



Lignins from enzymatic hydrolysis and alkaline extraction of steam refined poplar wood: Utilization in lignin-phenol-formaldehyde resins



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ABSTRACT

In this study, a steam refining process, optimized earlier with respect to carbohydrate yield, was used to extract lignins from non-debarked poplar wood from short growth plantations by enzymatic hydrolysis (EHL) and alkaline extraction (AEL) for the utilization in lignin-phenol-formaldehyde resins (LPF). Three different pretreatment conditions were chosen at 190 °C and 16 min, 210 °C and 15 min and 200 °C, 15 min, 2.5% SO₂. Characterization of the lignins revealed that the carbohydrate content decreased about 47% (210 °C, 15 min) to 58% (200 °C, 15 min, 2.5% SO₂) with intensification of the pretreatment conditions. Furthermore, the average molecular weight and polydispersity increased. The chemical and physico-chemical properties of lignin-phenol-formaldehyde resins synthesized with these lignins were evaluated and gluebond performance was tested by the Automated Bonding Evaluation System (ABES). LPF resins with AEL and EHL (190 °C, 16 min) were used to produce particleboards. LPF resins with Organosolv lignin (OL) and Kraft lignin as well as neat PF resins served as references. The mechanical properties of these panels were evaluated. The results showed high dry (EHL: 0.64 N mm⁻², AEL: 0.73 N mm⁻²) and wet internal bond strength (EHL: 0.21 N mm⁻², AEL: 0.25 N mm⁻²) of LPF bonded particleboards. LPF resin with AEL fulfills the requirements for the relevant standard specifications P7 according to DIN EN 312:2010-12.

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1. Introduction

The generation of ethanol and other platform chemicals via fermentation of carbohydrates from lignocellulosic materials is an alternative to fossil feedstocks. One way to convert the cellulose and hemicelluloses of biomass to monomeric sugars is a steam pretreatment of the wooden material and subsequent enzymatic hydrolysis of the carbohydrates. An impregnation of the feedstock with acidic catalysts (e.g. H₂SO₄, SO₂) lead to higher carbohydrate yields (Sassner et al., 2005). Between steaming and enzymatic hydrolysis an alkaline extraction of lignin can be performed. The main advantage of this extraction is not an improved saccharification but a higher lignin purity, at least at high severity of steaming (Schütt et al., 2011).

After steam pretreatment of lignocellulosic material and enzymatic hydrolysis of the fibers, lignin remains as a valuable residue of this process. Ragauskas et al. (2014) estimated the annual amount of lignin incurring from an industrial cellulosic ethanol plant at 100,000 to 200,000 tons. Due to the high heating value of lignin,

combustion of the residues for energy recovery is a common and obvious possible use. However, a high value material utilization of the lignin is desirable to reduce the cost and keep steam pretreatment a competitive process (Doherty et al., 2011).

A prominent application for technical lignins are thermosetting polymers. Due to the chemical structure, lignin is supposed to be suitable for substitution of phenol in PF resins (Ghaffar and Fan, 2014). However, reports about the utilization of enzymatic hydrolysis and alkaline extracted lignins after steam refining for application in PF resins are limited. Gravitis et al. (2010) used lignin from steam exploded hardwood to produce self-binding fiberboards. They also mixed up to 10 wt% of the lignin with commercial phenol-formaldehyde resin. This mixture was used as a binder to manufacture plywood. The produced fibreboards showed improved form stability and the mechanical properties of the plywood were not negatively influenced by the addition of lignin. Jin et al. (2010) used cornstalk residues from bioethanol production to obtain lignin by alkaline extraction and modified phenol-formaldehyde adhesives. In contrast to the work of Gravitis et al. (2010) they used lignin as a copolymer for the preparation of LPF-resins. They replaced up to 20 wt% of phenol by lignin and varied the NaOH content. Qiao et al. (2015) replaced even up to 50 wt% of phenol in PF-resins by enzymatic hydrolysis lignin. Both, Jin

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et al. (2010) and Qiao et al. (2015) determined improved mechanical properties of the plywood bonded with their resins. However, both observed rising contents of free formaldehyde with increasing phenol substitution rate.

Recently, Schütt et al. (2011) optimized the steam pretreatment conditions for steam refining and enzymatic hydrolysis of non-debarked poplar wood with regard to the highest carbohydrate yield. Furthermore, Schütt et al. (2013) compared the optimal process conditions for steaming with and without SO₂. The technological less complex steam refining process was compared with steam explosion and no substantial differences could be found (Schütt et al., 2012). The authors investigated as well the alkaline extraction of lignin from steam pretreated fibers on the overall process balance. This extraction had no positive effect on the optimal saccharification yield based on wood. However, at high severity in steaming the alkaline extracted lignin exhibited high purity. Up to now, the suitability of the lignins incurring as byproducts of the steam refining processes are not investigated with regard to material utilization.

