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Purity improvement and efficient recovery of levoglucosan mist produced by fast pyrolysis of cellulose using corona discharge†

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Cellulose can be efficiently decomposed through fast pyrolysis. However, the mist products generated during this process are difficult to collect efficiently because they remain suspended in the gas phase for an extended period (20–30 min). In this study, we attempted to overcome this problem by using corona discharge treatment to add static electricity, which allowed us to collect the mist products more effectively. This method facilitated the rapid agglomeration of mist products, primarily composed of levoglucosan (LG), allowing for their easy recovery as condensate. Conversely, the aldehydes produced as by-products of the pyrolysis process remained in the gas phase and were unaffected by the static electricity. Consequently, the application of corona discharge improved the purity of LG compared to the untreated process, providing valuable insights into the production of fermentable sugar solutions *via* subsequent mild hydrolysis. These results demonstrate the feasibility of simultaneously recovering and refining products using static electricity.

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Introduction

Renewable and carbon-neutral biomass resources are ideal for producing chemical substances and energy sources that can replace fossil resources. Lignocellulose, the most abundant form of biomass, is garnering significant attention.[1] Cellulose is one of the major components of lignocellulose and has been used as a raw material for paper and pulp. However, its crystalline structure and chemical stability require an efficient conversion process to use cellulose as a chemical feedstock. Pyrolysis, involving heating and decomposition without oxygen, is promising for rapid cellulose decomposition.

Fast pyrolysis, characterized by rapid heating, converts cellulose into bio-oil, with levoglucosan (LG, 1,6-anhydro-β-D-glucopyranose) as the main component.[2–6] LG serves as a precursor for various chemicals and pharmaceuticals.[7,8] Additionally, since LG can be hydrolyzed to glucose under mild conditions, pyrolysis-based saccharification is a viable proposal.[9–11] However, the high temperatures required for fast pyrolysis lead to the decomposition of LG, resulting in a decrease in yield and selectivity.[12–16] Therefore, it is crucial to cool LG while simultaneously heating cellulose at high temperatures.

The fast pyrolysis of cellulose under infrared irradiation and nitrogen flow has been investigated.[17–19] The application of infrared irradiation allows for the selective heating of the cellulose, while the nitrogen remains unheated. Consequently, the volatilized LG can be stabilized by cooling it with nitrogen flow in the gas phase. In our previous research, a relatively high yield of LG was obtained, reaching a maximum of 52.3 wt%.[19] However, the mist products (aerosol) containing LG, produced by rapid cooling, were difficult to agglomerate and remained suspended in the gas phase for a relatively long duration, which complicates its recovery.

Various methods for bio-oil recovery are employed, including electrostatic precipitators, cooling, centrifugal separation, solvent traps, and filtration systems, often in combination.[20–23] Electrostatic precipitators are noted for their reduced susceptibility to clogging and their efficiency in recovering liquid products.[3,23–25] An electrostatic precipitator comprises a discharge wire and a dust collection plate. The bio-oil is ionized by the corona discharge from the discharge electrode and subsequently collected on the dust collection plate through Coulomb forces, thereby facilitating the separation of gaseous and liquid products.

In this study, an attempt was made to use static electricity to collect the volatile products from cellulose during fast pyrolysis under infrared irradiation. In addition, the effect of corona discharge-induced aggregation on products composition was also investigated. The composition analysis revealed that LG was selectively aggregated during the electrostatic collection process, resulting in improved purity.

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Materials and methods

Materials

Microcrystalline cellulose powder (Avicel PH-101, Asahi Kasei Corp., Tokyo, Japan) was used as received for pyrolysis reactions without further purification. The LG and glycolaldehyde dimer were purchased from Tokyo Chemical Industry (Tokyo, Japan) and Nacalai Tesque, Inc. (Kyoto, Japan) respectively, and used without purification.

