NOTE

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Saccharification of cellulose by dry pyrolysis

Abstract Pyrolysis of cellulose was studied for the purpose of practical production of 1,6-anhydro-β-D-glucopyranoside (levoglucosan, LG). To minimize secondary degradation of levoglucosan, two methods were examined: (1) conductive heating by glass bottle, and (2) radiation heating from the surface by CO_2 laser beam, both under vacuum and in a nitrogen atmosphere. Glass-bottle pyrolysis under vacuum gave levoglucosan yield of 50%–55% in the optimum temperature range of 350°–410°C, where placing the cold trap in the vicinity of heated area was effective in improving the yield. In contrast, glass-bottle pyrolysis under nitrogen gave low yields of 17%–20%, probably due to slower diffusion of pyrolysis product from hot region. The CO_2 laser pyrolysis under vacuum gave the product as aerosol (white smoke), causing difficulty in recovery of the product, and the maximum yield was 5%–17%. In this case the treatment under nitrogen flow was effective for recovery of aerosol, and the maximum yield reached approximately 25%.

Key words Cellulose · Pyrolysis · Levoglucosan · 1,6-Anhydro-β-D-glucopyranoside · CO_2 laser

Introduction

Production of large amounts of 1,6-anhydro-β-D-glucopyranoside (levoglucosan, LG) in the pyrolysis of cellulose has long been known, and numerous studies have been reported.[1–5] Anhydrosugars including levoglucosan and levoglucosenone are potentially useful as intermediates to glucose via acid hydrolysis, as well as starting materials for synthesis of oligo/polysaccharides[6,7] and other biologically active compounds.[8,9] While the levoglucosan yield from cellulose in pyrolysis is reported to be 30%–60%,[3] a large-scale process to utilize this reaction has not been realized. This situation appears somewhat surprising in view of the abundance and low cost of cellulose. Possible reasons for this situation are: (1) levoglucosan readily undergoes secondary decomposition at its formation temperature of 320°–360°C, giving various smaller species such as furfural, acetic acid, or methanol, and (2) the levoglucosan yield is sensitive to the purity of the starting cellulose, and is significantly reduced by small amounts of impurities, especially inorganic salts.[3]

The reported features of cellulose pyrolysis, however, strongly suggest that its primary process is the formation of levoglucosan, and it may be utilized as a practical saccharification process. Conventional methods of pyrolysis of solid materials employ heating of the material from the bottom, or introducing the material to a uniformly heated area. These methods, however, cannot minimize secondary decomposition, because the primary pyrolysis products are exposed to high temperature. To overcome this problem, alternative heating methods using CO_2 laser[10] or microwave[11] irradiation have been examined. The laser pyrolysis attracts special attention, because it can heat the material from its open surface, thus facilitating release of the primary pyrolysis products. However, Madison and Keehn[10] found that the major products from laser pyrolysis of cotton were gases (CO, CO_2, acetylene, ethylene, etc.), which were likely to have resulted from secondary degradation due to excessive heating. On the other hand, Suzuki et al.[12] analyzed the material deposited on the edge of laser-cut traces of filter paper, and detected significant amounts of monosaccharides or oligosaccharides and their anhydro derivatives including levoglucosan. Laser treatment products under similar conditions were examined by Hattori et al.,[13] who showed that the amount of deposit was greater when the laser beam was enlarged by a lens.

Based on these observations, we studied cellulose pyrolysis by comparing two methods of heating, which are

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expected to provide rapid removal of primary decomposition product from the heated area; namely: (1) CO_2 laser irradiation of the surface of the material, and (2) conventional glass-bottle pyrolysis, but with a cold trap placed close to the heated area.

Experimental

Cellulose materials

Whatman CF11 cellulose powder (acid-treated cotton) was used for glass-bottle heating as received. For laser treatment, the cellulose powder was formed into dense pellets, approximately 1.0 g (weighed accurately), by a metal die and hydraulic press. Quantative-grade filter paper, 5A (Advantec Toyo, Tokyo), was cut into pieces measuring approximately 30 × 30 mm, which were stacked to form a pile of approximately 1.0 g pile (weighed accurately). Corn starch (Wako, Tokyo) was used in the same way as cellulose powder.

