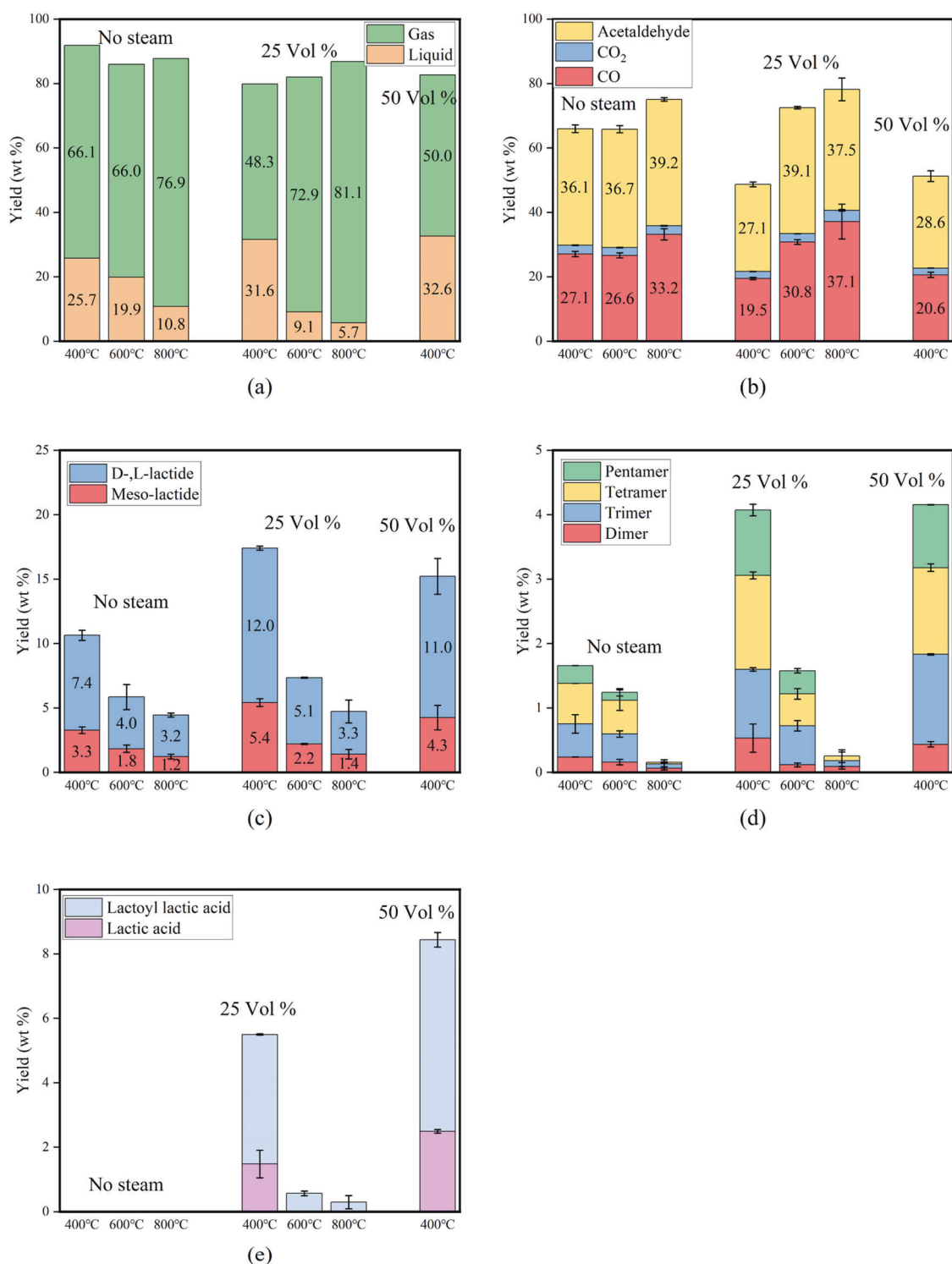


Fig. 2 a Mass balance, (b) yield of gas compounds, (c) yield of lactic acid, (d) yield of oligomers, and (e) yield of hydrolyzates obtained from PLA at different temperatures and steam concentrations

The chain-cracking reaction and secondary thermal cracking were promoted at higher temperatures. Figure 2b shows the yields of gaseous compounds. Acetaldehyde and CO were the major gas products. At 400 and 600 °C, no

significant difference was observed in the yields of the gas compounds, and the selectivity toward each compound was the same. At 800 °C, the yield of CO₂ was similar, whereas the yields of CO and acetaldehyde increased to 33.2 and

39.2 wt%, respectively. The weight compositions of CO and acetaldehyde in total gas yield slightly increased and decreased, respectively, suggesting that acetaldehyde was degraded to methane and CO at high temperatures [38].

