

A comparative study of reaction behaviors between cellulose and starch in supercritical methanol

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The chemical conversion of cellulose and starch as treated in supercritical methanol was made with a batch-type reaction vessel, and a comparative study was made on their decomposition rates and the product yields. The decomposition rate constants of starch obtained were considerably higher than those of avicel at a range of temperature from 255 to 300 °C. The maximal total yield of the monomeric compounds such as methyl α - and β -D-glucosides and levoglucosan was 78.1 wt% at 5 min treatment, which was more than twice that from cellulose. In addition, unlike cellulose, the total yield of methylated oligomers and monomeric compounds were not hardly changed under the prolonged treatment. These differences of the decomposition rate constants and the product yields between cellulose and starch could be explained by the differences in the molecular structure and the cage effect of methanol

Introduction

Cellulose is a linear macromolecular compound of (1 \rightarrow 4)- β -D-glucopyranose, and the configuration of the C1 position is different from that of starch which occurs in two forms with helical structure, amylose and amylopectin. The former is made of (1 \rightarrow 4)- β -D-glucopyranose, while the latter is a branched molecule with α -(1 \rightarrow 6) glucosidic bond. As with starch, glucose is the only monosaccharide found in the hydrolysis products of cellulose. However, unlike starch, cellulose is linear and moderately crystalline, forming numerous hydrogen bonds inter- and intra-molecularly. This difference results in a difficulty in hydrolyzing cellulose, compared with starch. Therefore, a comparison between cellulose and starch is of great interest to evaluate a potential of the chemical conversion of cellulose by the supercritical fluid treatment. For the supercritical water treatment, Saka and Ueno reported that cellulose was hydrolyzed to, more or less, the same degree as corn starch for 5-10 seconds with a semi-batch-type reaction vessel [1]. However, there is a possibility that some noticeable differences between cellulose and starch can be observed for the supercritical methanol treatment because its treatment is considerably milder than that of water [2]. In this study, therefore, a supercritical methanol treatment of starch was investigated, and a comparative study between cellulose and starch was made. To put it concretely, the decomposition rates and the product yields of cellulose and starch was compared, and the decomposition mechanisms of these natural polymers were discussed.

Material and Methods

As starch sample, corn starch which consists of about 18 % amylose and 82 % amylopectin was selected for the supercritical treatment of methanol. Methanol was fully fed to the 5 ml reaction vessel with 150 mg of starch sample, and then it was attached to the batch-type supercritical methanol biomass conversion system. To start supercritical treatment of the sample, the reaction vessel was quickly heated by immersing it into the tin bath preheated at various temperatures and maintained at designated temperature and pressure with swaying left and right. To stop the reaction, the reaction vessel was moved into the water bath to quench. The reaction mixture obtained after the treatment was filtrated with 0.2 μ m membrane filter to separate methanol-insoluble and methanol-soluble portions. The methanol-insoluble portion was then dried and weighed to obtain its yield. The methanol-soluble portion was analyzed by using the liquid chromatography–mass spectrometry (LC-MS) and the high performance liquid chromatography (HPLC).

Results and Discussion

Figure 1. shows the arrhenius plot for the decomposition rate constants of starch with those of avicel and methyl

α - and β -D-glucosides in subcritical and supercritical methanol. The decomposition rate constants of starch were considerably higher than those of avicel in the range of temperature between 255 and 300 °C. This result was mainly due to the difference of the molecular structures. Starch is in helical structure and more amorphous nature with much less hydrogen bonds, while cellulose is composed of crystalline microfibrils with numerous hydrogen bonds. Therefore, the decomposition of starch in supercritical methanol can be expected to proceed considerably faster than that of avicel. Furthermore, unlike avicel, a rapid change of the decomposition rate constants at near 270 °C was not observed for starch. This result might suggest that some changes in crystalline microfibrils of cellulose, which became to be easy to decompose the microfibrils, occur in supercritical methanol above 270 °C and 26 MPa.

The main products from cellulose and starch were, methyl α - and β -D-glucosides, levoglucosan, methylated oligomers and 5-hydroxymethylfurfural (5-HMF). Figure 2. shows the yields of the products from starch as treated in supercritical methanol at 350 °C and 43 MPa. The maximal total yield of the monomeric compounds was 78.1 wt% at 5 min treatment, which was more than twice than that of avicel. This result would be due to the difference of the treatment time. Starch was decomposed considerably faster than avicel due to the difference of the molecular structures. Therefore, the monomeric compounds produced from starch could be recovered smoothly before the pyrolysis of both starch and the monomeric compounds occurs in supercritical methanol. Furthermore, it is surprising that the sum of the methylated oligomers and monomeric compounds from starch remained almost unchanged during the treatments from 1 to 7 min, although that from avicel decreased under the prolonged treatments. This result might be due to the difference in the degree of the cage effect of methanol, which would be caused by the difference of liquefaction degree between avicel and starch [3]. These results indicated that the crystalline structure of cellulose affected both the decomposition rate and the product yield for the supercritical methanol treatment of cellulose seriously, and these lines of information must be important for the chemical conversion of cellulose by the supercritical methanol treatment.

References

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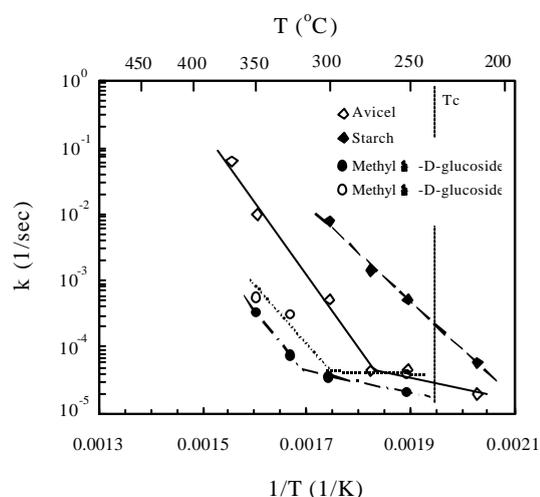


Figure 1. Arrhenius plot for the decomposition rate constants of avicel, starch and methyl α - and β -D-glucosides in sub- and supercritical methanol.

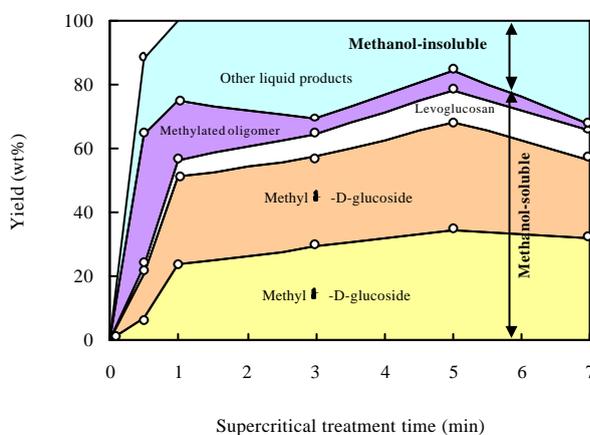


Figure 2. The yield changes of the products from starch as treated in supercritical methanol at 350 °C and 43 MPa.