§24. Study on the Mechanism for Direct Saccharification of Cellulosic Materials under Microwave Irradiation

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The conversion of biomass into fuels and valuable chemicals has attracted considerable interest because biomass is recognized as renewable source of energy and organic carbon. Among a wide variety of biomass sources, cellulose has been known as the most abundant material, and has attracted much attention because of its digestible nature for humans. The direct saccharification of cellulosic materials is a key technology to convert biomass into fuels and valuable chemicals. Recently, our research group discovered that microwave irradiation to cellulose in the presence of tungstosilicic acid gave glucose (direct saccharification) with highly efficiency. The highest yield of glucose from cellulose reaches 44% with 95% conversion in the presence of large amount of tungstosilicic acid resulting in 46% selectivity. However, the mechanism of the direct saccharification of cellulose under microwave irradiation in the presence of tungstosilicic acid has not been elucidated. In this study, the effects of solvent as well as crystal structure of tungstosilicic acid onto direct saccharification under microwave irradiation.

Cellulosic material used in this study is cellulose powder purchased from Nacalai tesque (code 07748-75). Reagent grade of tungstosilicic acid hydrate (H_4SiO_4 · $12WO_3$ · xH_2O) and the other heteropoly acids were purchased from Alfa Aesar and used without further purification. Commercially available microwave apparatus of National NE-EH21A with power generator of 1.26kW at 2,450 MHz was used for microwave irradiation.

The selective saccharification could not proceed by the simple heating of cellulose in the presence of inorganic acid such as H_2SO_4 and HCl. On the other hand, microwave irradiation to cellulose in the presence of tungstosilicic acid could degrade crystallinity of cellulose effectively, and simultaneously produce glucose. Moreover, it was found that tungstosilicic acid revealed the effect of degradation for cellulose crystalline and the production of glucose in spite of acidity of solvent. Besides the tungstosilicic acid, Hetero-poly acids such as phosphotungstic acid, molybdosilicic acid and molybdophosphoric acid also showed the same effect of tungstosilicic acid on cellulose degradation as well as direct saccharification. Thus the effect is not only characteristics for tungstosilicic acid but also for hetero-poly acids in common. The direct saccharification could not proceed when iso-poly acids were used instead of hetero-poly acids. Based on these results, the direct saccharification of cellulose under microwave irradiation is owing to the characteristics of hetero-poly acids. These results indicate that β-1,4 glycosidic bonds as well as inter- and intra-molecular hydrogen bonds in cellulose could be ruptured selectively to produce simple building blocks of glucose by microwave irradiation in the presence of tungstosilicic acid.

The effect of solvent was investigated. Microwave irradiation in the presence of tungstosilicic acid in 1-propanol or 2-propanol solvent didn't produce glucose. On the other hand, ethanol solvent produces glucose although the yield was low. However, the mixed solvent of water and ethanol could produce glucose from cellulose with highly yield of 80%. Thus the effect of solvent is meaningful for the direct saccharification.

The effect of crystal structure of tungstosilicic acid onto direct saccharification was investigated. The drying pretreatment on tungstocilicic acid was done by the simple heating and microwave irradiation. Judging from the X-ray diffraction patterns of dried tungstocilicic acid, the crystal structure was changed from untreated sample to dried samples. Moreover, the differences in crystal structure of the dried sample between simple heating and microwave irradiation were observed. Thus, the state of water molecules in the crystal structure of tungstocilicic acid depends on the drying processes. It was also found that the drying treatment is effective to improve the glucose yield. These results indicate that the direct saccharification of cellulose under microwave irradiation in the presence of tungstocilicic acid depends strongly on the amount of water and its characteristics in the crystalline of tungstocilicic acid. The highest yield of direct saccharification from cellulose to glucose reached 99% by using the pre-treated tungstocilicic acid. Thus, it can be concluded that the high glucose yield can be achieved when the suitable condition such as solvent and pre-treatment of tungstocilicic acid was adopted.

The microwave absorption was investigated by using cellulose and tungstocilicic acid (Fig. 1). The experimental results reveal that cellulose itself can't absorb microwave at any frequency. On the other hand, tungstocilicic acid dissolved in water solvent absorb microwave indicating that the tungstocilicic ions absorb microwave to be activated for rupturing β-1,4 glycosidic bonds as well as inter- and intra-molecular hydrogen bonds in cellulose crystalline.

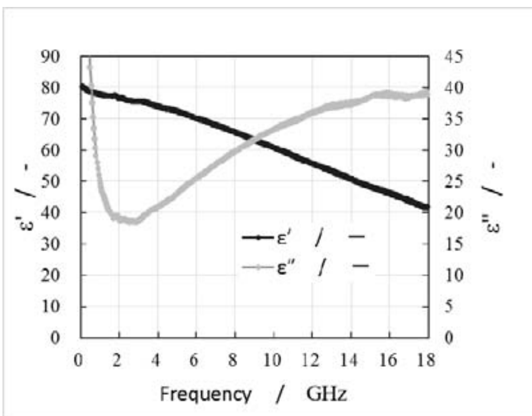

Fig. 1 Complex permittivity of cellulose dispersed tungstocilicic acid aqueous solution.