Technical Paper

Ring and Rod Media Combination Effects on Continuous Pulverization by Tandem Ring Mill

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In this study, scale-up and continuous pulverization of a vibration mill with ring media were promoted for pretreatment of lignocellulose biomass. In continuous pulverization, coarse powder that passes through the inside of the ring media without being crushed was generated. Then continuous pulverization with a ring and rod combination was examined to suppress the powder flow passing through the ring hole and to increase pulverization force. First, batch pulverization with the ring and rod combination was examined. Results demonstrate that filling the rod media inside the hole of the ring media improved the micronizing efficiency in large amounts of Japanese cedar powder and increased the saccharification efficiency during the initial stage of pulverization. Based on the results, continuous pulverization was examined. The powder flow suppression effect was fundamentally confirmed. Furthermore, powder properties by continuous pulverization were confirmed to be improved in median size and the enzymatic saccharification efficiency by the filling rate of rods from 40% to 50%. Therefore, the ring and rod combination was found to be effective for continuous pulverization using a tandem ring mill.

本研究では、リグノセルロースの微粉碎前処理に用いるリング媒体利用粉碎機のスケールアップと連続粉碎に取り組んでいる。その連続粉碎ではリング媒体の内側を未粉碎物が通過する問題が生じている。そのためリング媒体の穴を通過する粉体流を抑制し、粉碎力を高めるために、リングとロッドの組み合わせによる効果を検討した。まず、リングとロッドの組み合わせによるバッチ式粉碎でその粉碎効果を検討した。その結果、大量のスギ粉末の粉碎において、リング媒体の穴にロッド媒体を充填することにより、微粉化効率が向上し、粉碎初期における酵素糖化率が向上した。その結果に基づき、連続粉碎を検討した。粉体流動が抑制され未粉碎物が通過することなく連続粉碎できることを確認した。また、連続粉碎による粉体特性は、ロッドの充填率が40%から50%になることでメジアン径および酵素糖化効率が向上することも確認された。したがって、リングとロッドの組み合わせは、タンデムリングミルによる連続粉碎に有効であった。

Key Words

Continuous pulverization, Enzymatic saccharification, Japanese cedar, Pretreatment, Ring and rod media

1. Introduction

Demands for economic growth and solutions to environmental problems together are imposing unprecedented social pressure caused by increasing energy demand, fossil fuel consumption, and petrochemical production. Given that background, developing sustainable biorefinery technologies that include bio-ethanol and biopolymers from pretreatment, enzymatic saccharification, and microbial fermentation of lignocellulosic biomass has become an important trend in many countries. Bio-

refineries processing lignocellulosic biomass are anticipated for their enormous potential to provide sustainable fuels and chemicals and to decrease greenhouse gas emissions.

Lignocellulosic biomass is fundamentally composed of cellulose, hemicellulose, and lignin. Both cellulose and hemicellulose are designated collectively as holocellulose. Enzymes hydrolyze holocellulose to monosaccharides such as glucose, arabinose, and xylose. Subsequently, microbial fermentation of these monosaccharides produces bio-ethanol via ethanol fermentation and produces biodegradable plastic as polylactic acid biopolymer by lactic acid fermentation. However, the structural compositions of lignocellulosic biomass are recalcitrant against the direct use of enzymatic hydrolysis. Mechanical pulverization has been used to

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obtain cellulose in a noncrystalline state in lignocellulose to achieve high enzymatic saccharification¹⁾. Many mechanical pretreatment processes have been studied for rotary ball milling to attain an efficient lignocellulosic biomass conversion state²⁾, such as oscillating ball milling³⁾, convergent ball milling⁴⁾, and planetary ball milling⁵⁾. However, mechanical milling of lignocellulose biomass was fundamentally assessed using a batch scale. Few studies have examined continuous pulverization⁶⁾.

For our earlier research, we developed a vibration mill using cog-ring media called a ‘tandem-ring mill’, which replaces the ball medium with a cog-ring media to achieve high-impact pulverization with sub-kilogram scale pulverization capacity⁷⁾. The tandem-ring mill shortened the pulverization time by one-fifth and attained similar saccharification efficiency to that of a conventional vibration ball mill⁸⁾. Moreover, Japanese cedar, rice straw, rice husk, eucalyptus, and other powders pulverized using the tandem-ring mill showed high enzymatic saccharification efficiency^{9) 10)}.

