2P4-7

Catalytic Effect on Ultrasonic Decomposition of Cellulose

セルロースの超音波分解に及ぼす触媒の影響

Shinfuku Nomura[1], Kosuke Wakida[1‡], Shinobu Mukasa[1], Hiromichi Toyota[1]
([1] Grad. School Sci. Eng., Ehime Univ.)
野村信福 [1], 脇田孝祐 [1†‡], 向笠忍 [1] ([1] 愛媛大学大学院 理工学研究科)

1. Introduction

Cellulose the organic compound which is the chief ingredient of the cell walls of the plants exists in large quantities in nature, however, it is discarded in large quantities without effective utilization of its potential as biomass energy. In previous work, it was clarified that filter paper containing a high cellulose content can be decomposed into 5-hdroxymethy furfural (5-HMF) and furfural by applying the ultrasonic welding method (1). Additionally, nomonosaccharide glucose was confirmed as being present during this method. If the glucose could be obtained by this method, ethanol could then be generated by a general fermentation process. Cellulase, which hydrolyzes cellulose, is well known as a catalyst for producing glucose. In the present study, the effect of introducing a catalyst into the decomposition by ultrasonic welding in water is investigated. The ultrasonic welding method occurs through contact with materials, which are decomposed either physically or chemically. Adding a catalyst to the filter paper in water to trigger glucose production, and performing the ultrasonic welding methods, can be expected to enhance the generation of glucose from cellulose.

2. Experimental Apparatus and Method

A diagram of the experimental apparatus is shown in Fig. 1. The configuration is almost same as previously reported. Ultrasonic waves of 19.5 kHz are irradiated downward using a horn-type transducer. The horn tip diameter is 7 mm. Output power of ultrasonic waves is recorded using a wattmeter. Filter paper (No. 3, Toyo filter paper Co., Ltd.) which has a high cellulose content is used as a cellulose specimen. 30 sheets of the 7×7 mm square filter paper (200 mg) were stacked at the bottom of the reaction chamber, and were submerged in 5 mL of pure water. The horn for ultrasonic vibration was lowered and pressurized the specimen by operating a manual adjustable device. The ultrasonic irradiation time is 60 s. Cellulase (C1184, Sigma-Aldrich) is utilized as the catalyst. After the experiment, the residential liquid in the reaction chamber was collected, and the ingredients of the product were analyzed by high performance liquid chromatography (HPLC).

3. Experimental Results and Discussion

Before conducting the ultrasonic decomposition experiments, the characteristics of decomposition of filter paper by cellulase were investigated. After adding 0.2g cellulase to reaction chamber, the liquid was kept at 50 to 60°C in a thermal insulator to optimize the temperature for cellulose decomposition. Figure 3 shows the elapsed time for the production of glucose with after adding cellulase. The amount of glucose produced increases with the time until 48 hours, afterwards saturation occurs. Cellulase is added as a pretreatment in the chamber after 60s of ultrasonic irradiation at 100W and shown in Fig. 2. The amount of glucose produced with pretreatment is greater than that without ultrasonic pretreatment. The saccharification process is enhanced by ultrasonic welding as pretreatment through hydrolysis and thermolysis. This pretreatment suggests that it is an effective method to reduce the processing time of glucose production, however, after the elapse of 48 hours, it shows a tendency to become saturated.

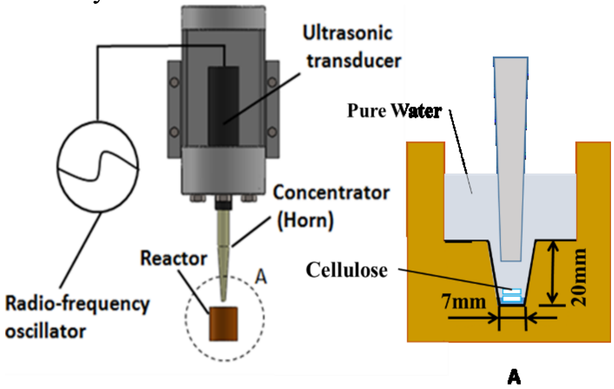

Fig. 1 Experimental apparatus. The lower section of the reaction container is formed in a tapered shape, and the bottom has a 7mm diameter, which is the same size of the horn tip.

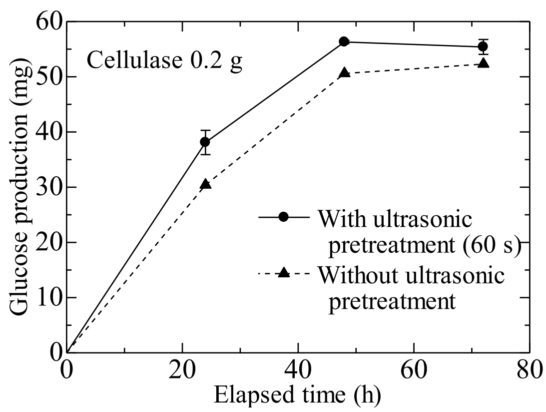

Fig. 2 Comparison of with and without ultrasonic pretreatment. Here, ultrasonic welding time is 60 seconds.

Fig. 3 shows the ratio of glucose production with and without ultrasonic pretreatment. The vertical axis shows the ratio of ultrasonic pretreatment to that without ultrasonic application. The enhancement ratio increases with the amount of quantity of catalysis, with nearly 1.4 times enhancement of glucose production obtained at 0.5 g. The amount of cellulase also increases further as the enhancement ratio increases.

