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From Lignin to Oil by Microwaves

Pulsed microwaves break down lignin into its sub-compounds, where methoxyphenols are the main product.

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An obstacle in the production of second generation bioethanol from plant residues is the presence of lignin. Although new experiments with enzymes suggest promising results, lignin remains a problem.

In 2009, several large-scale experiments converting hundreds of kilos of straw into bio crude oil indicated that microwaves could degrade lignin.

Further experiments have now been carried out on a small scale in a laboratory plant at BFT Bionic Fuel Technologies in Groß-Gerau, Germany. This plant converts between 200 g and 1 kg at a time. The current study used lignin that was supplied by Claus Felby, Faculty of Life Sciences, University of Copenhagen.

Laboratory experiment

The heart of the conversion is a reactor that works with pulsed microwaves adjustable up to 6 kW, as well as a catalyst of synthetic zeolite. The expression "pulsed" means that the microwaves are emitted as pulsations instead of continuously.

The lignin experiment is carried out like any other experiments with various organic raw materials:

First, a glass flask is filled with lignin and 1 weight-% catalyst. Before heating, the reactor vessel is evacuated to an underpressure of approximately 0.4 bars, and a nitrogen blanket is applied. Then, the microwaves are turned on, and the process is regulated so that a gradual increase in temperature is achieved. The microwaves can be stopped at any time and the reaction vessel can be inspected.

Products that are liquid at room temperature are condensed in flasks and poured into bottles that are closed immediately. Storage in open bottles will often change oil made from biomass in less than a day, while the same product remains stable in a closed bottle for at least one year. The product is immediately tested for colour, inflammability, density, etc.

The equipment used in this experiment can only capture molecules with boiling points higher than that of propane.

