LIGNIN DEPOLYMERISATION UNDER SUPERCRITICAL PROCESS CONDITIONS FOR AROMATIC CHEMICALS PRODUCTION

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ABSTRACT

Valorisation of lignin plays a key role in the further development of biorefinery processes for biofuels and the production of biobased materials from lignocellulosic biomass. Today's increased demand for alternatives to fossil carbon based products, such as the production of transportation biofuels and bulk "green" chemicals, expands the interest and the need to create added value to the unconverted lignin fraction. As a consequence of its poly-aromatic structure, lignin is the obvious candidate to serve as a source for aromatic chemicals.

In this work organosolv hardwood lignin was converted in a mixture of super critical carbon dioxide, acetone and water (300 – 370°C, 100 bar) to aromatic monomeric compounds with a total yield of 10% based on dry lignin. Addition of formic acid increases the yield of aromatics from 7% to 10%. Main monomeric lignin derived products were 2,6-dimethoxyphenol, 4-hydroxy-3,5dimethoxybenzoic acid, 2-methoxy-4-methylphenol and 2-methoxyphenol. During this process a strong competition occurs between depolymerisation of lignin and recondensation of fragments. This leads to a residual lignin fraction representing 40% of the starting material consisting of a substantially reduced oxygen/carbon ratio and a similar structure to carbon black.

I. INTRODUCTION

Today's increased demand for alternatives to fossil carbon based products, such as the production of transportation biofuels and bulk "green" chemicals, expands the interest and the need to create added value to the unconverted lignin fraction. By far the most available bio-based feedstock that seems feasible for the preparation of aromatic (bulk) chemicals like phenol is lignin. Lignin is found in trees and other lignocellulosic plant-based materials representing 15-25% of its weight and about 40% of the biomass energy content.

In biorefinery processes, lignin will be produced in large quantities, additionally to lignin production in the paper and pulp industry, and can serve as a future aromatic resource for the production of green chemicals (Bozell et al. 2007).

Traditionally, the use of lignin has been as a fuel source in the pulp mills, component in binders, or additive in cement. However, due to its chemical nature, and in particular the presence of large amounts of aromatic structures, lignin may be an attractive raw material for the production of base aromatic chemicals, such as benzene, toluene, xylene and phenol, reducing CO_2 emission and the need for fossil resources.

Lignin conversion to phenolic monomers described in the literature starts from biomass including lignin or with extracted technical lignin. The latter has the important advantage that non-lignin components, like carbohydrates, have been removed to a large extent. Most lignin conversion processes have been studied at elevated temperatures 250 - 600°C, with and without catalysts, as reviewed by Zakzeski et al. (2010). These high-temperature processes for "cracking" of the lignin led to the formation of a phenolic complex mixture of polyhydroxylated and alkylated phenol compounds next to char and volatile components. This, of course, provides the challenge of further upgrading these mixtures to a higher content of phenol and of downstream processing in order to separate the phenolic-like compounds that are derived. The highest percentages of phenols reported (based on total lignin feed) are in the range of 5–10%. Here it seems a prerequisite that in addition to the production of phenols, outlets for all side products formed should be developed (Haveren van et al., 2007).

In this work development of a novel process for depolymerisation of lignin under supercritical conditions for aromatic chemicals production is described. Carbon dioxide was chosen because of its non-toxic character, its fluid behavior under supercritical conditions (>31°C, 74 bar) and its established industrial use, for example in decaffeination of coffee beans (Zosel, 1974) and dying of textile fibres. In this novel process the aromatic products were separated from residual lignin and char by adiabatic pressure release. Carbon dioxide based solvents consequently will lower the temperature in the solvent stream facilitating condensation of formed aromatics and leaving no solvent or salts in the obtained product mixture. So, downstream processing will become easier.

In the conversion of lignin into monomeric phenolics two main overall reactions strongly compete. These are depolymerisation and recondensation yielding a residual lignin char fraction. Although this char can represent a certain value as bio-char the main focus is to minimize the formation of this carbon residue. The use of H-donating solvents, such as formic acid, and other stabilizing compounds like alcohols diminish the formation of char (Kleinert et al., 2008, 2009). Because of the lignin solubility, in our work we used a mixture of acetone/water to dissolve lignin and pump this solution into a pre-heated reactor at elevated temperature. Formic acid was added to stimulate the stabilization of aromatic radicals.

