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Delignification of rye straw using hydrogen peroxide

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Abstract

Alkaline peroxide delignification of rye straw has been first investigated in this paper. The results showed that treatment of dewaxed and water-extracted rye straw with 2% H_2O_2 at pH 11.5 for 12 h at 20, 30, 40, 50, 60, and 70°C resulted in a dissolution of 52.7, 75.7, 81.8, 83.1, 85.8, and 87.8% of the original lignin, and 44.2, 52.5, 70.0, 70.0, 71.3, and 71.9% of the original hemicelluloses, respectively. The isolated pure lignin fractions contained rather low amounts of neutral sugars, 0.4–1.1%, and had weight-average molecular weights between 2420 and 3480 g mol^{-1}. They contained almost equal amounts of noncondensed guaiacyl and syringyl units with fewer *p*-hydroxyphenyl units. The β–*O*–4 ether bonds together with β–β and β–5 carbon–carbon linkages were found to be present in the lignin structural units. Hydroxycinnamic acids such as *p*-coumaric and ferulic acids appeared to be strongly associated to lignin molecules. Comparison of these lignin samples indicated that the alkaline peroxide treatment of the straw under the conditions given did not affect the overall structure of lignin. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Rye straw; Hydrogen peroxide; Lignin; Hemicelluloses; Degradation

1. Introduction

World production of rye, one of the major cereal crops, exceeds 30 million tons per annum, which yields about 40–50 million tons of straw (Ghaly and Ergudenler, 1994). This straw and other agricultural residues exiting as waste streams from commercial crop processing plants have little inherent value and have traditionally constituted a disposal problem. These materials represent an abundant, inexpensive, and readily available source of renewable lignocellulosic biomass. However, their utilisation as a carbohydrate source for glucose and ethanol production, and as a metabolic energy source in ruminant feeds, has been severely hampered by the low efficiency with which organisms and enzymes are able to convert the polysaccharide portion of the residue into monomeric sugars (Gould, 1989). The low conversion efficiency for lignocellulosic materials and low digestibility is largely due to the lignin component of the cell wall and its association with other cell wall polysaccharides, which prevents the degradation of cellulose mainly by acting as a physical barrier between the cellulose enzyme and it substrate.

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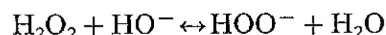
Lignin is an aromatic biopolymer, an integral cell wall constituent in all vascular plants including the herbaceous varieties. Lignin is unique among biopolymers in that there is limited control over its biosynthesis, and the factors guiding this process are not yet fully understand (Ammalahti et al., 1998). Lignin is built up by oxidative coupling of three major C_6–C_3 (phenypropanoid) units, namely, syringyl alcohol (S), guaiacyl alcohol (G), and *p*-coumaryl alcohol (H), which form a randomised structure in a tridimensional network inside the cell walls. The major interunit linkage is an aryl–aryl ether type. Besides the some 20 different types of bonds present within the lignin itself, lignin seems to be particularly associated with the hemicellulosic polysaccharides. Owing to its crosslinking, lignin in situ is usually insoluble in all solvents, unless it is degraded by physical or chemical treatments (Sun et al., 1999).

There is no known method for release of unaltered lignin from plant cell walls, and chemical or biochemical degradation methods produce low molecular weight products in modest yields only. However, numerous treatments have been developed in an effort to increase the removal of lignin from straw and grass. These processes utilise physical, chemical, and/or biological methods to remove lignin and decrease cellulose crystallinity. Among these, the processes such as autohydrolysis, alkaline cooking, and steam explosion require substantial energy input in the form of heat and tend to generate toxic side products. Other drawbacks typical of conventional treatments include loss of the hemicelluloses with the solubilized fraction (Gould, 1989). For example, in the cooking such as chemical pulping processes lignin is dissolved from the raw material at high pressures and temperatures under aqueous alkaline, neutral or acidic conditions. Important delignification reaction include the cleavage of phenolic α–O–4 linkages, cleavage of non-phenolic β–O–4 linkages, and removal of residual lignin fractions, either by cleavage of carbon–carbon linkages or by carbohydrate degradation, releasing lignin-carbohydrate fractions, which are mainly oxidised into aliphatic carboxylic acids.

It is well known that hydrogen peroxide reacts with lignin under alkaline conditions and has widely been used for many years to bleach high-lignin wood pulps. The bleaching effect of hydrogen peroxide has been attributed to its ability to react with various coloured carbonyl-containing structures in lignin. This reaction has been explained through the reactions of the hydroperoxide anion (HOO^-), formed in an alkaline medium according to the equilibrium:



$$H_2O_2 + HO^- \leftrightarrow HOO^- + H_2O$$

where the $pK_a = 11.6$ at 25°C.

