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Assessment of the structural factors controlling the enzymatic saccharification of rice straw cellulose

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ABSTRACT

In this study, the structural factors controlling the enzymatic saccharification of rice straw cellulose were examined by preparing structure-modified rice straw samples such as dewaxed, alkali-treated, oxidized, and swollen rice straw. It was found that the initial enzymatic saccharification rate of the various structure-modified samples was largely controlled by the initial cellulose surface area of the cellulose unit. Although the presence of lignin limited the cellulose surface area, there was no strong relationship between the lignin content and the initial reaction. On the other hand, the long-term enzymatic saccharification of rice straw cellulose highly depended on the lignin removal rate (lignin content). It was also found that silica is not a crucial factor in controlling the enzymatic saccharification.

1. Introduction

The securement of sustainable feedstock is one of the most important factors affecting the feasibility of biorefinery. For this reason, lignocelluloses have attracted great attention as sustainable feedstock for biorefinery. Lignocelluloses can be classified into the following four groups [1]: 1) forest products/residues (e.g., eucalyptus, pine, and poplar), 2) agricultural residues (e.g., corn stover, wheat straw, sugarcane bagasse, and rice straw), 3) agricultural processing by-products (e.g., corn fiber, rice hull, and barley hull), and 4) dedicated energy crops (e.g., hybrid poplar, switchgrass, and willow). Since the factors affecting availability of the above lignocelluloses, including the land use for their cultivation, are geologically and seasonally diverse, a strategy for biorefinery from these sources cannot be generalized. This is the reason why many countries have been evaluating the potential of indigenous biomass for biorefinery.

For many Asian countries including Japan, among the agricultural residues, rice straw accounts for the major portion of the available biomass [2]. According to statistics supplied by the Japanese government, the annual generation of rice straw in 2005 reached about 9 Mt; however, most of this product is plowed down, with a little effective utilization (i.e., animal feed and composting) that accounts for only about 20% of the total production. Considering this situation, the utilization of rice straw as feedstock of biorefinery is quite meaningful in those Asian countries in which the land use for energy crop cultivation is highly limited in terms of establishing an agricultural society for carbon circulation. From this viewpoint, the feasibility of sugar-based biorefinery (e.g., ethanol production) using rice

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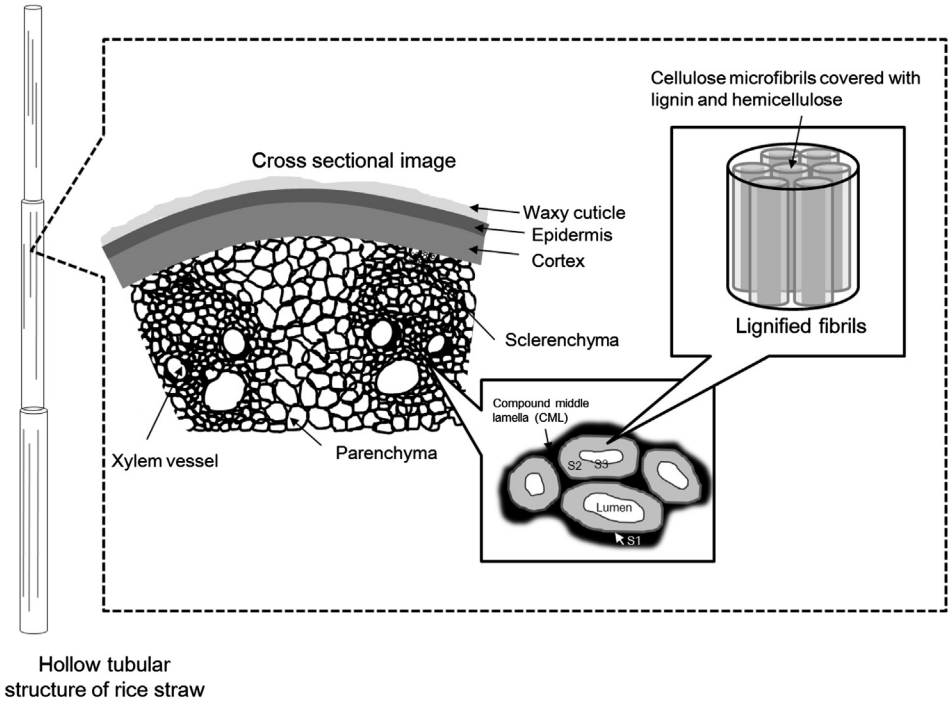

Fig. 1 – Schematic image of the structure of rice straw.

straw has been widely discussed [2,3]. However, basic studies on the pretreatment and enzymatic saccharification of rice straw, taking into account its intrinsic structural features, have not been fully carried out, even though it is very important to optimize the sugar-based biorefinery using rice straw.

In contrast to wooden stem, the stem of the rice straw monocots lacks a cambium, but it has numerous vascular bundles in different layers consisting of a waxy cuticle, silicated epidermis, cortex (collenchyma), a thick lignified layer (sclerenchyma), and ground tissue (parenchyma), as shown in Fig. 1 [4].

Compared to woody biomass and other monocots, one of the intrinsic features of rice straw is its silica-enriched body, which is known to be the main physical barrier to material transportation along with the lignin that reduces the susceptibility to enzymatic degradation [5]. Jin and Chen [4] reported that the proportion of lignin and the silica content in different parts of rice straw (e.g., the leaf blade, node, and internode) showed a negative correlation with the hydrolysis performance of cellulose.

Nonetheless, the enzymatic saccharification cannot be fully explained based on the proportion of lignin to silica, because rice straw has a three-dimensional structure consisting of various layers. Moreover the negative effects of lignin and silica on the digestibility of rice straw as an animal feed have been elucidated extensively for the last several decades [6], but the structural factors governing the enzymatic saccharification of rice straw cellulose are still not clear. Therefore, in this report, the structural factors controlling the enzymatic saccharification of cellulose in rice straw have been studied taking into consideration the intrinsic structure of rice straw. Based on the results, an effective pretreatment strategy for rice straw was also discussed.

2. Material and methods

2.1. *Preparation of structure-modified rice straw samples*

Straw of Japanese rice (*Akitakomachi*) harvested at maturity on October 2011 from a single paddy field in Shinano (36°48′ N, 138°12′ E, Nagano prefecture, Japan) was kindly supplied by the rural rice farmer. Air-dried rice straw was coarsely cut to less than 30 mm by cutting machine and stored in a dry space until further use. Rice straw was crushed to (3 ± 2) mm × (10 ± 5) mm pieces by using a manual roll crusher and air-dried to reduce the water content (below 10%, weight fraction). The crushed raw rice straw is termed RAW. The authors intended to modify the rice straw structure in a stepwise approach to estimate more clearly how each modification step (e.g. removal of wax and silica-enriched layers) contributes to changes in the accessible cellulose surface area, since various components of rice straw affect exposure of the cellulose surface together. First, ethanol Soxhlet extraction was carried out for 24 h to remove the wax from the cuticles of rice straw. The dewaxed sample is hereafter termed DW. DW was treated to control silica-enriched layer (i.e. epidermis) by immersion in a 940 mol m^{-3} Na_2CO_3 (soda ash) solution under the following conditions: liquid-to-solid ratio (L/S) of 20 (dm^3 kg^{-1}), temperature of 62 °C, and reaction times of 20, 40, 90, and 180 min. For the modification of densely lignified layer, DW was treated by immersion in the oxidizing agent (25% CH_3COOH + 15% of 30% H_2O_2 + 2.5% H_2SO_4 + 57.5% distilled