II. EXPERIMENTAL

Mixed hardwoods organosolv lignin (Alcell[tm], Repap Technologies, Canada) was dissolved in acetone/water 8:2 (v/v) at 0.7 gram per 2 ml. 0.7 gram of lignin was pumped with acetone/water 8:2 (v/v) via an sample loop of 2 ml by a HPLC pump (Waters, model 515) into a pre-heated 100 ml Hastelloy PARR reactor (PARR Instruments Co., model 4590) at 300 – 370°C. After introduction of lignin in the pre-heated reactor, the pressure was adjusted to 100 bar with carbon dioxide by another pump (Isco, model 260D). Formic acid was introduced in the process via the same sample loop of 2 ml and subsequent pumping by the HPLC pump. In total 25 ml of solvent was used to pump lignin and catalyst into the pre-heated reactor.

Headspace sampling was performed by pressure release from 100 to 75 bar and capturing the products in 2 serial connected gas washing flasks filled with about 200 ml acetone. After 90 min pressure release was performed from 100 to 0 bar. At each sampling time fresh solvent acetone/water 8:2 (v/v) and CO_2 was added to adjust the pressure to 100 bar. Products were identified and quantified by GC-MS and GC-FID on a Restek RXI-5 column. Residual char was weight after drying at 50°C.

Residual char was analysed by FT-IR on an ATR crystal and by its elemental composition.

III. RESULTS AND DISCUSSION

After introduction of organosolv hardwood lignin into the pre-heated reactor at 300°C in a carbon dioxide/acetone/water solvent mixture some monomeric aromatic products have been formed as shown in figure 1 (1.8% on dry lignin). An uncatalysed treatment of lignin at 300°C yielded about 7% identified monomeric phenolic compounds based on dry lignin. A product spectrum with 17 identified aromatic compounds was found. 2,6-dimethoxyphenol, 4-hydroxy-3.5-dimethoxybenzoic acid, 2-methoxyphenol (guaiacol), 2-methoxy-4-methylphenol are the main products. These can be expected from a hardwood (SG) lignin.

Addition of 14% formic acid just before the first sampling point finally lead to a higher production of phenolics to a level of 10 wt%. Till 60 minutes a lag phase can be observed maybe due to a decreased solubility of lignin in the acidic solvent mixture. After that, a substantial increment in the production of monomeric phenols was observed resulting from the depolymerisation of lignin. Repeated addition of formic acid starting from 30 minutes does not lead to a higher yield compared to an uncatalysed supercritical treatment of lignin. In particular, after 60 minutes the production of monomeric phenols stopped. This is probably due to the strong acidic nature of the mixture in which the lignin and char are mostly insoluble.

Uncatalysed depolymerisation of lignin at 370°C results in a lower production of monomeric phenols (4%) and the char amount is higher compared to the treatment at 300°C (figure 2). Recondensation probably dominates the formation of stable monomeric phenols.
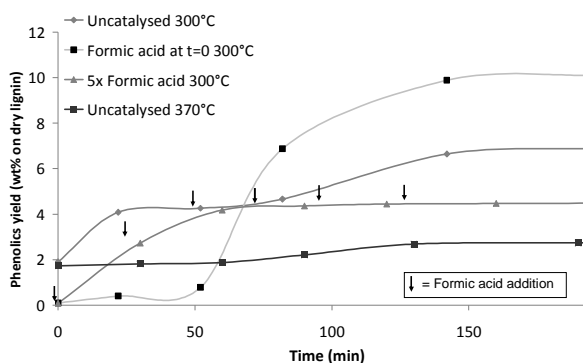

Figure 1. Cumulative formation of identified monomeric phenolics during supercritical depolymerisation of Alcell lignin at 300 – 370°C and 100 bar in a carbon dioxide/acetone/water mixture. 14% (based on lignin) Formic acid was added as catalyst.

