



Isolation of high quality lignin as a by-product from ammonia percolation pretreatment of poplar wood



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HIGHLIGHTS

- Isolation of significant amount of pure poplar lignin using ammonia pretreatment.
- Limited condensation of the soluble lignin through using percolation mode.
- Homolytic cleavage of lignin β -O-4 bonds favoured at low ammonia concentration.
- Nitrogen incorporation increased with increasing cleavage of lignin β -O-4 bonds.
- Lignin recovery decreased with increasing nitrogen incorporation.

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ABSTRACT

A two-step process combining percolation-mode ammonia pretreatment of poplar sawdust with mild organosolv purification of the extracted lignin produced high quality, high purity lignin in up to 31% yield and 50% recovery. The uncondensed fraction of the isolated lignin was up to 34%, close to that the native lignin (40%). Less lignin was recovered after pretreatment in batch mode, apparently due to condensation during the longer residence time of the solubilised lignin at elevated temperature. The lignin recovery was directly correlated with its molecular weight and its nitrogen content. Low nitrogen incorporation, observed at high ammonia concentration, may be explained by limited homolytic cleavage of β -O-4 bonds. Ammonia concentrations from 15% to 25% (w/w) gave similar results in terms of lignin structure, yield and recovery.

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1. Introduction

The pretreatment step, in which lignin is dissociated from cellulose, is the key to economic conversion of lignocellulosic biomass to liquid biofuel (Agbor et al., 2011). The most important factor in the choice of pretreatment technology is therefore how efficiently the lignin is solubilised or otherwise rendered innocuous towards the enzymatic depolymerisation of cellulose. However it is widely agreed that the economic viability of biofuel production will depend on adding value to the by-products, including lignin. Efficient solubilisation will then improve the yield of both the primary fuel product and the lignin as a secondary product, but it is necessary to ensure that the quality of the lignin is not degraded.

The best prospects for adding value to lignin are through its conversion to aromatic fine chemicals by controlled depolymerisation (Bozell et al., 2007; Zakzeski et al., 2011). The quality of the

isolated lignin can then be defined in terms of its structural suitability for depolymerisation. Recent research on lignin model compounds has suggested that lignin should be efficiently broken down into low molecular weight compounds if the starting material contains a high proportion of alkyl–aryl ether (β -O-4) bonds (Parsell et al., 2013). This bond accounts for up to 60% of the *in situ* linkages in hardwood lignins. Lignins also contain more stable carbon–carbon (β -5, β - β , β -1 and 5–5) and diaryl ether (4-O-5) bonds (Ralph et al., 2004), and are termed condensed if the carbon–carbon bonds are abundant and the polymer structure is heavily cross-linked.

For efficient delignification it is necessary, although not sufficient, to maximise the aryl–ether linkages that are broken (Pan et al., 2006). Unfortunately, severe thermal conditions, required in wood pretreatment, increase the degree of condensation, leading to lignin that is harder to break down (Choi and Faix, 2010; Li et al., 2007). For example the well-established organosolv process has proved to be efficient for hardwood delignification and the isolated lignin, with low molecular weight and high phenolic

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hydroxyl content, has interesting anti-oxidant properties, but high temperature and acidity led to significant structural alteration, including loss of the γ -methylol group and increased condensation (El Hage et al., 2010; Pan et al., 2006), reducing its suitability for conversion to fine chemicals.

