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Steam explosion lignins; their extraction, structure and potential as feedstock for biodiesel and chemicals

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ABSTRACT

In the present study, a steam explosion wood pre-treatment process, optimized earlier with respect to ethanol production, has been applied to both softwoods (*Picea abies* and *Pinus sylvestris*) and hardwoods (*Betula verrucosa* and *Populus tremula*). The alkaline extractable lignins have then been isolated to investigate lignin separation efficiency and lignin structure and to evaluate their potential for producing value-added products, such as biodiesel components or chemicals, in terms of the purity, molecular size, functional groups, β-*O*-4′ inter-unit linkage content, and degradability in a subsequent processing treatment. The mechanism of lignin modification and possible improvements to the steam explosion pre-treatment process are discussed.

1. Introduction

The biomass-to-ethanol process has been considered as one of the potential solutions for the worldwide need for environmentally sustainable energy resources. The major steps in the process are the hydrolysis and fermentation of carbohydrates, normally with the defibration of wood as the first step. Among the alternative processes for this defibration, steam explosion is considered to be one of the most important. Its attractive features, in comparison to autohydrolysis, pulping, and other methods, include the potential for significantly reducing the environmental impact, the investment costs, and the energy consumption (Avellar and Glasser, 1998). A process applying steam explosion to facilitate the subsequent enzymatic/acidic hydrolysis and fermentation has been presented by several researchers (Palmqvist et al., 1996; Stenberg et al., 1998; Soederstroem et al., 2004). Steam explosion, together with an SO_2 pre-impregnation, has been optimized for the ethanol yield from softwood (Soederstroem et al., 2004).

The production of ethanol is, however, not economically competitive without an effective application of the lignin components in the raw material. Use of the lignin as a biofuel is one solution, while further lignin conversion with formation of useful chemicals, e.g. phenols, and/or biodiesel components, can be of further value. In the latter cases, a homogeneous mixture of low molecular mass products would be desirable, preferably via a direct isolation of lignin from the process, and an efficient degradation of the isolated lignin could be applied. At present, however, there is a large heterogeneity in terms of purity and chemical structures in lignins resulting from the steam explosion process, as well as in most of the other technical lignins. Moreover, there is not a general protocol available for the judgment of lignin degradability and the potential for fragmentation reactions.

The present work aims at establishing an analytical protocol by which the chemical changes and their influence on the structure heterogeneity and degradability can be identified for steam explosion lignins from various wood species, after applying different conditions in the process. Therefore, Norway spruce, Scots pine, birch, and aspen wood chips were subjected to the steam explosion process by applying conditions similar to the optimal conditions reported in the literature for ethanol production (Soederstroem et al., 2004). On all samples, the portion of lignin extractable with aqueous alkali solution was further quantified and characterized by a comprehensive set of analytical methods, including TGA, SEC, FTIR, UV, ^{13}C,^{13}C–^{1}H 2D HSQC and ^{31}P NMR, and thioacidolysis followed by GC and SEC. Milled wood lignin from corresponding wood species was analyzed for comparison. It is expected that the lignin potential for direct application or for further processing is closely related to its purity, molecular size and distribution, and the amounts of different chemical functional groups. Thioacidolysis-GC and thioacidolysis-SEC analysis could illustrate the degradability into monomeric or dimeric aromatic or phenol products.

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2. Methods

2.1. Raw material

Fresh and chipped Norway spruce (*Picea abies*), Scots pine *(Pinus sylvestris*), birch (*Betula verrucosa*), and aspen (*Populus tremula*) were provided by several Norwegian companies. The wood chips were screened to a chip size between 3–13 mm (pine), 7–13 mm (aspen and birch), or 13–45 mm (spruce) before use.

2.2. Steam explosion

The workflow procedures shown in Fig. 1 were followed after a steam impregnation performed with 2e + 5 Pa steam for 30 min. The SO_2 impregnation was performed at room temperature by introducing SO_2 gas to reach the designed charge (Table 1), and maintaining it in the sample for 30 min before ventilating out the gas. The steam explosion was carried out at the conditions shown in Table 1, using equipment consisting of a 10-L pressure vessel and a flash tank to collect the steam-exploded materials as described in detail in the literature (Stenberg et al., 1998).

2.3. Alkaline extractable lignin and extracted steam-exploded fibers

As shown in Fig. 2, the steam-exploded fibers were subjected to an alkaline extraction by 1.5 mol/L NaOH at 70 °C for 120 min in a wood to liquid ratio of 1:10. This was followed by filtration. The solid residues were then washed to neutral pH and dried to obtain the extracted steam-exploded fibers for further analysis. The liquid was neutralized to pH 4 by addition of sulphuric acid, and the precipitates were isolated by filtration followed by drying at 40 °C to obtain the alkaline extractable lignins.

2.4. Analyses

The ash content was determined after burning the lignin under oxygen (50 mL/min) using Thermogravimetric Analysis (TGA) equipment at a temperature range from 40 °C to 800 °C and then maintaining the sample at 800 °C for 15 min.