Pyrolysis and product analysis

Fig. 1 shows a schematic diagram of the apparatus used in this study. Avicel cellulose powder (100 mg) was placed in a quartz sample boat and positioned at the center of a quartz reaction tube (inner diameter: 30 mm, length: 495 mm) on a stainless steel mesh. This is because the infrared radiation is concentrated at the center of the furnace used in this study. A mist collection tube (Pyrex glass, inner diameter: 30 mm, length: 495 mm) was connected downstream of the reaction tube, with a stainless steel rod installed inside as a cathode electrode, positioned so that its tip was centered in the collection tube. Using a T-joint, a 10 L gas bag was connected downstream of the collection tube, and the other end of the cathode rod was led outside through a rubber seal. A negative electrostatic potential up to 50 kV was applied to the cathode rod using a corona discharge gun (GC90N, Green Techno, Kanagawa, Japan), while the cellulose sample was subjected to fast pyrolysis with an infrared heating device (RHL-E45N, Advance Riko, Inc., Kanagawa, Japan) at 1 kW for 30 s under a nitrogen flow at 5 L min^{-1}. During discharge, the voltage decreases and does not remain constant, resulting in the actual voltage being lower than the set value.

After pyrolysis, the condensates in the gas bag and on the inner wall of the collection tube were each extracted with methanol (100 mL). The methanol was evaporated under vacuum, and the resulting products were dissolved in dimethylsulfoxide-d$_6$ (DMSO-d$_6$) (0.7 mL) containing maleic acid as an internal standard and hydroxylamine hydrochloride (NH_2-$OH \cdot HCl$, 10 mg) for derivatizing aldehydes and ketones in the products into their corresponding oximes.[26] The products were then quantified using ^{1}H nuclear magnetic resonance spectroscopy (^{1}H-NMR) on a Bruker AC-400 spectrometer (400 MHz, Bruker, MA, USA). The yield and purity of LG were determined from the area of ^{1}H-NMR signals assigned to LG and other products such as aldehyde oximes relative to that of maleic acid used as an internal standard. The compositions of char and gaseous products have been reported in our previous paper.[19]

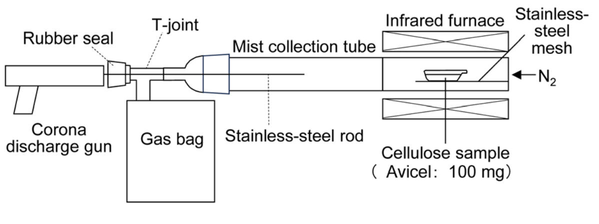

Fig. 1 Schematic diagram of infrared fast pyrolysis and mist recovery equipment.

Results and discussion

As shown in Fig. 2 (A), under the condition without corona discharge, mist products did not agglomerate in the mist collection tube and reached the sample bag at the latter stage, and agglomerates were collected by leaving the bag for about 30 min. On the other hand, when static electricity was added using corona discharge, mist products were trapped in the collection tube as shown in Fig. 2(B), and almost no mist products were observed in the sample bag. Thus, corona discharges can efficiently coagulate and collect mist products.

The products collected in the sample bag and mist collection tube were analyzed. According to the NMR analysis, the major product was LG (Fig. S1†). The yields of LG and aldehydes are shown in Fig. 3. The produced LG accumulated predominantly in the sample bag in the absence of an electrostatic charge. Conversely, when a negative electrostatic potential of 50 kV was applied, the majority of LG was collected in the mist collection tube. This observation is consistent with the mist behavior shown in Fig. 2. As shown in the ^{1}H-NMR spectra in Fig. 4, most aldehydes, including glycolaldehyde (GA, bp 131 °C), formaldehyde (Falde, bp −19 °C), glyoxal (GO, bp 50.4 °C) and methylglyoxal (MeGO, bp 72 °C), were collected in the sample bag regardless of the presence or absence of an electrostatic charge. This suggests that these aldehydes were not influenced by static electricity. Furthermore, the absence of mist in the sample bag under electrostatic conditions, where these aldehydes were collected, implies that the aldehydes were generated as invisible gas products. This is probably because the boiling point of aldehydes is lower than that of LG (bp 385 °C (ref. 14)). Consequently, the application of static electricity promoted the selective recovery of LG, increasing its purity from 95.9% to 99.6% (based on NMR analysis) at the positions where the mist products were mainly collected—namely, the sample bag at 0 kV and the mist collection tube at 50 kV, respectively.