Figure 2c summarizes the lactide yields obtained from the PLA pyrolysis liquid. As shown in the figure, the maximum yield of lactides was obtained at 400 °C (10.7 wt%). Although radical intermediates were not detected in these experiments, lactide production through transesterification and radical reaction mechanisms during PLA pyrolysis has been reported [39]. As the pyrolysis temperature increased, the lactide yield decreased rapidly. Only 4.5 wt% lactide was obtained at 800 °C. Lactides are thermally unstable and decompose into acetaldehyde and CO [20, 40]. Although oligomers were converted to lactide at 800 °C, the lactide yield was significantly reduced, indicating that the lactide decomposition rate was greater than the lactide production rate. Under the tested experimental and analytical conditions, oligomers from dimers to pentamers were identified and quantified, and their total yields decreased from 1.7 wt% at 400 °C to 1.2 wt% at 600 °C. Less than 0.2 wt% oligomers, except for the pentamer, was quantified at 800 °C. Thus, low temperatures are preferred for PLA pyrolysis to effectively recover lactides.

PHBH

The total recovery rate of the PHBH pyrolyzates ranged from 90.1 to 99.0 wt%. Only 0.5 wt% gas was observed at 400 °C, and the gas yield increased from 2.4 to 6.3 wt% when the pyrolysis temperature was increased from 600 to 800 °C. The liquid yields were 98.5, 92.6, and 87.8 wt% at 400, 600, and 800 °C, respectively. The degradation of PHBH proceeded via the β -elimination reaction [41]. Therefore, monomeric, dimeric, and trimeric products were the dominant pyrolyzates in the liquid. The pyrolysis gas consisted primarily of propylene, CO₂, and CO. The yields are shown in Fig. 3b. Propylene and CO₂ are generated by the thermal decomposition of crotonic acid [29, 42]. In addition, propylene and other hydrocarbons can be formed via bond cleavage and dehydration of the PHBH chain at higher temperatures [43]. Therefore, as the temperature increased from 400 to 800 °C, the propylene yield increased

from 0.1 to 2.3 wt%. In addition, methane, ethane, and ethylene were also detected at 800 °C, with yields of 0.12, 0.04, and 0.19 wt%, respectively. At 800 °C, CO was detected with a yield of 0.44 wt%.

Isocrotonic acid, crotonic acid, and 2-hexenoic acid were the major compounds in the liquid. As shown in Fig. 3d, as the pyrolysis temperature increased, the yields of isocrotonic acid, crotonic acid, and 2-hexenoic acid increased from 1.8, 30.1, and 2.5 wt%, respectively, at 400 °C to 11.2, 71.8, and 5.3 wt%, respectively, at 800 °C. Notably, no significant difference in the yield of 2-hexenoic acid was observed between 600 and 800 °C, which can be attributed to the relatively low content of the 3-hydroxyhexanoate (3HH) unit (6%) in PHBH. Approximately 30.7 wt% oligomers was observed at 400 °C, which decreased to 7.6 wt% at 600 °C. At 800 °C, the oligomers were completely degraded.

Effects of steam on the product distribution

PLA

Figure 2a shows that the trend of the total gas yield with temperature was the same in the presence of steam. High temperatures facilitate gas production. During steam degradation at 400 °C with a steam concentration of 25 vol%, the yields of CO₂, CO, and acetaldehyde were 2.2, 19.5, and 27.1 wt%, respectively, which were lower than those obtained without steam. The hydrolysis and pyrolysis reactions progress simultaneously under steam degradation. In our previous study, we showed that hydrolysis occurs faster than pyrolysis at lower temperatures during the steam degradation of polyesters [34]. Therefore, the current results suggest that the addition of steam increases the yields of hydrolysis products and inhibits the further fragmentation of degradation products by pyrolysis. However, the gas yields above 600 °C were slightly greater than those in the absence of steam. The yields of CO and acetaldehyde increased to 30.8 and 39.1, respectively, at 600 °C in the presence of steam. The CO yield further increased to 37.5 wt% at 800 °C, whereas the acetaldehyde yield remained comparable (37.1 wt%).

