

# Phenols and aromatics from fast pyrolysis of variously prepared lignins from hard- and softwoods



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## ABSTRACT

This study reveals that catalytic and non-catalytic fast pyrolysis of lignin is influenced by the lignin separation method. Lignin of the same soft- and hardwood source was prepared by the Dioxane-, Klason- and Organsolv-methods and pyrolyzed at different temperatures using H-USY zeolite. The product selectivity demonstrated temperature dependence, changing from phenol alkoxy ketone products to phenols at high temperatures. Hardwoods produced more monophenols with carbonyl groups, and softwoods generated more phenols at high temperature. Relative yields and selectivities varied between each lignin type. The yield in liquid products and gases depends on the overall bond structure in the lignin. The presence of aryl ether bonds increases the conversion above 600 °C, but has the inverse effect at lower temperatures. High selectivity for one group of products could be achieved under optimized conditions. Commercial Kraft lignin demonstrated the smallest change in yield and selectivity with temperature.

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## 1. Introduction

Lignocellulosic biomass is the only renewable resource for carbon-based chemicals. It consists of 35–45% cellulose, 25–30% hemicellulose and 20–35% lignin, which is the third-most-abundant polymeric structure [1]. Today, lignin is generally considered a waste material with no practical industrial application except for energy production by direct incineration [3,4]. In contrast to cellulose and hemicellulose, lignin is a highly irregular polymer based on the three basic, phenolic building blocks, *p*-coumaryl (H-unit), synapyl (S-unit) and coniferyl (G-unit), as shown in Fig. 1. Selective abstraction of desired aromatic and phenolic products from lignin would constitute a renewable resource for these valuable chemicals. However, lignin's complexity and structural variety make it difficult to use and study [5]. The exact structure of lignin is not precisely known and depends largely on the bio-resource [6,7] and separation method utilized [8]. Wood, especially softwood, contains a very high amount of lignin compared to grass and other non-woody biomass [9]. Notably, the relative amount of building blocks differs between the lignins. Hardwood lignins contain up to 70% syringyl (S-units), whereas softwoods consist of 85–100% coniferyl (guaiacol-, G-units) [10].

*P*-coumaryl and H-units only make up a minor fraction in lignin. (Fig. 1)

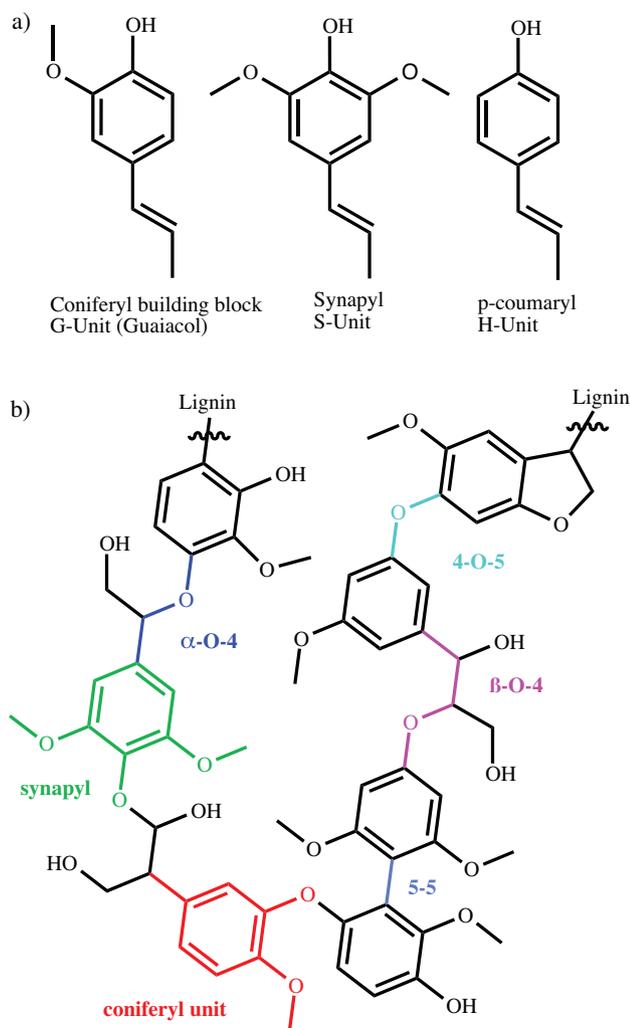
Since the lignin polymer is chemically bound to the hemicellulose, its separation has to occur chemically. There are several separation methods that result in differently structured lignins [7]. The “Kraft” method is the most common in the paper and pulp industry. Kraft separation, steam explosion and other dilute acid hydrolysis separation methods focus on the liberation of cellulose rather than on the quality of the obtained lignin [11]. Whereas other lignin separation methods, such as Organosolv, attain larger yields of high quality lignin. For example, the resulting lignin may have a structure resembling the original one but with a lower sulfur content.

In this study, hardwood and softwood lignins of the same biore-source were prepared by various preparation routes and tested in catalytic fast pyrolysis to determine the influence of the lignin separation methods on the pyrolysis product yield [12].