Glass-bottle heating

A 1-liter, three-mouth glass bottle was equipped with a cold finger at the large center mouth. One small mouth was used as an exhaust leading to a rotary pump or to atmosphere, and the other was used for feeding cellulose powder from a small glass bottle that was rotated at the tapered glass joint. The dry weight of cellulose powder was 1.0 g for each experiment. The treatment was performed under vacuum or under nitrogen flow. The main bottle was heated from the bottom with a mantle heater thermostated by a feedback thermocouple. The effectiveness of cold trapping was examined by comparing the long finger (8.5 mm above bottle base), the short finger (35 mm above bottle base), and no trap. The vacuum condition was not determined accurately, but was estimated to be below 1.0 mmHg based on the performance of the pump used.

Laser pyrolysis

The infrared beam source was a 1.7-kW CO_2 laser (RS-1700M, 10.6 μm wavelength, Rofin-Marubeni). The chamber was a transparent plastic desiccator (250 × 250 × 100 mm), to which a laser irradiation window made of zinc selenide (36 mm wide and 3 mm thick, Oyo Koken, Tokyo) and a gas inlet/outlet were fitted (Fig. 1). The laser output was 100 W (power density 2.84 W/cm²) to 300 W (power density 8.51 W/cm²). The duration and interval of laser pulse were varied for repeated pulse irradiation.

Analysis of pyrolysis products

In both glass-bottle and laser treatments, the pyrolyzate that had accumulated on the trap, the inner wall of the vessel, or the adsorbent cotton in the exit tube was collected
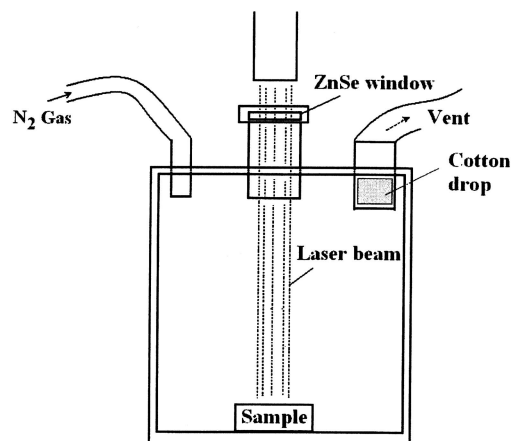

Fig. 1. Apparatus for CO_2 laser pyrolysis of cellulose

by rinsing with water. The aqueous solutions were combined and concentrated in a rotary evaporator into syrup (called "tar" by some researchers) at approximately 80°C. The chemical composition of the syrup was analyzed by gas chromatography (GC) without derivatization as follows. The syrup was dissolved in methanol and subjected (without derivatization) to a gas chromatography-mass spectrometry (Shimadzu GCMS-QP5000, with GC column TC1701, 0.25 mm I.D. × 30 m, film thickness 0.25 mm, GL Sciences, Tokyo) for identification of chemical species. The amount of levoglucosan in the syrup was determined by a gas chromatograph (Shimadzu GC1700, with GC column TC17, 0.25 mm I.D. × 30 m, film thickness 0.25 mm, GL Sciences). In both cases gas chromatography was performed with the following conditions: evaporation chamber 250°C, helium flow of 2.6 ml/min, split ratio of 3.0, and heating rate of column of 10°C/min from 120° to 280°C. Levoglucosan yield was determined by comparing the peak area from the syrup with that of authentic levoglucosan (Wako).

The levoglucosan yield from cellulose or starch was calculated by: LG yield (%) = [GC value/(starting material weight − residual weight)] × 100. The residue in the glass-bottle treatment was the char remaining on the bottom, corresponding to 2%–5% of the starting material. The residue in the laser treatment consisted of char and the unirradiated portion of starting material. In this case the LG yield was calculated based on the treated material. Although reproducibility of levoglucosan yield was not assessed quantitatively, the variation of the results for the same condition was within ±5%.