For energy conservation using the tandem-ring mill, continuous pulverization had been examined. An effective pulverizing result¹¹⁾ was obtained by continuous pulverization testing using a tandem-ring mill (TR-1500 type; Chuo Kakuki Shoji Co., Ltd.), which consisted of a 155 mm inner diameter mill chamber and ring media with 123 mm outer diameter and 69 mm inner diameter. To scaled up of a continuous tandem-ring mill, TR-3000 type (TRU LCC) was developed, consisted of a 280 mm inner diameter mill chamber with ring media of 248 mm outer diameter and 190 mm inner diameter¹²⁾. However, continuous pulverization using, failed pulverization because of powder flow through the large holes of the ring media.

This study investigated continuous pulverization using a tandem-ring mill with ring and rod combined media to suppress powder flow through the hole. First, batch pulverization was conducted to confirm the combined media effects. Then a continuous pulverization test was conducted. Finally, the ring-rod combined media effects on continuous pulverization are discussed.

2. Materials and methods

2.1 Materials

Japanese cedar (*Cryptomeria japonica*) sawmill chips without bark from a Honjoyuri Forest Owner's cooperative was used for pulverization tests conducted for this study. Coarse Japanese cedar powder was prepared from sawmill chips using a drying crusher (KDS-2; JP Steel Plantech Co.) with initial particle size of less than 2 mm and moisture content of less than 20%. Table 1 presents the Japanese

Table 1 Composition of Japanese cedar used for this study

	Japanese cedar
Cellulose (wt.%)	39.6
Hemicellulose (wt.%)	28.4
Lignin (wt.%)	31.5
Ash (wt.%)	0.5
(Holocellulose)(wt.%)	(68.0)

cedar composition used for this study. The monosaccharide component conversion efficiency was estimated as the saccharification efficiency from a ratio of the amounts of monosaccharides to those of holocellulose in terms of weight, as defined by the total weight of cellulose and hemicellulose.

2.2 Batch pulverization test

Fig. 1 presents the appearance of a tandem-ring mill (TR3000; TRU LCC.) in batch pulverization system. The tandem-ring mill has two vertically aligned mill chambers, with a revolving eccentric mass as a vibration generator, a 30-kW motor, and four support springs. The overall size of the tandem-ring mill was 2775 mm in length, 1155 mm in width, and 2052 mm in height. The mill chamber was also shaken by rotary vibrations generated by the rotations of a motor combining the eccentric mass during pulverization examination. The upside and downside mill chambers have lids at both ends, and Japanese cedar powder installed was pulverized by grinding media in batch.

Fig. 2 presents schema depicting the mill chamber interior contrasting the ring media and the ring and rod combined media. The mill chamber was made of steel and had 280 mm inner diameter and 1640 mm interior length. The ring media were made of steel with 248 mm outer diameter, 190 mm inner diameter, and 21 mm thickness

Fig. 1 Appearance of a TR-3000 type tandem-ring mill (batch pulverization system)

Fig. 2 Schema depicting the mill chamber interior contrasting the ring media and the ring rod combined media

in its basic shape. Ring media with 2 mm high cogs were installed in the upside chamber. Ring media with a smooth surface were installed in the downside chamber. The ring medium weight was 3 kg. The steel rod media were of 19 mm diameter and 1500 mm length. The ring media pulverization test was conducted using 76 media in each of the upside and downside mill chambers. Furthermore, the pulverization test on the ring and rod combined media was conducted by filling a plurality of rods in the installed ring media. The filling numbers of rods were, respectively 10, 20 and 30. Furthermore, the enclosed Japanese cedar powder in the mill chamber was 5, 6, and 7 kg. Samples of pulverized Japanese cedar powder were collected every 10 min for 60 min.

Moreover, the electric energy consumption was measured during pulverization. Also, the energy consumption as the pulverization power per unit of the pulverized amount was evaluated.

