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### Converting lignin to aromatics: step by step

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**Publication date**  
2014

[Link to publication](#)

#### **Citation for published version (APA):**

Strassberger, Z. I. (2014). *Converting lignin to aromatics: step by step*. [Thesis, fully internal, Universiteit van Amsterdam].

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## *Summary*

Lignin, the glue that holds trees together, is the most abundant natural resource of aromatics. In that respect, it is a far more advanced resource than crude oil. This is because lignin already contains the aromatic functional groups. Thus, catalytic conversion of lignin to high-value aromatics is environmentally attractive, but can also be an economically viable option. The aim of this PhD thesis is to understand the fundamentals of lignin depolymerization reactions through the study of monomeric and dimeric model compounds and then move towards the actual lignin as feedstock. The latter was used for a solubilisation and fractionation study using an unconventional solvent, liquid ammonia. The main reactions envisaged are demethylation and hydrodeoxygenation leading to aromatic building blocks such as benzene, toluene and xylene (BTX) and phenol using heterogeneous catalysts.

**Chapter 1** discusses the potential short- and long-term applications of lignin. The isolation of different lignin streams will become more and more available in the near future thanks to improvement in the field of biomass separation processes. Hemicellulose and cellulose upgrading to high-value chemicals is already present in a commercial scale applications, but lignin has not yet reached this level. However, its valorisation to aromatic platform chemicals could become economically interesting in the near future. We present different scenarios where the application of lignin varies from fuel to BTX production and polymer applications.

A general overview of lignin catalytic depolymerization research is provided in **chapter 2**. Catalytic reduction and oxidation are presented, covering different studies from conventional catalysts to noble metal supported catalysts. The development and improvement of selective catalytic reactions, such as hydrodeoxygenation, are fundamental to enhance the catalytic valorisation of lignin towards high value aromatics.

Methoxy groups are one of the most abundant functional groups in the lignin structure. Therefore, the study of a simple model compounds such as anisole (methoxy benzene) was the first field of investigation in this thesis. Demethylation/dealkylation

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reactions are known to require acidic sites to increase the substrate adsorption, but the addition of basic sites can enhance the selectivity toward demethylation and hydrodeoxygenation. With this in mind, we investigated in **chapter 3** the selectivity of phenol in the dealkylation reaction of anisole and phenetole over several alumina and magnesium mixed oxide catalysts which had different MgO:Al<sub>2</sub>O<sub>3</sub> ratio. A set of five magnesia-alumina mixed oxides were screened in the dealkylation of alkyl phenyl ethers (R–O–Ph) as lignin model compounds. Interestingly, the more basic the catalyst, the higher the selectivity to phenol. The results concur with the formation of phenoxide PhO<sup>-</sup> and CH<sub>3</sub><sup>+</sup> fragments on the catalyst surface. These can then react than with H<sup>+</sup> and H<sup>-</sup> species formed by the heterolytic dissociation of hydrogen on the MgO surface, giving phenol and hydrocarbons. Nevertheless, above 60% of MgO content, the conversion drops considerably due to substrate adsorption on acidic sites.

Lignin polymer structure is mostly defined by β–O–4 linkages. Therefore, we focused on finding a catalytic alternative that can cleave selectively this bond and then hydrodeoxygenate the smaller fractions obtained to target molecules such as phenol and BTX. We first synthesised two model compounds mimicking the β–O–4 linkage and synthesised catalysts active in hydrodeoxygenation reaction. We show in **chapter 4** that copper-based catalysts are suitable and active catalysts towards hydrodeoxygenation (HDO). Copper on γ-alumina and on mixed magnesia/alumina catalyse HDO of β–O–4 lignin-type dimers, giving valuable aromatics like phenol and ethylbenzene. The typical selectivity to phenol is as high as 20%. By changing the support's acidity we can modify the dispersion of copper. Interestingly, more HDO occurs with larger copper agglomerates than with finely dispersed particles. Three different pathways are hypothesized for the reaction on the catalyst surface; (i) cleavage at the C–O–aryl bond, (ii) cleavage of the OC–CH<sub>2</sub>O(aryl) bond and followed by (iii) hydrodeoxygenation. Introducing basic sites on the support hinders HDO and the selectivity to ethylbenzene drops considerably. Thus, copper activates ketones more and especially more selective towards cleavage than their corresponding alcohols. DFT calculations of bond dissociation energies correlate well with this experimental observation. Excitingly, ethylbenzene is formed in proportional amounts to phenol, showing that these catalysts can reduce the oxygen content of lignin-type product streams. Considering its low price

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and ready availability, we conclude that copper on alumina is a promising alternative catalyst for lignin depolymerization.

In **chapter 5**, we report the synthesis and characterization of new  $V_2O_5/Al_2O_3-MgO$  catalysts and their application in anisole deoxygenation, oxidative dehydrogenation and epoxidation reactions. The IR and UV-Vis spectra of these catalysts indicate the presence of monomeric vanadium species at 5 wt.%  $V_2O_5$  loading, along with small amounts of polymeric species at 10 and 15 wt.%  $V_2O_5$ . Electron paramagnetic resonance (EPR) spectroscopy reveals the presence of ferromagnetic  $VO^{2+}$  dimers following calcination at 773 K. The catalysts were then tested in three reactions: (i) anisole deoxygenation, (ii) gas phase oxidative dehydrogenation of *n*-butane under flow conditions at 773 K and (iii) liquid phase epoxidation of limonene with  $H_2O_2$ . The deoxygenation reaction with anisole showed no activity. The dehydrogenation reaction gave butenes and 1,3-butadiene in moderate selectivity at 8-10% conversion. The epoxidation of limonene yielded 50-70% selectivity to the 1,2-epoxide at 10-20% conversion.

After studying monomers and dimers, we moved on to the real lignin. The challenge of working with technical lignin is described in **chapter 6**. The standard conditions applied in the solubilisation of lignin encounters several disadvantages, e.g. alkaline salts saturation. We demonstrate that using liquid ammonia as a solvent, lignin can be solubilised under mild conditions. A special autoclave and setup were designed and constructed for this purpose (see **appendix**). We discuss the fundamental similarities and differences between ammonia and water, and show that using liquid ammonia helps overcome many of the drawbacks of water/acid or water/base solutions. Several analytical tools like SEC, elemental analysis and 2D NMR were used to understand the interaction between ammonia and the lignin polymer.