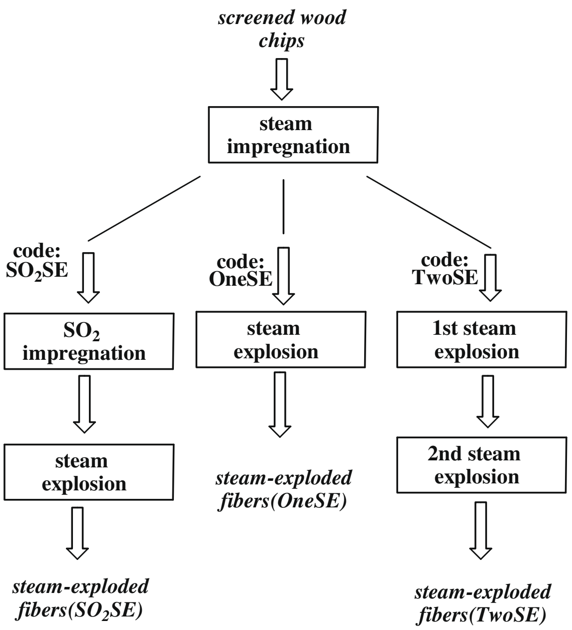

Fig. 1. Steam explosion workflow procedures.

Quantitative ^{13}C and ^{13}C–^{1}H 2-Dimensional Heteronuclear Single Quantum Coherence (2D HSQC) NMR spectra of lignin dissolved in acetone-d_6-D_2O (5:1) were recorded on a Bruker Avance 400 MHz instrument using the standard Bruker pulse programs (Zhang and Gellerstedt, 2007).

^{31}P NMR was performed as described in the literature (Granata and Argyropoulos, 1995) with a delay time of 10 s.

The UV spectra were recorded using dioxane:water 9:1 as a solvent. The FTIR spectra were recorded by applying an Attenuated Total Reflectance (ATR) crystal.

Thioacidolysis was performed according to the literature (Rolando et al., 1992).

Size Exclusion Chromatography (SEC) analysis of the lignin samples before and after thioacidolysis was carried out after acetylation (prepared according to the literature (Gellerstedt, 1992)) using three (HR4 + HR2 + HR0.5) Styragel columns (7.8 × 300 mm each) coupled in series with THF as the mobile phase, and using UV-detection at 280 nm. The SEC calibration was performed with commercial polystyrene standards, having M_w between 580 and 210,500 Da.

GC analysis was performed at an Rtx 5 column obtained from the Restec Corporation (45 m, 0.32 μm I.D., 0.25 μm film thickness) with a temperature program of 180 °C/0 min to 270 °C/15 min, and then to 300 °C/5 min at a rate of 4 °C/min. The injector and detector temperatures were 250 °C and 280 °C, respectively, with helium as the carrier gas in a constant flow mode with a split injection.

The lignin content, carbohydrate analysis, and extractives content (by acetone) were determined according to the Tappi standards, T222 om-88, T249 cm-85, and T204 om-88, respectively.

The kappa number of lignin with a pre-dissolution of lignin in a small amount of dioxane (5 mL) was determined automatically by using a "Kappamat" instrument according to the ISO 302 method.

3. Results and discussion

Generally, softwoods are more difficult to defiber by steam explosion than hardwoods. A pre-impregnation of SO_2 was found to be necessary in aiding this process. A maximum ethanol yield could be achieved by a steam explosion at 215 °C for 5 min in combination with a 30 min SO_2 pre-impregnation (Soederstroem et al., 2004). In order to study lignin as a by-product for value-addition to a biomass-to-ethanol process, this optimal combination (process code SO_2SE) was followed (Fig. 1 and Table 1) for testing two softwood species, Norway spruce and Scots pine. A slightly lower temperature (205 °C) was conducted for two hardwoods, birch and aspen, since they were more easily defibered. To investigate the effects resulting from SO_2, steam explosion without SO_2 impregnation (code OneSE) was performed at a higher temperature, 225 °C and 210 °C for the softwoods and hardwoods, respectively. For the hardwoods, the treatment time was also increased to 10 min to better suit the low temperature (Table 1). Since a two-step steam explosion was found to give a higher ethanol yield than a one-step treatment (Soederstroem et al., 2004), a two-step steam explosion process (code TwoSE) was applied for the two softwoods (Fig. 1 and Table 1). To compare different steam explosion conditions, a severity factor (R_0) as suggested by Overend and Chornet (1987), which is calculated based on the temperature and retention time of the treatment, is also listed in Table 1. However, the usefulness of this factor was found to be rather limited when a steam explosion was performed after SO_2 impregnation, or with other types of pH adjustments, since the effects of acidity were not included in the calculation.

After steam explosions, an alkaline extraction was performed, applying much milder conditions than an ordinary alkaline delignification (cooking) in order to avoid severe chemical structure alternations by the latter. The latter is also considered not desirable