2.3 Characterization of pulverized powder

The median size of the pulverized powder was estimated using a particle size analyzer (Microtrac MT3300II; Nikkiso Co. Ltd.). Furthermore, enzymatic

saccharification for hydrolysis of holocellulose was conducted using 0.04 g pulverized powder, 2 mL acetic acid buffer (5.5 pH and 0.1 M), and 0.002 g enzyme (Meicelase; Meiji Seika Pharma Co. Ltd.) as 9 FPU/g-biomass. The enzyme activity was measured related to reports¹³⁾ issued from NREL. The amount of cellulase enzyme used for this study was 9 FPU/g-biomass, which was similar to the amount of enzyme used in other studies^{14)~18)}: 5–20 FPU/g-substrate. The incubation temperature, agitation speed, and reaction time in enzymatic saccharification were 50 °C, 150 rpm, and 48 hr. The saccharification efficiency of holocellulose was estimated using a spectrophotometer (U-3900H; Hitachi High-Technologies Corp.) with 420 nm wavelength using Schales' reagent method¹⁰⁾ and a standard curve of glucose. The amount of monosaccharide after the tube test was calculated by multiplying the monosaccharide concentration by the acetic acid buffer volume.

3. Experimental results

Fig. 3 presents variations of the median size achieved during pulverization comparing the pulverized weights of Japanese cedar powder of 5, 6, and 7 kg. At the median size change of 5 and 6 kg pulverization, the median sizes decreased rapidly as the filled number of rods increases in initial pulverization time of 10 min. Then the median size decreased to less than 40 μm and continued gently to be flat during pulverization under each condition. However, at enclosed powder weights of 7 kg in Fig. 3 (c), the median size decreased as the number of rods decreases. The smallest median size was confirmed in pulverization without rod media.

Fig. 4 presents variations of the enzymatic saccharification efficiency during pulverization comparing the pulverization weight of Japanese cedar powders of 5, 6, and 7 kg. At the saccharification efficiency of 5 kg pulverization, the saccharification efficiency increased concomitantly with increasing pulverization time. Saccharification efficiency in 60 min pulverization was achieved higher as the number of rods increased. And when the filled numbers of rods were 30, increased saccharification efficiency during the initial stage of pulverization around 20 min was confirmed. However, at the saccharification efficiency of 6 and 7 kg pulverization, a relation between the saccharification efficiency and the number of rods was unclear.

Fig. 5 shows the saccharification efficiency change along with the unit consumption energy based on the pulverized powder weight in each condition. At 5 kg pulverization, regarding the relation between saccharification efficiency and the unit consumption energy,

a) 5 kg

a) 5 kg

b) 6 kg

b) 6 kg

c) 7 kg

c) 7 kg

Fig. 3 Variation of median size compared in mill weight of 5, 6, and 7 kg in batch pulverization

Fig. 4 Variations of the saccharification efficiency comparing in pulverization weight of Japanese cedar powder of 5, 6, and 7 kg

a) 5 kg

b) 6 kg

c) 7 kg

Fig. 5 Saccharification efficiency change with unit consumption energy in each condition

the saccharification efficiency increased concomitantly with increasing unit consumption energy. However, the unit consumption energy fluctuated according to the number of rods. Therefore, pulverization by the ring and rod combined media might indicate unstable pulverization behavior when

the powder amount is small. Hence, if the number of rods increased when the amount of powder was low, it was considered that the unstable pulverization behavior of rods leads to an increase in consumption energy, which make little contribute to the pulverization.

However, at 6 and 7 kg pulverization, the saccharification efficiency increased concomitantly with increasing unit consumption energy, irrespective of the number of filled rods. Therefore, in this pulverization, it was considered that increasing the energy consumption contributing to the pulverizing led to the improvement of the saccharification efficiency. In fact, the pulverization with higher the number of rods resulted in higher saccharification efficiency than the pulverization without rods. Furthermore, pulverization with saccharification efficiency exceeding 50% was possible with lower energy than with the 5 kg pulverization. Results demonstrated that pulverization with the ring and rod combined media with 30 rods improved saccharification efficiency, even when the powder amount was large.

