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学位論文の内容の要旨

Chitin is a simple β-(1-4) glycan, and is widely distributed in nature as a component of bacterial cell walls and exoskeletons of, for example, crustaceans and insects. Chitosan is also a natural polysaccharide, which has been produced industrially by the deacetylation of chitin. On the other hand, cellulose was found to be a major component of plant cell walls. These two kinds of biomass resources, cellulosic materials and chitinous materials (which are both major components of biomass) are expected to be valuable renewable resources for energy, chemicals, food and feedstock. Depolymerization of these biomass resources for their successful utilization in various fields is an important area of study, since improved solubility and essential biological activities of the corresponding depolymerized products have recently been discovered. These polysaccharides are hydrolyzed with concentrated hydrochloric acid, sulfuric acid or hydrolase, and decomposed with other reagents. Transformation of these biomass molecules into their low molecular weight homologs usually needs catalysts or reagents, because chitinous and cellulosic materials are highly crystalline. However, these methods include the following drawbacks: the acidic treatment method leads to corrosion of the reactor, and the enzymatic method is very expensive.

Recently, supercritical water treatment has been considered to be an attractive alternative for hydrolyzing cellulose, compared with enzymatic saccharification and acidic hydrolysis methods. Some researchers have reported that supercritical water treatment can rapidly convert cellulose to glucose.

Water is the most commonly used, and most environmentally friendly solvent. It is a unique fluid with interesting properties. Because of its high critical points for temperature and pressure, much attention has recently been given to its use in the supercritical state. The fundamentals of the characteristics of water as a reactive solvent can be understood from the viewpoint of an ionic product and a dielectric constant. The ionic product plays a role in estimating the activation of hydrolytic and hydrogen-bonding sites of substrates and reactants, and the dielectric constant is useful as a measure to evaluate the solubility of various solutes. Water has a comparatively high ionic product under high temperature. Supercritical water is a non-polar solvent with a low dielectric constant. It is able to dissolve organic compounds, while simultaneously retaining high hydrolysis performance. However, control of the reaction conditions for decomposition of chitinous and cellulosic materials in supercritical and sub-critical water is too difficult, because these materials are rapidly decomposed to monosaccharide, oligosaccharide, and pyrolyzed products. Furthermore, the experimental device used is very expensive, because the process requires both high temperatures and high pressures.

Chitin and cellulose are usually not decomposed easily with aqueous acid or enzyme under moderate subcritical conditions (below 200 °C), because their molecules contain rigid crystalline areas. Therefore, the present author tried to destroy the rigid hydrogen bonding structures in these biomasses before carrying out the depolymerization experiments. In this study, it is shown that decrystallization of chitinous and cellulosic materials accelerates the depolymerization reaction, even under hydrothermal conditions (120-200 °C), in the absence of catalysts, or with a dilute acid. For the mechanistic study, hydrolysis of various acetals under hydrothermal conditions is also investigated.

In chapter 1, the relationship between crystallinity and ease of hydrolysis of chitinous materials under hydrothermal conditions without any catalyst addition is discussed. Although transformation of commercially available chitin and chitosan into their low molecular weight homologs needs some catalysts or reagents, chitin and chitosan decrystallized with concentrated sodium hydroxide were found to be good substrates for catalyst-free decomposition under hydrothermal conditions (120-180 °C). The decomposition of chitin and chitosan under hydrothermal conditions is regarded as a hydrolysis reaction, because IR analysis of chitin and chitosan decomposed under these conditions did not show any structural change, and the number of reducing groups increased.

In chapter 2, hydrolysis of cellulosic materials as chitin-like polysaccharides under hydrothermal conditions without any catalyst. Cellulosic materials such as decrystallized cellulose, water-soluble cellulose derivatives and cellooligosaccharides were decomposed effectively under hydrothermal conditions of 120-180 °C in the absence of catalyst. In contrast to these substrates, avicel, which is highly crystalline, was difficult to decompose. Therefore, decomposition of cellulosic materials under hydrothermal conditions is influenced by the degree of crystallinity of the substrates. Because molecular weights decreased and the number of reducing groups increased after the hydrothermal reaction, decomposition of cellulosic materials under hydrothermal conditions is regarded as a hydrolysis reaction.

