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Cellulose accessibility determines the rate of enzymatic hydrolysis of steam-pretreated spruce

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HIGHLIGHTS

- Degradability and surface characteristics of steam-pretreated spruce were studied.
- A clear correlation between rate of enzymatic hydrolysis and BET area was found.
- Higher pretreatment severity resulted in a more accessible cellulose fraction.
- The influence by cellulose accessibility was larger than by surface lignin content.

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ABSTRACT

Spruce chips steam-pretreated at various conditions, according to a central composite design, were used for investigating the influence of pretreatment conditions on enzymatic hydrolysis, accounting for the individual effects of pretreatment temperature (194–220 °C), time (3–11 min) and sulfur dioxide uptake (0.7–2.5%). The materials were analyzed for several surface characteristics, including IR absorption, enzyme adsorption capacity, total surface area, cellulosic surface area, and cellulosic pore sizes.

This work showed a clear correlation between rate of enzymatic hydrolysis and specific surface area. Although the lignin content of the particle surface increased at higher pretreatment temperature and residence time, the initial rate of enzymatic hydrolysis increased. Enzyme adsorption measurements and staining methods revealed that the higher rate of hydrolysis of these materials was due to increased accessibility of the cellulose. An accessible cellulose fraction is thus more important than a low surface lignin content for the enzymatic hydrolysis of steam-pretreated spruce.

1. Introduction

Due to the recalcitrant nature of native lignocellulose, the cost for pretreatment and enzymatic hydrolysis of lignocellulose is substantial. Improvements in pretreatment efficiency and development of new enzymes require better understanding of the factors that determine the rate of enzymatic hydrolysis.

Factors that are generally indicated to influence the enzymatic hydrolysis include non-productive enzyme adsorption on lignin, cellulose crystallinity and degree of polymerization. A limiting factor for enzymatic hydrolysis is also cellulose accessibility to cellulases, which may be reduced by hemicellulose or lignin and is influenced by cellulose porosity (Zhang and Lynd, 2004). The relative importance of these factors is still unclear.

In a comparison of the enzymatic hydrolysis of delignified and non-delignified steam-pretreated spruce, Várnai et al. (2011) found non-productive binding of cellulases to lignin to be the dominant inhibiting factor during enzymatic hydrolysis of steam-pretreated softwood. Thermal denaturation on the hydrophobic lignin surface is a likely cause of the observed activity loss (Rahikainen et al., 2011). Nakagame et al. (2011) found that although non-productive binding to lignin was more extensive, the enzymatic hydrolysis of the pretreated spruce was more efficient at higher pretreatment temperatures. Hence, the study concluded that cellulose accessibility to cellulases plays a greater role during hydrolysis than enzyme–lignin interactions. The same conclusion has also been drawn for other materials (Jeoh et al., 2007; Rollin et al., 2011).

The rate of enzymatic hydrolysis of pretreated lignocelluloses has previously been related to measures of the cellulose accessibility. Grethlein (1985) found a linear correlation between pore volume accessible to a molecule of 51 Å and rate of enzymatic

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