

Thermochemical conversion of cellulose in sulfolane as a solvent for levoglucosan into low molecular-weight substances

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Pyrolysis of cellulose in sulfolane as a solvent for initially formed levoglucosan (LG) is presented as a selective conversion method into low molecular-weight (MW) substances, and the pyrolysis mechanism of cellulose is discussed focusing on the effect of the solvent.

Introduction

Although cellulose, which is a major component of woody biomass, has simple chemical structure based on α -D-glucose, selective conversion into specific lower MW chemicals or gas and liquid fuels is still difficult. In our laboratory, reaction mechanism in pyrolysis has been studied in order to control the pyrolysis reaction for specific chemicals or fuels. In cellulose pyrolysis, condensation reaction of initially formed LG into polysaccharides has been clarified to be a key reaction to produce carbonized products, and the pyrolysis in the solvent for LG was found to be effective for complete prevention of the carbonized products formation [1]. In this paper, pyrolysis of cellulose in sulfolane as a solvent for LG is presented, and the mechanism is discussed focusing on the effect of the solvent.

Materials and methods

Cellulose powder (10.0 mg, 100.200 mesh, Toyo Roshi Co.) in 0.5 ml of sulfolane was heated in an ampoule at 200.330°C. After immediate cooling, inner part of the ampoule was filtered and washed with sulfolane to give residues and sulfolane-soluble fraction. The residues were analyzed by IR spectroscopy and X-ray crystallography [Rigaku RINT 2000V(Cu-K α , λ =1.542, 40kV, 30mA)], and soluble fraction was analyzed by HPLC (column: ODS) and GPC (column: Shodex KF-803) chromatography.

Results and discussion

Cellulose was found to decompose into the products completely soluble in sulfolane for 3, 10, 60, and 480 min at 330, 280, 240, and 200°C, respectively (Fig. 1). MWs of the soluble products were found to be less than that of cellobiose by GPC analysis. From HPLC analysis, substantial amount of LG was formed initially, and then, LG was transformed into various kinds of the products including levoglucosenone and furfural. Arrhenius plot of the decrease rate of the residues gave a straight line (Fig. 2), and the activation energy was calculated into 21.2 kcal/mol.

Residues in sulfolane were obtained as colorless solids under all conditions and had no absorption at 1700 cm^{-1} (C=O), which was characteristically observed for carbonized cellulose, in their IR spectra (Fig. 3). Furthermore, X-ray diffraction patterns of the residues is almost identical with the original cellulose. These results indicate that the residues in sulfolane are cellulose itself without suffering any pyrolysis reactions.

Pyrolysis mechanism of cellulose is proposed as shown in Fig. 4. Focusing on a cellulose fiber, pyrolysis reaction starts to occur at the surface molecules because intermolecular forces such as hydrogen bonding stabilize the inner part. The pyrolysis proceeds continuously from outer to inner side at the newly generated surface cellulose molecules with forming carbonized layer. In sulfolane, initially formed LG is dispersed into homogeneous solution, and this prevents the carbonization by inhibiting the polymerization reaction of LG. Thus, pyrolysis of cellulose in solvent for LG is expected to be a selective conversion method of cellulose into low MW substances.

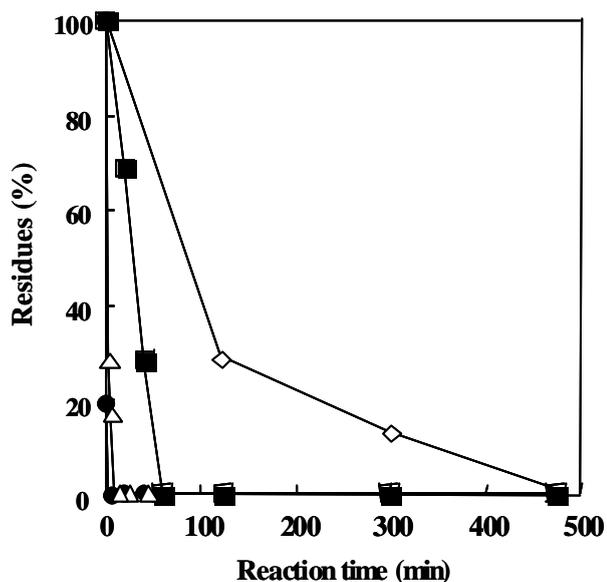


Fig. 1 Decomposition behavior of cellulose in sulfolane at 200~330°C.
 . : 330°C, . : 280°C, . : 240°C, . : 200°C