Results and discussion

Pyrolysis of cellulose under inert atmosphere is known to proceed rapidly in the temperature range of 320°–360°C. Figure 2 shows the thermogravimetric curves for Whatman cellulose powder and corn starch, for comparison. When cellulose powder was supplied to the bottom of a glass
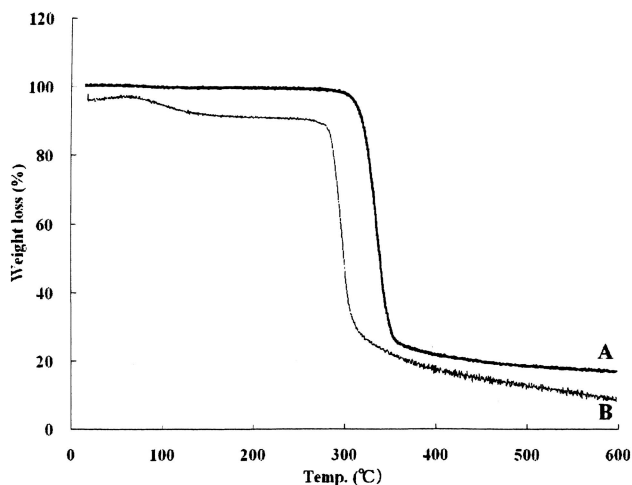
Fig. 2. Thermogravimetric curve of Whatman CF11 cellulose powder (*A*) and corn starch (*B*). Heating rate: 10°C/min in nitrogen
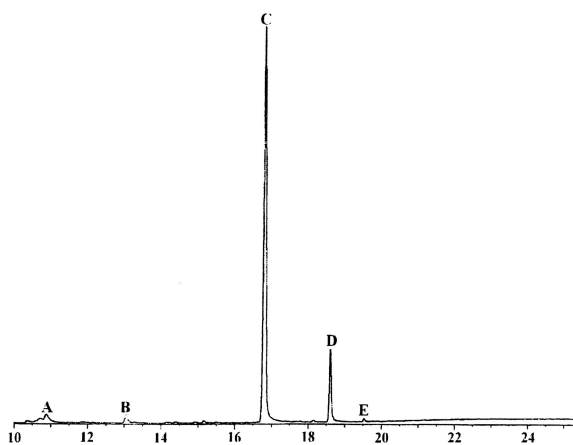

Fig. 3. Gas chromatogram of pyrolysis product from Whatman CF11 cellulose powder by vacuum flask pyrolysis. T = 370°C; levoglucosan yield 56%. *A*, 1,4:3,6-dianhydro-α-D-glucopyranose; *B*, unknown; *C*, 1,6-anhydro-β-D-glucopyranose (levoglucosan); *D*, 1,6-anhydro-β-D-glucofuranose; *E*, unknown

Fig. 4a–c. Mass spectra of the characteristic pyrolysis product from Whatman CF11 cellulose powder **a** 1,6-anhydro-β-D-glucopyranose (levoglucosan); **b** 1,6-anhydro-β-D-glucofuranose; **c** 1,4:3,6-dianhydro-α-D-glucopyranose