The liquid yield obtained from steam degradation decreased with increasing temperature. The yield of lactides at 400 °C was significantly increased by adding steam. The yield of meso-lactide increased from 3.3 to 5.4 wt%, and the D-, L-lactide yield increased from 7.4 to 12.0 wt% (Fig. 2c). Increased lactide production was also observed at higher temperatures. The yields of meso-lactide and D-, L-lactide increased from 1.8 and 4.0 to 2.2 and 5.1 wt%, respectively, at 600 °C. However, the difference in yield between the treatments with and without steam was not significant at 800 °C. Thus, the effect of steam-induced hydrolysis was

Table 2 Main fragment ions of PLA oligomers observed by GC/MS analysis

Compound	Main fragment ions (<i>m/z</i>)
Dimer	32, 56, 100, 128, 200
Trimer	32, 56, 100, 128, 200, 272
Tetramer	32, 56, 100, 128, 200, 272, 344
Pentamer	32, 56, 100, 128, 200, 272, 344, 416

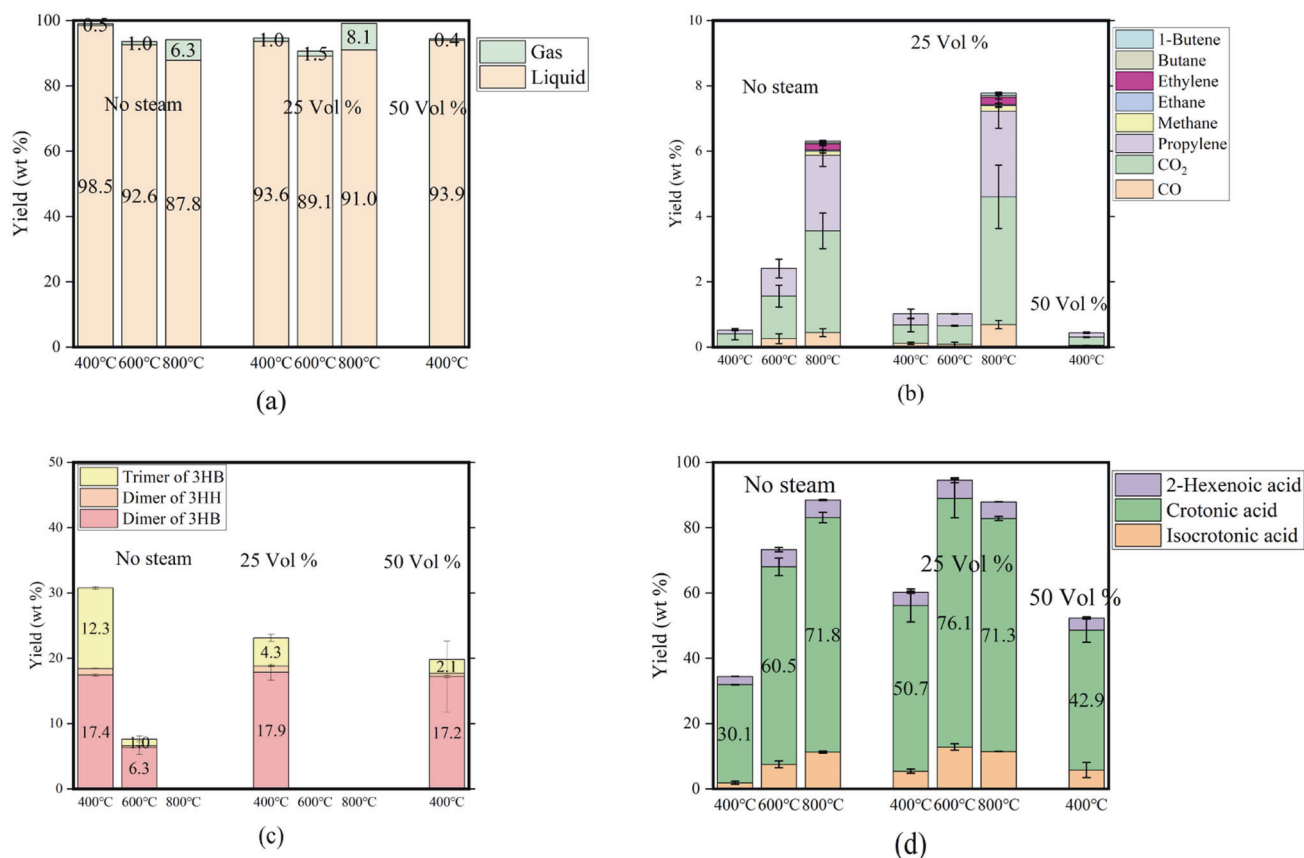


Fig. 3 a Mass balance, (b) yield of gas compounds, (c) yield of oligomers, and (d) yield of monomers obtained from PHBH at different temperatures and steam concentrations

not noticeable because of the promotion of pyrolysis at higher temperatures. This tendency is consistent with that observed in our previous study on the steam degradation of polyesters [34].