The experiments on poplar wood that we describe here were focused on the optimisation of the pretreatment step to combine minimal chemical alteration of the solubilised lignin with high cellulose digestibility in the residue. Ammonia pretreatments are known to increase cellulose digestibility while avoiding condensation of the lignin (Yoon et al., 1995). The efficiency of ammonia-based pretreatments (Ammonia Fibre Expansion, Soaking Aqueous Ammonia, Ammonia Recycling Percolation) for biofuel production has been extensively studied (Bals et al., 2011; Gupta and Lee, 2009; Kim et al., 2003; Kumar et al., 2009), but few studies have considered the lignin structure after ammonia treatment (Chundawat et al., 2011; Liu et al., 2013). In a recent patent (Balan et al., 2013), lignin fractions were characterised after batch-mode ammonia extraction of corn Stover, and 2D NMR analysis of a fraction enriched in lignin showed that a moderate percentage of β -aryl ether linkages were preserved. AFEX pretreatment of corn stover at 130 °C, which retained the lignin in the residue, altered its structure only to a moderate extent (Chundawat et al., 2011). The mild temperatures (120–130 °C) used in the ammonia pretreatment of corn stover partially explained the limited structural alteration of the lignin. However in the case of hardwoods, higher temperatures (160–180 °C) are generally needed to produce residues suitable for enzymatic saccharification. Under these conditions the lignin will suffer more condensation. An interesting question is whether lignin is more vulnerable to condensation in its native, solid state or after solubilisation. If condensation occurs more readily when the lignin is soluble, then removing the solubilised lignin immediately by adopting a percolation mode should lead to less condensed lignin than with batch mode, where the lignin remains in solution at high temperature for longer. In this study poplar sawdust was subjected to both batch and percolation ammonia pretreatments to extract lignin. The extracted lignin was then purified by a very mild organosolv post-treatment to produce high purity, high quality lignin in excellent yield.

2. Methods

2.1. Materials

Hybrid poplar sawdust was provided by a UK sawmill. The sawdust was sieved and the particle size range from 125 μm to 1080 μm was used. The dry matter content of the sawdust was 92.6%. All reagents and solvents were purchased from Sigma-Aldrich and used without further purification.

The poplar sawdust was subjected to batch and percolation (continuous) ammonia pretreatments to extract lignin. Each extracted lignin was then purified by mild organosolv post-treatment (see Section 2.3) to produce an ethanol-soluble, purified lignin after precipitation in water. The multistep process is illustrated in Fig. 1.

2.2. Ammonia extraction of poplar lignin

2.2.1. Batch mode

A stainless steel reactor (75 ml) was packed with 5–6 g of poplar sawdust. The reactor was filled with 15% (w/w) aqueous NH_3 (60 ml) and soaked for 2 h at 40 °C. The pressure was then increased to 20 bar and the temperature was raised to the cooking temperature at 25 °C/min. The cooking temperature was held for 120 min, then dropped to 80 °C in order to flush the reactor with

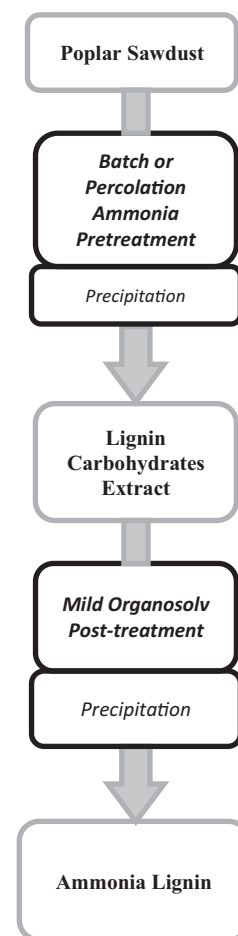


Fig. 1. Global flow-chart for ammonia lignin isolation from poplar sawdust.

nitrogen. The residue was washed twice with water at 80 °C. The residue was transferred to a sealed bag and weighed. Aliquots were taken for measurement of moisture and lignin content (2×2 g). The extracted lignin was recovered by precipitation in water.

2.2.2. Percolation mode

The percolation device, inspired by previous works, is illustrated in Fig. 2 (Kim et al., 2009). The stainless steel reactor (75 ml) was packed with 18–19 g of poplar sawdust, filled with 15% (w/w) aqueous NH_3 (40 ml) and soaked for 1 h at 40 °C. The pressure was increased to 20 Bar and the temperature was raised to the cooking temperature at 25 °C/min. Once the temperature of the oven reached 180 °C, more liquid extractant was percolated through the reaction vessel at 3 ml/min for 90 min. Deionised water was then percolated at 5 ml/min for 40 min, after which the temperature was reduced to 60 °C before flushing the reactor with nitrogen. The residue was transferred to a sealed bag and weighed. Aliquots were taken for measurement of moisture and lignin content (2×2 g). The extracted lignin was recovered by precipitation in water.

2.2.3. Extracted lignin recovery

The liquor was reduced in pH to 7–8 by evaporation of the ammonia and then acidified to pH 2 (HCl 2 M). After leaving overnight at 4 °C, the precipitate was recovered by centrifugation, washed three times with HCl at pH 2 and freeze dried.

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