4. Continuous pulverization

Fig. 6 presents the appearance of a tandem-ring mill in continuous pulverization system. In the continuous pulverization system of tandem-ring mill has a feeder as powder supply part, a flexible duct structure connecting the upside and downside mill chamber, and vent part as powder discharge, replacing the lid which closed the both ends of the mill chamber of batch system in Fig. 1. In continuous pulverization, the coarse powder was pulverized by sequential passage through the feeder, the upside chamber, flexible duct, the downside chamber and

Fig. 6 Appearance of a continuous pulverization system

vent. In the examination, the process of pulverizing 90 kg of powder by this sequential passage was defined one pass. It was repeated up to 10 passes to evaluate the continuous pulverization.

The continuous pulverization test was carried out using the ring and rod combined media in Fig. 2 (b). And from batch pulverization results, the maximum number of rods in the ring was 77. Therefore, the filling ratio with 30 rods was about 39%. We conducted continuous pulverization with 40%, 50%, and 60% rod filling ratios, with respective numbers of rods of 31, 39, and 46, including examination of powder passage suppression.

Fig. 7 presents continuous pulverization results. The horizontal axis of each figs shows the number of passes of repetition. Regarding the discharged amount of pulverized powder in Fig. 7 (a), the discharge amount after one pass was only 0.8 kg/min for all rod filling ratios, but in the passes after 1 pass, it was increased to around 4 kg/min.

Results suggest that the discharge rate decreased because the coarse powder was bulky at the initial stage of pulverization. In other words, the powder passage through the hole of ring media was restricted by the rod presence.

As a result, the retention time was secured. Regarding the median size change after continuous pulverization in Fig. 7 (b), the median sizes decreased gently to less than 40 μm during the four-pass pulverization irrespective of the rod filling ratio. Subsequently, the median size was maintained at around 40 μm irrespective of the number of passes. Regarding the saccharification efficiency change of continuous pulverization in Fig. 7 (c), the saccharification efficiencies by filled ratios of rods 40% and 50% reached nearly 50% during one pass. Subsequently, the saccharification efficiencies increased gently by around 56% with additional passes. However, at a 60% rod filling ratio, the saccharification efficiency remained at 30–40%. Results suggest that the increased number of rods in the ring media hole hindered the pulverizing behavior. Even in continuous pulverization, the pulverization with the sufficient impact force acts repeatedly led powder micronizing and internal structure destruction that leading to improvement in saccharification efficiency of the powder. These results demonstrate the possibility of continuous pulverization with high efficiency. The ring and rod combination can allow setting of the filling ratio of rods from 40% to 50%.

Fig. 8 shows the unit consumption energy with the number of passes of repetition. Results confirmed that the unit consumption energy was the largest at the rod filling ratio of 40%. And it decreased in the order of the rod filling ratio of 40%, 50% and 60%. Compared with the

a) Discharge amount of powder

b) Median size

c) Saccharification efficiency

Fig. 7 Continuous pulverization results by the ring and rod combined media

saccharification rates shown in Fig. 7 (c), there was no difference in the saccharification rates at 40% and 50% filling rates of rods. Therefore, for energy efficiency, the rod filling ratio of 50% was an appropriate condition in this pulverization.

Fig. 8 The unit consumption energy with the number of passes of repetition

4. Conclusion

In this study, to develop scale-up and continuous pulverization of tandem-ring mill with ring media, the mill chamber size was increased from 155-mm to 280-mm in inner diameter. However, continuous pulverization was failed by powder flow through the large holes of the ring media. As a countermeasure, the ring and rod combined media was examined. A pulverizing effect of the combined media was confirmed using batch pulverization. Then a continuous pulverization test was conducted. The main conclusions are summarized below.

- 1) At batch pulverization using the ring and rod combined media, stable micronizing was possible by filling a sufficient number of rods. However, fewer rods led to the opposite effect.
- 2) Pulverization with the ring and rod combination using 30 rods confirmed the improvement of the saccharification efficiency at the initial stage, even when the powder weight amount was large.
- 3) Continuous pulverization in the tandem-ring mill using ring and rod combined-media device was possible with setting of the filling ratios of rods from 40% to 50%.
- 4) Saccharification efficiency increased linearly with increasing unit energy consumption.
- 5) The 50% rod filling ratio was an energy-efficient pulverization condition in this study, producing a powder with high saccharification efficiency produced from small input energy.

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