別　紙

論 文 の 内 容 の 要 旨

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論文題目　**Sulfurous acid prehydrolysis pulping for the total utilization of wood polysaccharides**
（木材多糖類総合的利用のための亜硫酸前加水分解パルプ化）

The biggest present industrial process for the chemical utilization of woody biomass is the chemical pulping process. Annually, about as huge as more than 200 million ton of wood undergo this process all over the world. Huge knowledge and technology has been accumulated for the chemical utilization of biomass during the over 100 years history of this industry. What is interesting to note is that the science of woody plant cell wall has developed together with the development of this industry. Therefore, new development of chemical utilization of woody biomass must be constructed by taking the full advantage of the science and technology related to the chemical pulping process.

Through the chemical pulping process, cellulose which is a main component of plant cell wall is utilized efficiently as pulp. Lignin, next abundant material in the plant cell wall, is utilized as a source of energy. However, hemicellulose, which is a mixture of different structure of polysaccharides and account for about 25% of woody plant cell wall, is converted into various types of degradation products during pulping process and, thus, not utilized in an efficient way. Therefore, one of the most important targets in the research of chemical utilization of woody biomass is the hemicellulose.

One promising way to make the hemicellulose utilization possible is to recover hemicellulose from wood as monosaccharides prior to chemical pulping process. By conducting such a prehydrolysis, hemicellulose is saved from useless degradation and could be subjected to wide variety of utilization methods. The purpose of this research is to obtain basic knowledge on the behavior of wood cell wall components (hemicellulose, lignin, cellulose) during the prehydrolysis stage and find a effective way to obtain monosaccharides from hemicellulose while depressing the hydrolysis of cellulose. To find out a efficient combination of prehydrolysis process and following chemical pulping process is also an important purpose of this research.

In Chapter 1 (ntroduction) d introductory parts of following chapters, the basic knowledge of the woody plant cell wall and technology of chemical pulping process as well as recent development of bio-refinery technology were reviewed.

In Chapter 2 (Dilute acid treatment of Radiata Pine), behavior of hemicellulose in wood cell wall during prehydrolysis stage by the use of hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and sulfurous acid (H_2SO_3 or H_2O-SO_2) was investigated. Even though sulfurous acid is a weak acid compared with other two acids, hydrolysis of hemicellulose proceeded quite well and yield of monosaccharide from hemicellulose was comparable with other two acids. Importantly, the hydrolysis of cellulose was suppressed effectively during the prehydrolysis stage and the proportion of cellulose in the polysaccharides in the prehydrolysis residue was pretty high when sulfurous acid was employed. Therefore, it was concluded that selective and efficient hydrolysis of hemicellulose into monosaccharides was possible during the prehydrolysis stage by the use of sulfurous acid.

In Chapter 3 (Degradation of monosaccharides in dilute acid system), acid catalyzed reaction of monosaccharides into further degradation products in hydrochloric acid, sulfuric acid, and, sulfurous acid was kinetically investigated. Monosaccharide yield from hemicellulose depends not only on the efficiency of hydrolysis of glycosidic linkage but also on the preservation of once produced monosaccharides from the further degradation. Results obtained in Chapter 3 suggested that monosaccharides are preserved from further degradation rather well in sulfurous acid. In order to confirm this point, monosaccharides themselves were subjected to acid treatment by the use of above three acids, and degradation behavior was analyzed as second order reaction with respect to both substrate (monosaccharide) and acid concentration. Second order reaction rate constant as well as activation energy obtained by analyses confirmed that monosaccharides were preserved well in sulfurous acid comared with other two acids. As the mechanism of preservation effect of sulfurous acid, the adduct formation of carbonyl group of monosaccharide with bysulfite (hydrogen sulfite) ion was suggested. By comparing the stability of monosaccharides in sulfuric acid with and without addition of bisulfite ion, it was confirmed that the bisulfite ion has a protective effect on monosaccharides from the acid catalyzed degradation.

In Chapter 4 (Pulping of prehydrolsis Residue), pulpability (delignification efficiency) of hydrolysis residue was examined. If a good pulping (delignification) method can be established to obtain cellulose from the prehydrolysis residue as a form of pulp, the combination of such pulping method and sulfurous acid prehydrolysis enables the total utilization of wood polysaccharides. Prehydrolysis residue obtained by not only sulfurous acid but also hydrochloric and sulfuric acids were subjected to pulping reaction under various conditions. Pulping of prehydrolysis residues obtained by hydrochloric acid or sulfuric acid were rather difficult under any conditions examined. On the other hand prehydrolysis residue obtained by sulfurous were found to be easily delignified by simple alkali cooking and give pulp in rather high yield (about 42% based on the original wood) with rather high purity as cellulose (about 92%) .

Based on the above results, it was suggested the combination of sulfurous acid prehydrolysis and simple alkali cooking is a selective and efficient way to utilize wood polysaccharides.