As shown in Fig. 2d, steam-induced hydrolysis promoted the transformation of long-chain PLA into cyclic oligomers. In addition, lactic acid and its linear dimers were detected as new products of steam degradation. The formation of hydroxyl and carboxyl groups supported the progress of hydrolysis under the current steam degradation conditions. As shown in Fig. 2e, the yields of these hydrolysis products decreased significantly with increasing temperature. When the temperature was increased from 400 to 800 °C, the yield of linear dimers decreased from 4.0 to 0.3 wt%, and lactic acid was observed only at 400 °C, with a yield of 1.5 wt%. This result confirmed that the impact of hydrolysis was hindered by the dominance of pyrolysis reactions at higher temperatures.

The effects of steam concentration on PLA steam degradation at 400 °C are summarized in Fig. 2. As discussed above, the gas and liquid yields decreased and increased, respectively, at 400 °C in the presence of steam. However, no noticeable changes in the yield or composition

of the gaseous products were observed when the steam concentration increased from 25 to 50 vol%. The yields of CO, CO₂, and acetaldehyde at 50 vol% were 20.6, 2.1, and 28.6 wt%, respectively (Fig. 2b). However, the yield of lactides obtained as liquid products decreased from 17.4 to 15.3 wt% when the steam concentration was increased from 25 to 50 vol%. In the presence of steam, the ester bonds in lactide can be hydrolyzed to form lactic acid and linear dimers. Notably, their yields increased from 1.5 to 2.5 wt% and from 4.0 to 5.9 wt%, respectively, at a 50 vol% steam concentration.

PHBH

The trends in the changes in the gas and liquid yields in the presence of steam were similar to those observed under pyrolysis conditions: the liquid yield decreased and the gas yield increased with increasing degradation temperature. The primary gaseous compounds were CO₂ and propylene. Although a slight increase in gas yield was observed at 800 °C, this increase was negligible compared with that in the liquid yield. C₁, C₂, and C₄ hydrocarbons, which were produced by the secondary cracking of

pyrolyzates, with yields of less than 0.3 wt%, were observed [29].

Figure 3d shows the yields of the primary target compounds, such as isocrotonic acid, crotonic acid, and 2-hexanoic acid, in the liquid. Interestingly, their yields were substantially increased by the addition of steam, reaching 5.4, 50.7, and 4.1 wt%, respectively, at 400 °C. By increasing the temperature to 600 °C with steam addition, maximum yields of 12.8 wt% (isocrotonic acid), 76.1 wt% (crotonic acid), and 5.6 wt% (2-hexenoic acid) were achieved. This suggested that steam effectively decomposed PHBH into these compounds. However, these yields decreased slightly as the temperature increased to 800 °C and were comparable to those obtained by pyrolysis at 800 °C. Therefore, the effects of steam were hindered by the dominance of pyrolysis reactions at 800 °C. At 400 °C, the yields of the 3HB and 3HH dimers did not exhibit significant differences when steam was introduced (Fig. 3c), whereas the yield of the 3HB trimer decreased from 12.3 wt% to 4.3 wt%. These effects support the increased production of crotonic acid. All the oligomers were completely degraded at 600 °C.

The total gas yield was less than 1.0 wt% at all steam concentrations at 400 °C (Fig. 3a). When the steam concentration was 50 vol % at 400 °C, the yields of isocrotonic, crotonic, and 2-hexenoic acids were 5.8, 42.9, and 3.7 wt%, respectively. The oligomers obtained under these conditions exhibited similar trends. The difference was not significant, indicating that the hydrolysis selectivity was the same at these two steam concentrations.

Conclusions

In this study, we conducted steam degradation of PLA and PHBH to investigate the effects of steam on the product distribution. The addition of steam increased the production of lactide from PLA at 400 °C with a steam concentration of 25 vol%: the yield increased from 10.7 wt% to 17.4 wt%. In addition, the yield of crotonic acid, a primary product, from PHBH was significantly increased by the addition of steam, resulting in a maximum yield of 76.1 wt% at 600 °C with a steam concentration of 25 vol%. Thus, the study findings revealed that steam lowers the degradation temperatures of PLA and PHBH and increases the yield of chemical feedstock. These findings may suggest effective degradation methods for the treatment of biobased/biodegradable plastic wastes to maximize conversion efficiency and target product yields.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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