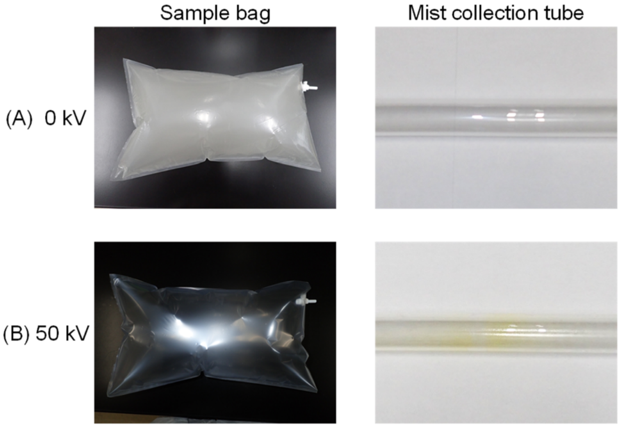

Fig. 2 Appearance of the sample bag and mist collection tube after the pyrolysis of cellulose conducted without (A) and with (B) static electricity.

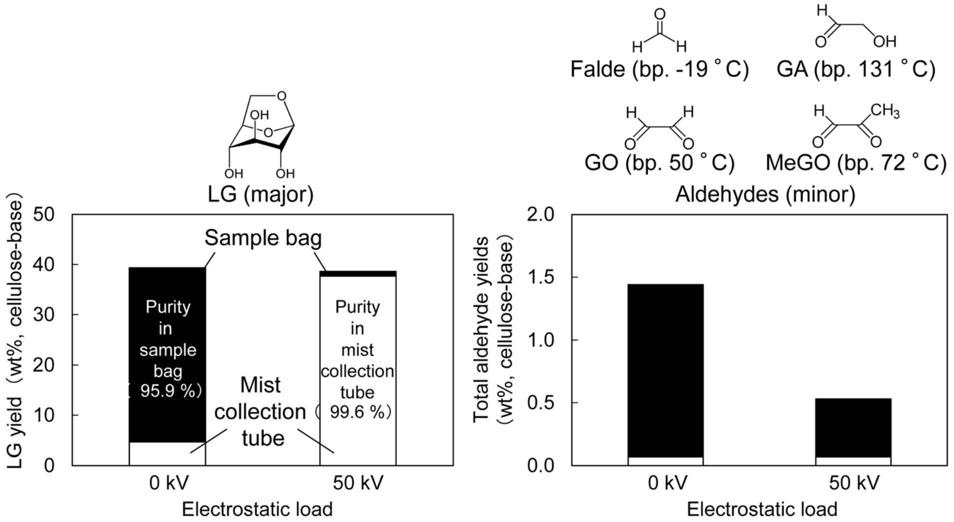

Fig. 3 Comparison of the yield and purity of LG and the yield of aldehydes collected in the sample bags or mist collection tubes under the electrostatic load of 0 kV and 50 kV.