Catalytic and non-catalytic pyrolysis are two of the most promising lignin conversion processes, which potentially can meet feasible process conditions for large-scale chemical production [5,13]. Other processes involve additional solvents and/or chemicals, thus requiring more complicated up- or down-stream treatment. This study is performed in a conventional pyrolysis microreactor connected to a GC/MS, thereby enabling rapid analysis of product distribution with high reproducibility. The wood specific S/G-ratio in the pyrolysis oil analyzed by Py-GC/MS represents well the S/G

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**Fig. 1.** Building blocks of lignin and a representative lignin structure depicting chemical bonds and functional groups important in pyrolysis processes.

ratio in the starting lignin [14]. Microreactor pyrolysis is widely used for structural analysis of commercial polymers [15] and more recently for biomass pyrolysis [1,3]. Previous studies with commercial Kraft lignin showed that a very fast heating rate (20 °C/ms) at 650 °C yield the highest amount of monophenols [16]. Zeolites are effective catalysts for oxygen removal and aromatic formation [17]. Porous systems without any Brønsted or Lewis acid sites (silicalites) could stabilize intermediates and increased yield in monomers. Introduction of acid sites enhances deoxygenation and aromatization reactions so that high yield in aromatics, such as benzene, toluene and xylenes are favored. H-USY in particular has proven to be a highly active catalyst as a result of its relatively large micropores, high acidity, and minimal coking [16,18]. However, deactivation of the H-USY zeolite during catalytic fast pyrolysis is irreversible because its acid sites cannot be regenerated after the reaction [19]. Transition metal dopants such as cobalt and nickel increase a zeolites catalytic activity in deoxygenation reactions, but simultaneously enhance coke formation [20]. Intermediate stabilization is a critical step in this process and requires improvement so as to inhibit coke and char formation. Thus major radicals and their reaction pathways have been determined temperature dependently. We found that rearrangement and decomposition of the formed intermediate depends on the concentration and the stability of the radical [21]. Previous studies employing in situ EPR

measurement have shown that hard- and softwood lignins react to pyrolysis conditions differently with respect to both radical formation and stabilization. Hardwood forms radicals faster and demonstrates less recombination [12].

To determine the influence of the separation method upon the resulting lignin and its structure, Organosolv-, Klason-, and Dioxane-separated lignins from the same hard- and softwoods were tested. In addition, commercial alkali lignin (Kraft) from softwood was used. Commercial and Klason lignin are both treated with concentrated sulfuric acid, while Organosolv and Dioxane lignin are treated with diluted sulfuric or hydrochloric acid and organic solvents. The solvent/acid residues in the lignin samples arise due to the high boiling points of these impurities and their incorporation into the lignin structure. Sulfide ions are crucial in the commercial delignification of wood, where they promote high yields and initiate the cleavage of aryl-ether bonds that neighbor  $\beta$ -carbons [22]. Dissolution of undesired lignin is specific to each pulping process. In sulfite pulping (Klason process) most of the cellulose is preserved, while the alkali process xylan shows high stability towards alkali. The alkali separation process increases the tensile strength of the resulting product and decreases the lignin yield. Due to the structural differences of the lignin samples, it may be expected that each extracted lignin will show a different temperature dependent reactivity and product selectivity at different optimal conditions.

## 2. Materials and methods

### 2.1. Lignin samples and preparation

#### 2.1.1. Commercial lignin/Kraft lignin

Commercial lignin (TCI Europe) is produced by soda delignification followed by acidification with sulfuric acid [7]. This process uses large amounts of sodium hydroxide and sodium sulfide. Treatment at high pH value results in cleavage of the  $\alpha$ -aryl and  $\beta$ -aryl ether bonds in the first stage and to C–C bond formation in the last stage. Whether these C–C bonds exist originally in the lignin or not is still debated [22], but their abundance increases dramatically during the pulping process. Commercial lignin is produced from a softwood, but its exact origin is not known.

#### 2.1.2. Klason lignin

Klason lignin is obtained by a two step hydrolysis treatment of the extracted wood with concentrated (72%) and diluted (3%) sulfuric acid. The concentrated H<sub>2</sub>SO<sub>4</sub> treatment is carried out at room temperature for an hour and diluted at 100 °C for 3 h, while the volume is kept constant by the continuous addition of water. The lignin is finally filtrated off and dried at 50 °C in a vacuum oven.

#### 2.1.3. Organosolv lignin

Extracted wood is suspended in 60 vol% ethanol with 5 wt.% sulfuric acid and then reacted at 200 °C in a microwave reactor for 55 min. The resulting liquor is filtered and washed with acetone. The filtrate is concentrated, precipitated and filtered with water and acetone to yield around 20 wt.% of Organosolv lignin based on the extracted wood [23].

#### 2.1.4. Dioxane lignin

Extractive free wood was treated with dioxane and 1 M HCl (9:1) under inert atmosphere for 2 h at 100 °C. The mixture was filtered and the filtrate was precipitated using a large excess of water and dried in vacuo to yield 6 wt.% of lignin (based on the initial quantity of wood).

#### 2.1.5. Wood extraction

The wood for Klason, Organosolv and Dioxane lignin has been before the described separation step by the following treatment.

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