This anion is a strong nucleophile that, during bleaching, preferentially attacks ethylenic and carbonyl groups present in lignin. As a consequence, such chromophores as quinones, cinnamaldehyde, and ring-conjugated ketones are converted to nonchromophoric species during the alkaline solution (Dence, 1996; Pan et al., 1998). On the other hand, hydrogen peroxide is unstable in alkaline conditions and readily decomposes, particularly in the presence of certain transition metals such as manganese, iron, and copper. This metal-catalysed decomposition of hydrogen peroxide is undesired in the bleaching process, since it leads to a loss of bleaching capacity and generates more active radicals such as the hydroxyl radicals ($HO^\bullet$) and superoxide anion radicals ($O_2^{-\bullet}$), which participate in the delignifying mechanism. This dual role of hydrogen peroxide in delignifying and bleaching has been investigated in detail by Gould (1984, 1985). Approximately one-half of the lignin and most of the hemicelluloses present in agricultural residues such as wheat straw and corn stover are solubilized when the residue is treated at 25°C in an alkaline solution of 1% H_2O_2. The delignification reaction is most efficient when the ratio of H_2O_2 to substrate is at least 0.25 (w/w) and the pH is 11.5 (Gould, 1984). In the process of alkaline peroxide treatment, wheat straw is delignified and bleached by alkaline peroxide solution and subsequently defibrated mechanically to pulp. As a high-yield pulping method, it is important to produce a pulp of acceptable brightness with a significant dissolution of lignin but a minimal degradation of cellulose. This paper reports the effect of alkaline peroxide treatment temperature

on the solubilization of lignin from rye straw in our newly developed process in which straws are sequentially treated with water and alkaline peroxide solutions. The isolated lignin preparations are physico-chemically characterised and the results are reported.

2. Material and methods

2.1. Material

Rye straw was obtained from Compak Co. (Gainsborough, UK), and was ground to pass a 0.7 mm size screen. The composition (w/w) of the rye straw used was cellulose 37.9%, hemicelluloses 36.9%, lignin 17.6%, protein 3.3%, ash 3.0% and wax 2.0%. All weights and calculations were made on an oven-dried (50°C, 16 h) basis. All chemicals used were of analytical or reagent grade.

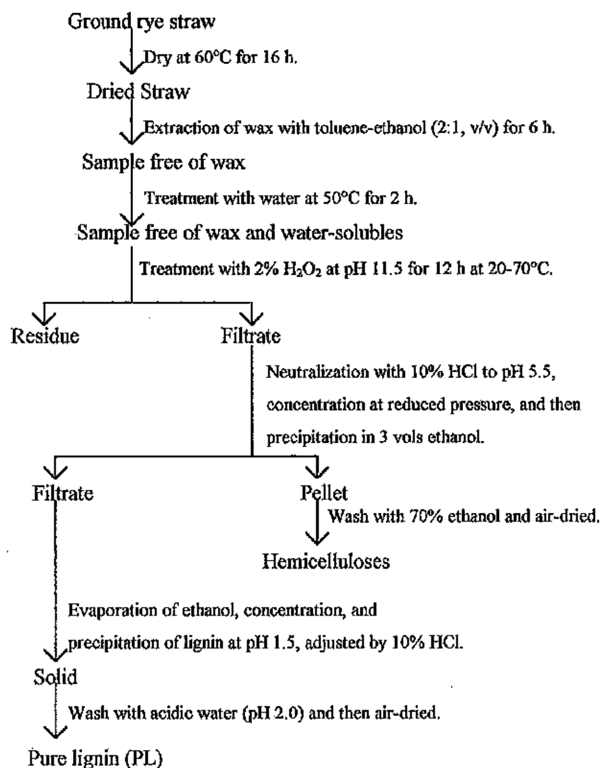


Fig. 1. Scheme for isolation of pure lignin (PL) from the hydrolystes of 20% H_2O_2 treatment of the dewaxed and water-extracted rye straw.

2.2. Alkaline peroxide treatment

The dried powder was first extracted with toluene–ethanol (2:1, v/v) in a Soxhlet for 6 h. The dewaxed straw was then treated with water at 50°C for 2 h. After isolation of the water-soluble hemicelluloses by precipitation of water-extracts in three volumes ethanol, water-soluble lignin fraction was obtained by reprecipitation at pH 1.5, adjusted by 10% HCl, from the supernatant solution. Samples free of wax and water solubles (10.0 g) were added to 250 ml of distilled water containing 2% H_2O_2 (w/v) in a jacketed reaction vessel heated with water from a thermostat-controlled circulating bath. The suspension was adjusted to pH 11.5 with 4 M NaOH and allowed to stir gently for 12 h at 20, 30, 40, 50, 60, and 70°C, respectively. In comparison, one sample was treated with dilute alkaline solution at pH 11.5 for 12 h at 50°C in the absence of H_2O_2 from water-soluble free and dewaxed rye straw. During initial stages of stirring, oxygen evolution was active, and substantial frothing occurred, requiring that extractions were conducted in vessels with volumes two to three times those of extraction mixtures. No further adjustments in pH were made during the course of the treatment. Under these conditions, the reaction pH remained nearly constant for 2 h before slowly rising to a final value of ca 13.0. The insoluble residue was collected by filtration, washed with distilled water until the pH of the filtrate was neutral, and then dried at 60°C. The supernatant fluid was adjusted to pH 5.5 with 10% HCl and then concentrated. The released hemicelluloses were precipitated by pouring the concentrated supernatant fluid into three volumes of ethanol. The solubilized lignins were obtained from the corresponding supernatants as the method above (Fig. 1).

2.3. Characterisation of the lignin fractions PL

FT-IR spectra were obtained on a FT-IR spectrophotometer (Nicolet, 750) using a KBr disc containing 1% finely ground samples. The solution-state ^{13}C-NMR spectrum was obtained on a Bruker 250 AC spectrometer operating in the FT mode at 62.4 MHz under total proton decoupled