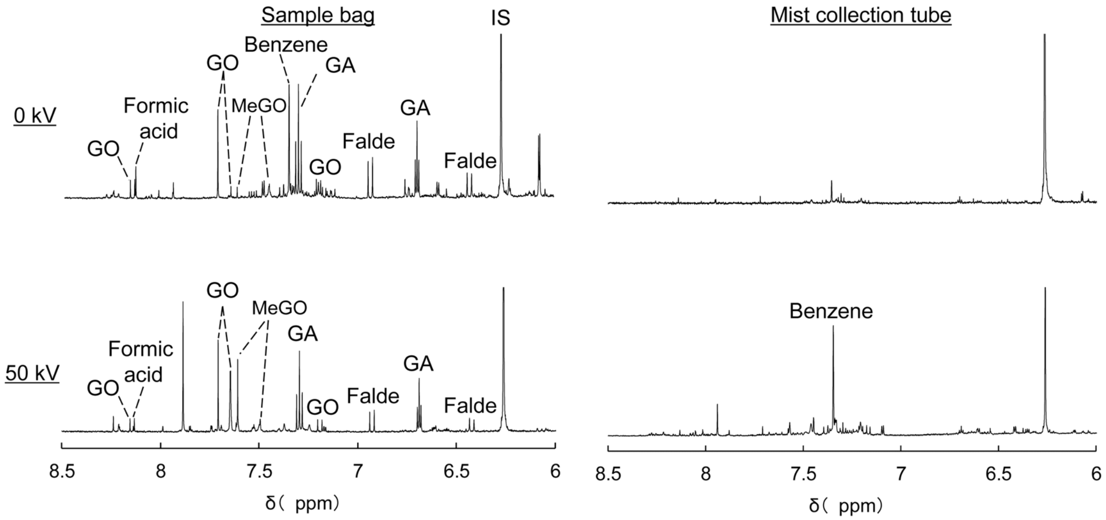

Fig. 4 ^{1}H-NMR spectra of the products collected in the sample bag and mist collection tube at the electrostatic load of 0 kV and 50 kV.

As shown in Fig. 3, the total yield of aldehydes decreased during electrostatic charging. In order to investigate this phenomenon, the volatility of GA in a methanol solution was examined. A 10 mL GA solution in methanol (25 mg L^{-1}) was placed in a 30 mL flask. Subsequently, the GA solution was distilled using an evaporator at 40 °C under 150 kPa for 15 min. The GA dissolved in methanol evaporated along with the methanol, and no GA remained in the flask. In contrast, when LG was added to the GA solution (LG concentration: 500 mg L^{-1}), approximately 30% of the GA remained even after evaporation. This retention is likely attributable to the acetalization of the aldehydes with LG (Fig. 5). The acetal intermediates formed subsequently react with other aldehydes to produce polyacetals. In our earlier study,[26] NMR analysis of pure GA dissolved in D_2O revealed the formation of a dimer and other products resulting from acetalization.

These results indicate that the yield reduction is attributable to the increased volatility of the aldehydes during the evaporation process of the product methanol solution, resulting from the separation of LG and aldehydes under the influence of an electrostatic charge.

The following implications are suggested by these results; low-molecular weight aldehydes when mixed with LG, became difficult to remove through vacuum distillation. Consequently,

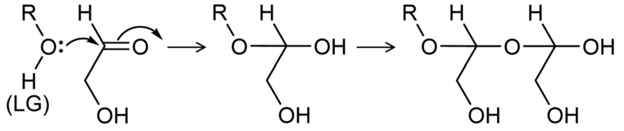

Fig. 5 Acetalization of the OH of LG with the aldehyde group of GA.

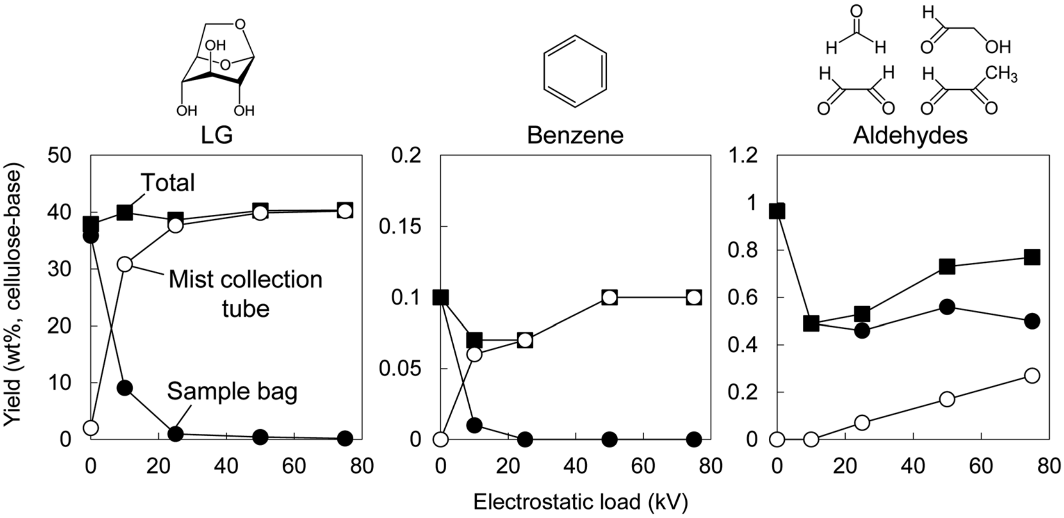

Fig. 6 Yields of LG, benzene and aldehydes at various electrostatic loads (■: total yield, ○: yield in mist collection tube, ●: yield in sample bag).