bottle preheated to 350°–400°C, the cellulose decomposed rapidly, and the pyrolyzate evaporated and accumulated on the trap and the inside of the upper part of the bottle. No smoke was observed in this case. When the same cellulose material was placed in the glass bottle and heated from room temperature, the cellulose powder started to move at above 310°C, and its volume reduced gradually. The evaporated material deposited on the cold trap and the upper part of the inner wall, forming a sticky liquid (syrup). Figure 3 shows an example of a gas chromatogram of the pyrolyzate syrup. The major peak was identified as levoglucosan, amounting to approximately 64% of the syrup. The minor component was 1,6-anhydro-β-D-glucofuranoside. This substance could not be quantitated due to unavailability of authentic reagent, but it was estimated to correspond to about one tenth of the levoglucosan based on the peak area. In additon, a trace of 1,4:3,6-dianhydro-α-D-glucopyranose
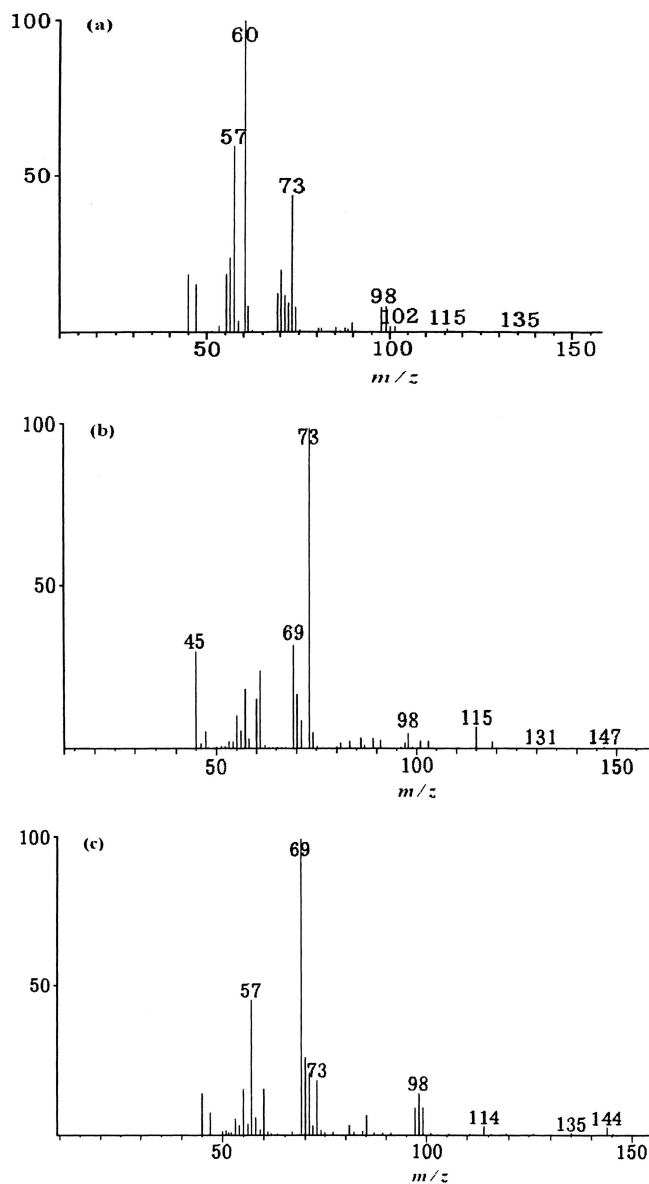
was detected. Figure 4 shows the mass spectra of the peaks identified as 1,6-anhydro-β-D-glucopyranose (levoglucosan), 1,6-anhydro-β-D-glucofuranose, and 1,4:3,6-dianhydro-α-D-glucopyranose. The spectrum of the levoglucosan peak was identical to that of pure reagent.

The levoglucosan yield by glass-bottle treatment (long trap, under vacuum or nitrogen, 1g cellulose powder dropped from small bottle) was nearly constant at 51%–56% for 350°–410°C treatments. Below this temperature range the decomposition of cellulose was slow, and the LG yield decreased due to increase of residual char. The decrease in yield above 430°C was probably due to increased secondary decomposition. The LG yield under 1 atm nitrogen was 17%–20%, less than half of that under vacuum. The

lower yield is considered to result from hindrance of diffusion of generated levoglucosan from the heated area. In the vacuum treatment, the LG yield was the highest for the long trap, with a maximum of 56%; use of the short trap caused it to decrease to about 45%, and the treatment without a cold trap gave only 35%. Therefore, the conditions favorable for levoglucosan recovery are use of vacuum treatment in which the cold trap is placed as close as possible to the site of pyrolysis. The levoglucosan yield of 51%–56% is in the highest range of reported values. Earlier values such as Golova's (63%) or Sandermann's (73%) were based on glucose assay after hydrolysis, which include glucose from components other than levoglucosan.[3]

A documented laboratory-scale method of levoglucosan preparation is described as placing dry starch powder in a vacuum glass bottle, which is connected to a second bottle serving as a condenser.[14] The described levoglucosan yield after isolation is about 25% of the starting material, while our present value for corn starch in the vacuum glass-bottle treatment (300°C, long trap) was 44% by GC assay. The difference reflects the loss in the isolation procedure. Because the corresponding value for Whatman CF11 (without isolation) was 56%, microcrystalline cellulose powder is an apparently superior material as a levoglucosan precursor. Also, the treatment of starch in the glass bottle was accompanied by notable expansion of the char material, causing difficulty in the procedure.