In the uncatalysed depolymerisation process 41% of char was formed from organosolv hardwood lignin (Alcell) as depicted in figure 2. Although an one time addition of formic acid (14% based on dry lignin) leads to a higher production of monomeric phenols while also a slightly higher amount of char was found (45%). More formic acid addition leads to the formation of a higher amount of char (48%) and a lower production of monomeric phenols. Supercritical treatment at 370°C results in a lower yield of phenols (3% based on dry lignin) and a higher char amount of 54%.
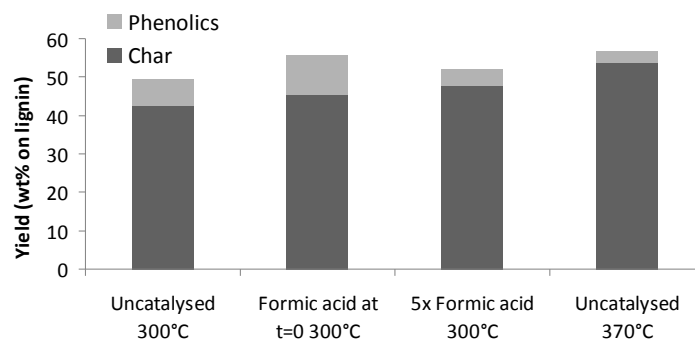
Figure 2. Char and identified phenolics formed from Alcell lignin after supercritical treatment in a carbon dioxide/acetone/water mixture. 14% (based on lignin) Formic acid was added as catalyst.

Figure 3 shows that the residual lignin chars lost substantially their functional groups and typical aromatic skeleton vibrations as measured by FT-IR. Their structure more and more resembles that of carbon black. This is probably due to partial deoxygenation, the removal of monomeric phenolics and recondensation of the remaining lignin fragments.
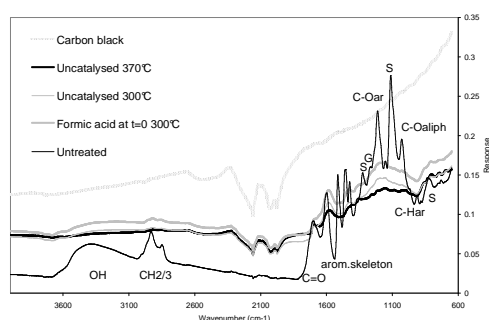

Figure 3. FT-IR of residual char after supercritical treatment of Alcell lignin compared to untreated lignin and carbon black

Figure 4 shows that lignin depolymerisation in a carbon dioxide/acetone/water mixture at 300°C leads to a substantial decrease of the oxygen/carbon ratio in the resulting char. The oxygen content decreases from 27 to 20%. A higher temperature (370°C) gives a further decrease in the oxygen content of the char formed (12.5%) and a oxygen/carbon ratio of 0.15.
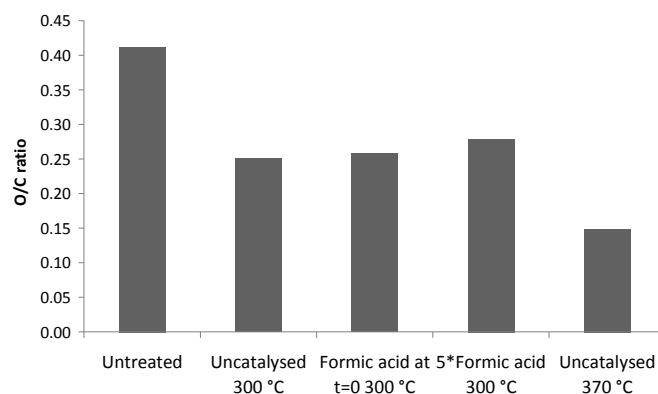
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Figure 4. Effect of supercritical treatment on the oxygen/carbon ratio in residual lignin char compared to untreated Alcell lignin

In this work, other depolymerisation products from lignin like reaction water, permanent gases and oligomeric lignin fragments were not quantified. More data on this novel lignin depolymerisation process will be published by Gosselink et al. (2010).

IV. CONCLUSIONS

In a supercritical carbon dioxide/acetone/water based solvent at 300°C and 100 bar hardwood organosolv lignin was converted to 10% identified monomeric aromatic compounds by using formic acid as a hydrogen donor and catalyst. In this novel process the products were separated from residual lignin by adiabatic expansion of scCO$_2$. During this process a strong competition occurs between depolymerisation of lignin and recondensation of fragments. This leads to a residual lignin char representing 40% of the starting material consisting of a substantially reduced oxygen/carbon ratio and a similar structure to carbon black. Further work is needed to improve the overall conversion of lignin to valuable products.

V. ACKNOWLEDGEMENT

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