separating LG from these aldehydes *via* mist formation induced by electrostatic charging is proposed as a critical approach for producing highly pure LG. Since aldehyde by-products in sugar solutions obtained through the subsequent hydrolysis of cellulose pyrolysis products inhibited the lactic acid fermentation,[27] this proposed process provides valuable insights into the production of fermentable sugar solutions *via* pyrolysis-based methods.

The effects of electrostatic load (kV) on product yield are shown in Fig. 6. The total yield of LG remained constant regardless of the set voltage, indicating that LG was not significantly degraded by static electricity. Most of the LG was collected in the mist collection tube when the voltage was increased to 25 kV. Benzene exhibited a similar trend to LG, suggesting that LG and benzene coexist in the mist products.

The formation mechanism of benzene is unclear, but it is likely produced from secondary decomposition of char rather than gas-phase degradation of volatile products. The char absorbs infrared radiation and reach temperatures sufficient for further thermal breakdown.

Contrary to this, aldehydes were mainly collected in the sample bag, but the amounts collected in the mist collection tube increased by increasing the electrostatic load. This increase is likely due to the decomposition of pyrolysis products into aldehydes at high load. These results indicate that, for efficient and selective recovery of LG, it is crucial to process it at the highest possible electrostatic load that does not degrade the pyrolysis products to aldehydes.

Based on these results, the following mechanism was proposed (Fig. 7). During the fast pyrolysis of cellulose, mist and gaseous products are generated. The mist products contain LG and a small amount of benzene, whereas the gaseous products contain aldehydes. Under electrostatic conditions, only the mist products become charged, promoting their aggregation. In contrast, the gaseous products are unaffected by static electricity and are separated from the mist products by nitrogen flow. This separation is attributed to the difference in boiling points: gaseous LG with a high boiling point of 385 °C readily forms aggregates, while the aldehydes with lower boiling points are not involved in this mist formation. Although benzene has a low boiling point, it is believed to coexist with LG through CH/π bonding. Complexation of sugars and their derivatives with aromatic substances through CH/π bonding has been re-ported in literature.[28–32]

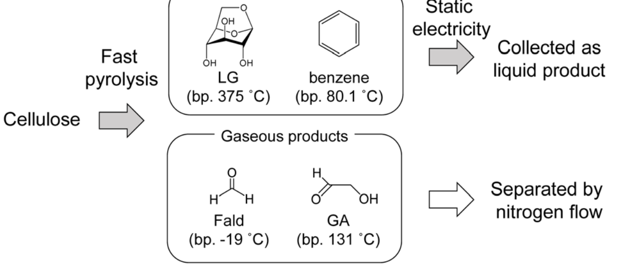

Fig. 7 The effect of static electricity on the pyrolysis products of cellulose in fast pyrolysis under infrared irradiation.

Conclusions

In this study, the fast pyrolysis products of cellulose were collected using static electricity. The following conclusions were reached. Without corona discharge, mist products remained uncoagulated and LG was mainly recovered in the sample bag. With a 50 kV charge, LG efficiently coagulated and was recovered in the mist collection tube. In contrast, low-molecular-weight aldehydes were unaffected by the charge and recovered in the sample bag. This indicates that electrostatic mist collection enables selective separation of LG from aldehydes, and facilitates the recovery of highly pure LG for fermentable sugar production. However, when mixed with LG, separation becomes difficult due to acetalization. Although the total LG yield was unaffected by the applied voltage, higher voltages promoted secondary degradation to aldehydes. Therefore, an optimal voltage should be selected to maximize LG recovery while minimizing its degradation. Future work will explore scale-up and application to cellulosic biomass such as waste paper.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

Author contributions

Conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing – original daft, T. N.; data curation, visualization, writing – review and editing, E. M.; conceptualization, funding acquisition, methodology, project administration, supervision, writing – review and editing, H. K. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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