In the laser treatment of cellulose, both under vacuum and in nitrogen, repeated pulse irradiation resulted in the formation of aerosol (white smoke), which remained floating indefinitely. This behavior is probably due to rapid cooling of evaporated levoglucosan, because the laser heating is limited to the irradiated part of the material. The formation of aerosol hampered product recovery under vacuum condition; in contrast, this problem could be overcome in nitrogen atmosphere by providing a continuous flow of nitrogen (2.5 l/min), which flushed the aerosol to the absorbent cotton trap fitted in the exit tube. Figure 5 shows the levoglucosan yield for cellulose powder pellet by laser treatments under nitrogen flow. The levoglucosan yield was 20%–25%, which is nearly the same yield as in the glass-bottle treatment.

We examined various pulse conditions in terms of the width and interval of the pulse, but could not find a systematic tendency, as seen in Fig. 6. Weak conditions (low power density, short pulse duration, and long pulse interval) did not give sufficient heating to the specimen, requiring processing times that were too long. In the laser treatment in nitrogen, filter paper gave lower levoglucosan yields of 7%–12%, about half of that for cellulose powder pellet. Scanning electron microscopic observation of the specimen after laser irradiation revealed the presence of spherical particles 20–30 μm wide. These particles probably comprise the same material reported by Nordin et al.[15] and Hattori et al.[13] Because these particles were removed by rinsing with water in our case, they were probably the same as the aerosol particles, consisting mainly of levoglucosan. Such trapping of product in the voids may be one reason for the low levoglucosan yield from filter paper.
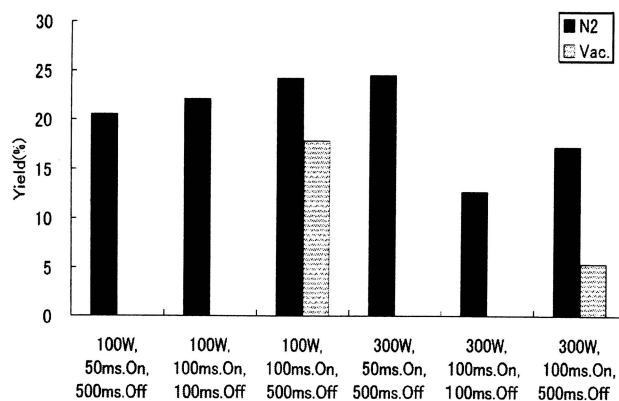

Fig. 5. Levoglucosan yield from Whatman CF11 cellulose powder pellet by laser pyrolysis under N_2 flow or vacuum
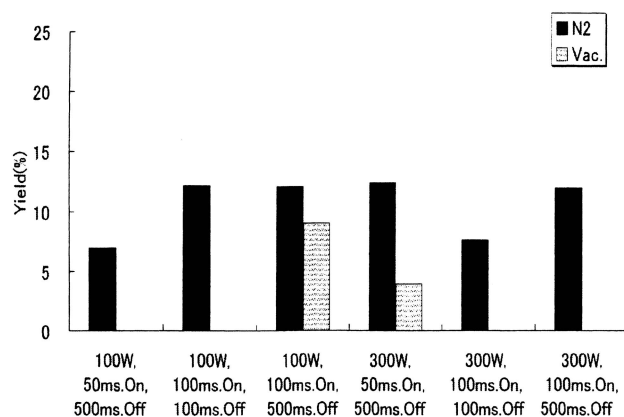

Fig. 6. Levoglucosan yield from filter paper by laser pyrolysis under N_2 flow or vacuum

Conclusions

The glass-bottle pyrolysis using a long cold trap (close to the pyrolysis site) gave a maximum yield of 56%. This method combined with the continuous feed of raw material is suitable for scaling up. Further improvements to the arrangement of apparatus may lead to a practical process for chemical conversion of cellulosic materials. In spite of the ablative condition, which was expected to be effective in preventing secondary degradation, the CO_2 laser pyrolysis gave lower levoglucosan yield than the glass-bottle method, especially under vacuum conditions. This behavior seems to result from the formation of aerosol, which may be characteristic of rapid radiative heating.

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