Fig. 4 show the results of HPLC of residual liquid after ultrasonic vibration. From the peak potions, 5-HMF, furfural, oligosaccharide components are confirmed in HPLC using a UV detector, and glucose could also be identified using a RI detector.

Fig. 5 shows the production of 5-HMF, furfural, and glucose after ultrasonic irradiation with and without cellulase. By catalytic feeding, the overall yield of the product increases, and the glucose is produced only when the catalyst is added. The amount of glucose at 100 W is approximately two times larger than that at 200 W, on the contrary, 5-HMF at 100 W is reduced in comparison with 200 W.

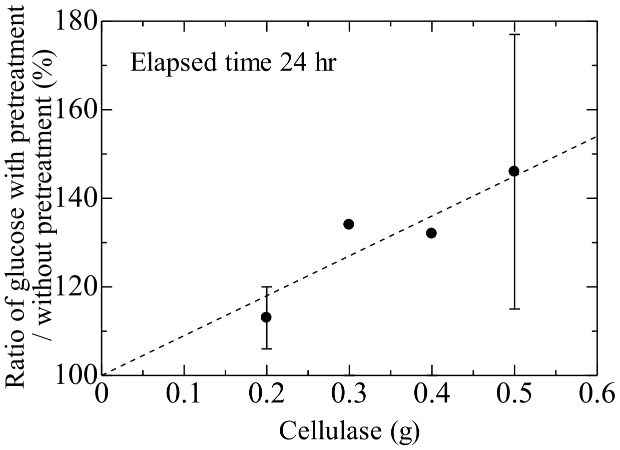

Fig. 3 Effect of ultrasonic pretreatment with the amount of cellulase. Here, temperature kept at 50 ℃ after adding cellulase.

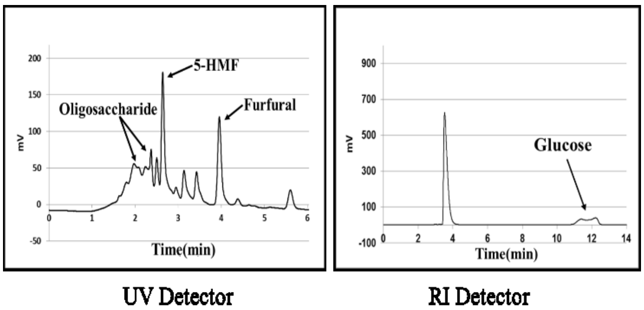

Fig. 4 HPLC after 60 seconds of ultrasonic vibration at 200 W. Here, a RI (Differential refraction) detector is used to detect the difference in refractive index between the specimen material and solvent (reference liquid) as moving layers. The UV (ultraviolet) detector is used to detect the property of ultraviolet light absorption of the specimen substance.

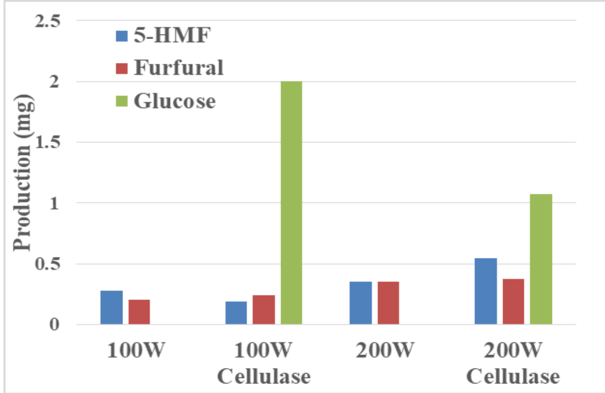

Fig. 5 Comparison of products after applying ultrasonic vibration for 60 seconds.

These results are related to the production process of 5-HMF from cellulose. It is considered that the main reaction process of 5-HMF production from cellulose is composed of 2 steps. One is hydrolysis of cellulose to glucose of the monosaccharides and the other is the dehydration reaction of glucose to 5-HMF (2). The preferable temperature for the hydrolysis of cellulose by cellulase is 50°C, while the most suitable dehydration reaction temperature of glucose to 5-HMF is 140-160°C. The temperature of the reaction field might be kept low to produce the glucose when the ultrasonic power is 100 W. The increase in ultrasonic output suggests that temperatures rise in the reaction field, and it is thought that the temperature reaches the dehydration temperature of glucose or oligosaccharides which are broken down into 5-HMF. Therefore, production of 5-HMF might be further increased by adding cellulase. On the other hand, there is little effect of cellulase feed on the production of furfural. The main reaction process of furfural is the hydrolysis of cellulose to saccharides such as xylose and the dehydration reaction of the xylose (2).The effect of cellulase feeding to promote generation of glucose is ineffective for furfural, moreover, a higher temperature is demanded for the reaction from from xylose.

5. Conclusion

The ultrasonic welding method can reduce the time of cellulose decomposition by adding catalyst. The injection of the catalyst is necessary for the production of glucose from cellulose, and the ultrasonic welding method is effective for the enhancement of glucose production rate with catalysis.

References

1. Nomura, Shinfuku; (2016), Decomposition of cellulose by ultrasonic welding in water, JJAP, Vol. 55, No. 7S1, 07KE02
2. Haraguchi, T; (1985), Chemistry of Wood, Buneido Publication, pp. 7-152.