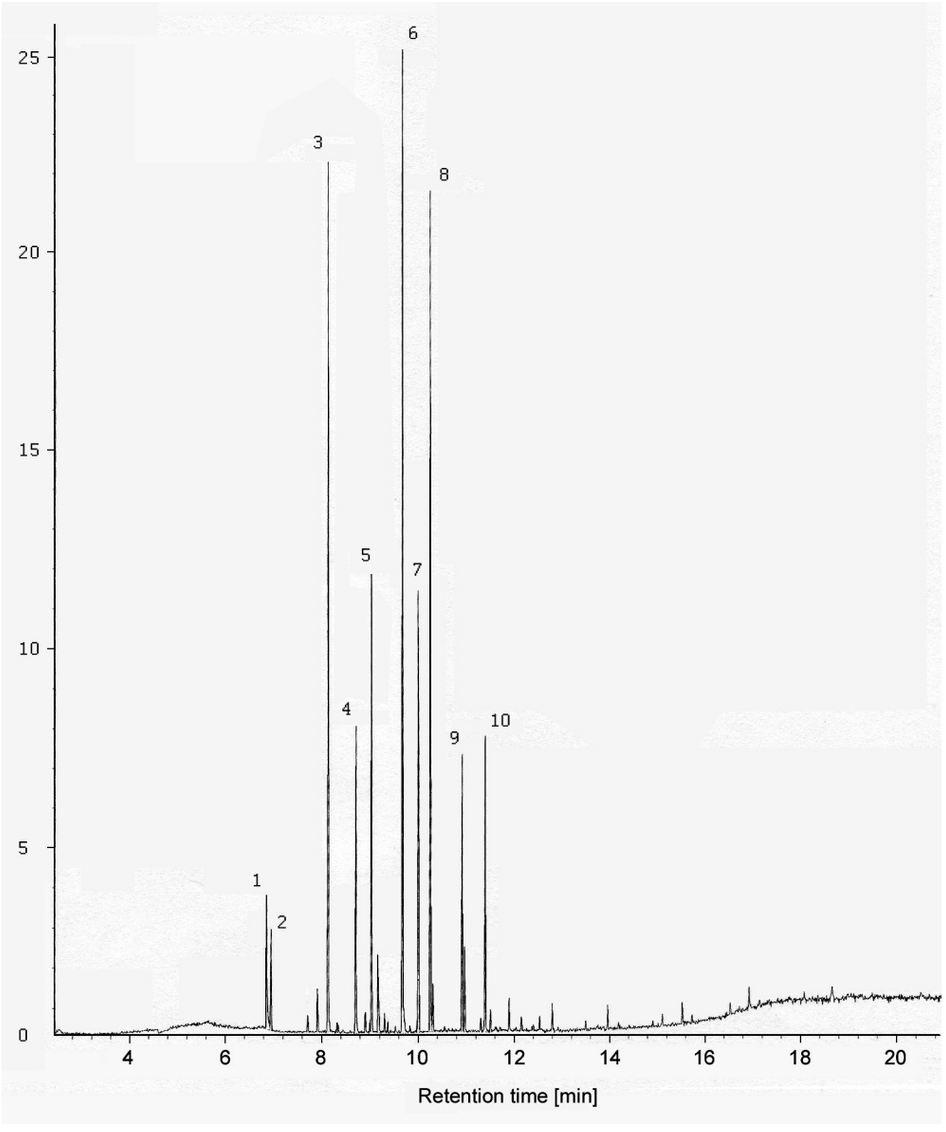

Figure 1. Gas Chromatogram for the conversion product of the lignin. The numbering corresponds to the numbering in table 1.

The converted product

The identification of the single molecules is done by GC/MS, followed by a comparison of the mass spectra with library spectra. First, the product is extracted with pentane, which has a short retention time so that the signal does not disturb the gas chromatographic analysis.

Lignin is an aromatic polymer, which mostly consists of different methoxyphenols and complex links between them [1]. Other products are alcohols, ethers and ketones, which come from the side chains of the lignin. Methoxyphenols have very strong antioxidative properties and may possibly be used as a stabilizer in fuels [2].

The actual experiment shows that pulsed microwaves are an easy way to convert lignin to methoxyphenols. Therefore, there is no reason why lignin, as a waste product from the bioethanol production, should end as a solid fuel in a power plant.

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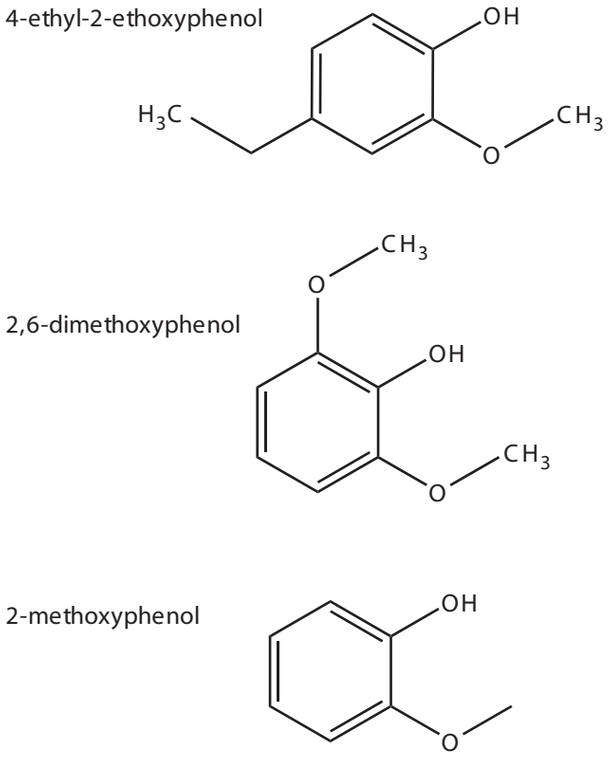

Figure 2. The structure of the three main products.

References
1. Palonen, H.: *Role of lignin in the enzymatic hydrolysis of lignocellulose.* VTT Publications 520, 2004.
2. Vasileva, T. m.fl.: *Phenolic antioxidants for fuels.* Journal of the University of Chemical Technology and Metallurgy, 43, 1, 2008, 65-68.

No.	Area %	Molecule
1	3.97	2,2-oxybis-ethanol
2	2.38	phenol
3	17.83	2-methoxy-phenol
4	6.72	2-ethyl-phenol
5	9.33	2-methoxy-4-methylphenol*)
6	21.49	4-ethyl-2-methoxy-phenol
7	10.08	2-methoxy-4-vinyl-phenol
8	17.52	2,6-dimethoxy-phenol
9	5.01	1,2,3-trimethoxy-benzene
10	5.67	1-(2,6-dihydroxy-4-methoxyphenyl)-ethanone

*) The analysis method does not distinguish between 4- and 5-methylphenol.

Table 1. The ten most frequent molecules in the product.