In chapter 3, hydrolysis of chitinous materials under hydrothermal conditions in the presence of dilute hydrochloric acid is discussed. In the case of chitinous and cellulosic material decomposition under hydrothermal conditions without any catalyst, only a small amount of water soluble oligosaccharide and monosaccharide fraction was formed. Usual industrial methods for the saccharification of chitinous materials consist of treatment with concentrated acid. In this chapter, decomposition of chitinous materials under hydrothermal conditions (120-180 °C) with dilute hydrochloric acid was examined. The chitinous hydrolysate obtained by this treatment contained a fairly large water-soluble fraction, and formation of chitooligosaccharide was confirmed.

In chapter 4, the transformation of several organic compounds in neutral water under hydrothermal conditions was attempted, and it was found that acetals and ketals were hydrolyzed to give their corresponding hydroxy and carbonyl compounds in high yields. This result provides additional evidence that the degradation reaction of chitinous and cellulosic materials under hydrothermal conditions can be regarded as a hydrolysis reaction of the acetal moiety in the biomass.

This thesis is comprised of 4 chapters. It shows that hydrothermal methods are promising for depolymerization of natural polysaccharides, and gives a convenient method for the chemoselective hydrolysis of acetal and ketal groups. This procedure using hydrothermal conditions is more environmentally friendly than conventional methods, which require strongly acidic conditions, and is expected to lead the way for the development of a key technology that will be necessary in the future.

論文審査の結果の要旨

カニ殻、エビ殻等の成分であるキチン及びその脱アセチル化体のキトサンは天然アミノ多糖であり、植物由来のセルロースと並ぶバイオマスである。特に、キチン、キトサンは、生体親和性の高さ、特異な免疫増強能、金属イオン等に対する優れた吸着能に代表される種々の特性が見出され、様々な産業分野での応用が試みられてきた。しかしながら、近年関心が高まっている中程度低分子化物、オリゴマー、モノマーの製造方法としては、強酸を用いる環境負荷型の方法や酵素を用いる高コスト型の方法が主流であり、環境適合性でしかも安価な方法の開発が課題となっていた。本学位論文は、セルロース、キチン、キトサン及びその誘導体を低分子化する簡便な方法の開発を目指し、水熱分解条件を詳しく検討した結果、新しい環境適合型の低分子化法を提案したものである。

一般に、超臨界水を用いる分解法は種々の長所があるものの、高価な装置を必要とする点で実践性に難点がある。そこで本研究では、高温水蒸気を利用して簡便に条件設定できる120−200 °Cの水熱領域において多糖の分解挙動を検討している。セルロース、キチン、キトサンのいずれについても、そのまま水熱処理を行っても分解の程度は低いが、初めに基質を非晶化することにより分解性が大きく向上することを見出した点は、極めて独創的である。また、ゲルパーミエーションクロマトグラフィーによる分子量の減少、還元末端定量による糖鎖の還元末端基の増大、さらに分解物の赤外スペクトル分析における原料多糖との相同性から、本水熱分解反応は基質の1, 4−グリコシル結合部分の加水分解反応であると解明している。反応機構に関して重要な点は、120−200 ℃の水熱領域において水のイオン積が常温常圧時の値よりも1000倍近く増大することである。従って、単に反応温度が上昇したのみにとどまらず、水素イオン濃度も上昇し、酸性のナノ反応場の提供が可能になったものと考察している。

次に、加水分解反応をさらに促進して水溶性生成物を増大させることを目指し、希酸存在下での水熱分解を検討し、目的を達成している。また、本水熱条件下で低分子アセタール化合物の加水分解反

応がほぼ定量的に進行することを実証し、本研究全体に関わる多糖類の 1, 4-グリコシル結合部分の加水分解機構を支持する知見を得ている。

以上、本論文は、多糖類を低分子化するための簡便かつ環境適合型の水熱分解法を開発し、バイオマス資源のより一層の利用拡大を可能とした。今後の資源循環型社会における重要なコンセプトを与えるものとして高く評価できる。よって本論文は、博士（工学）の学位論文に値するものと認められる。