Therefore, in this study lignins were isolated via enzymatic hydrolysis and alkaline extraction after steam treatment of non debarked poplar wood. The chosen steaming parameters with and without SO₂ were formerly found to be the optimal conditions regarding the carbohydrate yield (Schütt et al., 2013). Furthermore, a lignin sample obtained after mild steam pretreatment is included. A hardwood organosolv lignin (OL) and a softwood Kraft lignin (KL) were investigated as references. All samples were subsequently used as a copolymer in PF formulations. The lignins were characterized and the chemical and physico-chemical properties of the LPF resins synthesized with these lignins were evaluated. The gluebond performance was examined by an Automated Bonding Evaluation System (ABES). Furthermore, a lignin obtained from enzymatic hydrolysis and an alkaline extracted lignin after mild steam pretreatment were used to produce particleboards. The mechanical properties of these panels were evaluated and compared to particleboards bonded by neat PF resin, organosolv- and Kraft-LPF resins.

2. Materials and methods

2.1. Lignin isolation

The enzymatic hydrolysis lignins (EHL) and alkaline extracted lignins (AEL) were recovered from non-debarked poplar wood (*Populus balsamifera*) after steam refining. The steaming conditions were based on the findings of Schütt et al. (2011, 2013). The severity factor ($\log R_0$) was calculated according to Overend and Chornet (1987) as:

$$\log R_0 = e^{T-100/14.75} \times t$$

combining the duration of the treatment (t , min) and the temperature (T , °C). Steam pretreatment were performed at 190 °C, 16 min (SF 4; $\log R_0 = 4$), 210 °C, 15 min (Opt, $\log R_0 = 1.4$) and 200 °C, 15 min, 2.5% SO₂ (Opt/SO₂, $\log R_0 = 2.22$). Lignin recovery was also described by Schütt et al. (2011, 2013). Organosolv lignin (OL) was recovered from beech wood after pulping with ethanol/water at 170 °C for 90 min with 0.5% H₂SO₄ (based on dry wood). The lignins were isolated by filtration after water-induced precipitation. The Kraft lignin used was Curan 100, acquired from Borregard LignoTech.

2.2. Lignin characterization

Methoxy group content was determined according to the Vieböck and Schwappach method (Vieböck and Schwappach,

1930). The elemental composition of the lignins were analyzed with a Thermoquest elemental analyser EA 1112 at 900 °C purged with helium at 140 ml/min and oxygen at 100 ml/min. The protein content was calculated according to Robert et al. (1984) by the following equation:

$$\text{protein content}[\%] = N \times 6.25$$

with N as the nitrogen content of the lignin.

Mannich reaction was performed as described by Pan and Yoshihiro (1999). Results were corrected for carbohydrate and ash content.

The determination of the carbohydrate content in the hydrolysates was performed by borate-anion-exchange-chromatography as described by Schütt et al. (2011).

The hydroxyl group quantification was performed by ³¹P NMR spectroscopy using a Varian Mercury 400 MHz spectrometer according to the method of Granata and Argyropoulos (1995). The lignin samples were phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP). During acquisition 264 scans were accumulated at 25 °C with a pulse angle of 45° and a relaxation delay of 20 s.

Molecular weight distribution was analyzed by size-exclusion-chromatography. The separation was performed by two PolarGel-M columns (300 × 7.5 mm) in series and a PolarGel-M guard column (50 × 7.5 mm). Dimethyl sulfoxide (DMSO) with 0.1% LiBr was used as eluent. Before injection, samples and solvent were filtered using regenerated cellulose (Chromafil RC-45, Macherey-Nagel, 0.45 μm). The columns were calibrated with glucose and polyethylene glycol (180–82,250 g mol⁻¹, Agilent) as standard. Quantitative analyses were performed by refractive index (RI) detection and ultraviolet (UV) detection at 280 nm.

2.3. Resin synthesis

The lignins were used as replacement for phenol during resin synthesis (LPF-resins). In all resins the phenol substitution level was 20% (w/w). The formaldehyde to phenol molar ratio of the synthesized PF and LPF resins was 2. The sodium hydroxide to phenol molar ratio was set 0.4. In general, the synthesis was stopped when viscosity of the resin reached 400 mPa s–600 mPa s by rapid cooling and by final addition of NaOH. Prior to application to wood, potassium carbonate solution (K₂CO₃, 3% solid content based on total resin) was added.

2.4. Resin characterization

Bonding quality of the resins was tested using the Automated Bonding Evaluation System (ABES). Two veneer strips (*Acer saccharum* Marsh.) with a thickness of 0.6 mm (± 0.05 mm) and dimensions of 20 mm by 117 mm were bonded for a defined range of time under controlled conditions with a hydraulic press. After pressing, the glue bond was tested instantly by a tensile shear stress until failure. The amount of adhesive was 11.2 μl and was applied with an electronic pipette. The specimens were stored at 20 °C and 65% relative humidity (RH) before testing. Press temperature was 105 °C and the bond forming times ranged from 30 s to 420 s. For each time range, five replications were conducted.

Investigation on the influence of elevated carbohydrate contents in resin formulations on the wood bonding quality measured by the ABES was investigated by adding 30 wt% of microcrystalline cellulose (AviCel®) to LPF resin formulation (Kraft lignin). 5 g of KLPF resin (solid content 42.3%) was mixed with 0.13 g of microcrystalline cellulose (based on lignin in resin formulation) by mechanical stirring at room temperature until a homogenous solution was formed.

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