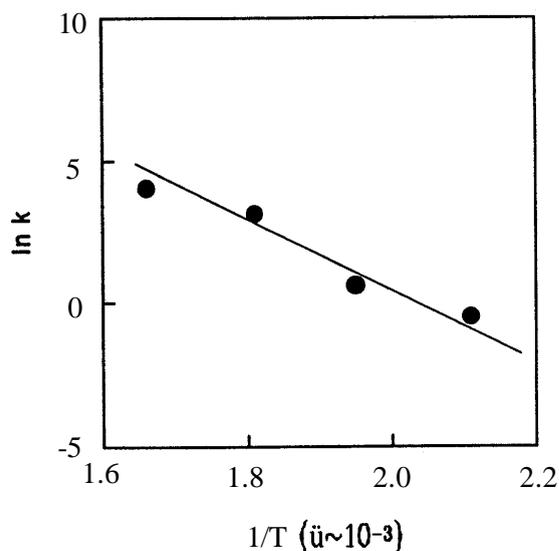


Fig. 2 Arrhenius plots of the decrease rate of the residues.

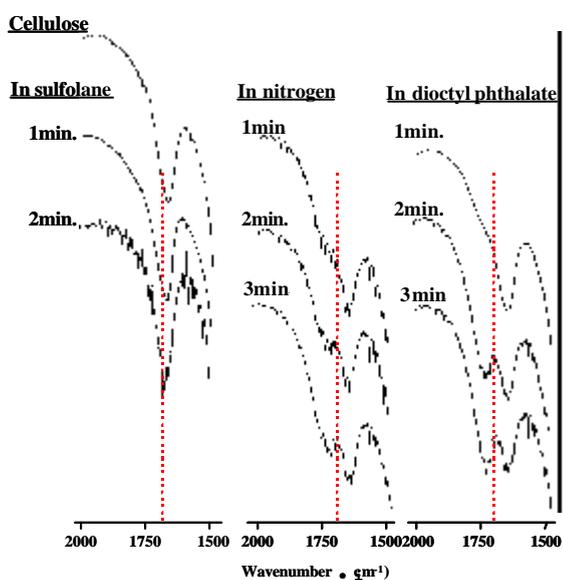


Fig. 3 IR Spectra of the residues obtained by the pyrolysis of cellulose in sulfolane, nitrogen or dioctyl phthalate at 330°C.

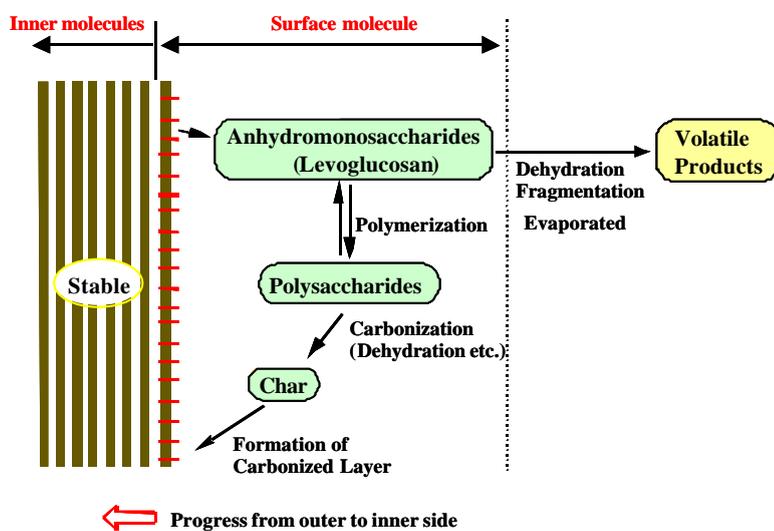


Fig. 4 A proposed mechanism starting from "inner molecule".

[1] H.Kawamoto, M Murayama, S. Saka: Proceedings of the XIXth International Carbohydrate Symposium, San Diego, August 9-14, 1998, DP059.