

# Influence of parameters on pyrolysis-GC/MS of lignin in the presence of tetramethylammonium hydroxide

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## Abstract

Thermally assisted hydrolysis and methylation (THM) with tetramethylammonium hydroxide (TMAH) was performed on spruce milled wood lignin (MWL) in order to investigate THM parameters. The objective was the maximization of information on lignin structure. The main emphasis was laid on the formation of lignin monomer derivatives with intact propane side chain, as these fragments are thought to be indicators of favourable THM conditions. In the tested temperature range (310–710 °C) the lowest temperature of 310 °C was found to produce the highest yield of these monomers. The elution of unmethylated lignin monomers, such as phenols and methoxyphenols, was also minimized at 310 °C. In addition, a number of different TMAH to sample ratios were applied. The yield of the most lignin monomer derivatives was increased by using the highest tested TMAH concentration, whereas some unmethylated products, such as phenol, were unaffected. Methanol as solvent for TMAH was compared to an aqueous solution of TMAH of same concentration in respect of the influence on degradation product yields. The elution of 3,4-dimethoxybenzoic acid methyl ester increased and the yield of 3,4-dimethoxybenzaldehyde decreased when methanol was used. At last a prolonged incubation time of the TMAH–sample mixture was shown to be useful to enhance especially the yield of lignin monomer derivatives with intact propane side chain in case of application of a low TMAH to sample ratio.

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## 1. Introduction

Pyrolysis-GC/MS has gained wide acceptance for structural analysis of complex biopolymers including lignins, lignocellulosics and humic materials. A major shortcoming of the conventional technique is the loss of structural information due to extensive fragmentation and due to the poor chromatographic behaviour of fragments containing polar functional groups. The combination of pyrolysis with in situ methylation using tetramethylammonium hydroxide (TMAH) was introduced by Challinor [1] to overcome the above-mentioned disadvantages. By depolarizing the fragments through methylation methyl esters from

carboxylic acids and methyl ethers from alcohols or phenols are formed, which are easily separable by gas chromatography.

It has been shown that, apart from the desired methylation, the strong alkaline character of TMAH causes dominant chemolytic reactions at elevated temperatures leading to the fragmentation of the analytes. As a result drastically different product patterns with higher overall yields compared to conventional pyrolysis are generated [2,3]. For this “thermally assisted hydrolysis and methylation (THM)” or “TMAH thermochemolysis” much lower temperatures have been reported to be sufficient for the generation of structural information in the case of lignin as analyte. In fact, it was noted that THM temperatures of 310 and 610 °C generate similar product patterns whereas lower temperatures are said to be advantageous for the reduction of

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pyrolytic reactions [4]. For the “off-line” thermochemolysis method even as low temperatures as 250 °C were applied for structural analysis of lignins [5,6]. But also temperatures of 360 °C [7], 500 °C [8,9] or 770 °C [10] were applied for lignin characterization.

A second important parameter is the TMAH to sample ratio, since generally a complete methylation at the highest possible yield is desired. 2 µl of 10% aqueous solution of TMAH for a sample of approx. 40 µg of spruce milled wood lignin (MWL) was reported to be sufficient for a complete methylation at 360 °C [7]. In another study 5 µl of TMAH (25% (w/w) solution in methanol) was added to a sample of approx. 70 µg of a synthetic lignin (DHP) applying thereby a TMAH to sample ratio [11] which was approx. 3.5 times higher than the ratio used in the previous mentioned work. In a recent study the influence of the ratio of TMAH to sample on the product pattern of various model compounds was lined out [12].

The thorough contact between reagent and sample is another aspect to be considered in sample preparation. A variety of approaches have been applied by different workers. After adding the TMAH, the samples were heated for 10 min at 100 °C [13], others preferred to dissolve the samples in TMAH-solution and let it dry under vacuum [8], or dissolved the sample in dioxane and dried it under a nitrogen stream after adding the reagent [7]. More recently Hermosin and Saiz-Jimenez [14] used ultrasonic treatment for thorough mixing of the sample–TMAH-mixture. Also solid TMAH pentahydrate (TMAH·5H<sub>2</sub>O) was utilized [9] whereas in this case the least contact between reagent and sample is to be expected.

Though a number of studies were carried out in order to optimize the conditions of the THM process for analysis of biopolymers [12–15], a standardization of the method has not yet occurred. Already the diverse nature of biopolymers seems to make it inappropriate to transfer conditions for analysis of e.g. humic acids or cellulose upon the analysis of lignins, although structural similarities are partially evident. Apart from the phenolic ring and the methoxy groups a glycerol-type side chain is a main characteristic of lignin monomeric units. This propane side chain is extensively degraded in conventional pyrolysis. Not only the evaluation of carboxylic acid groups in native lignin, which are known to be rare, or the categorization of the lignins by phenolic methoxy groups seem to bear a major interest to the authors. Also the extensive preservation of the propane side chain containing important structural information should be aimed for when the THM technique is applied.

The main aspect of the present work is the evaluation of the effect of THM parameters not only on the total yield, but also on single products. Especially under the scope of their usefulness for structural analysis of lignin it appears reasonable to distinguish between products in respect of their importance, as, for example, 1,2-dimethoxybenzene and 3,4-dimethoxytoluene only give little information compared to e.g. 1,2-dimethoxy-4-(1,2,3-trimethoxypro-

pyl)benzene, all being typical degradation products of the THM method.

Furthermore, the authors aimed for an optimization of the parameters of THM in order to apply these on the qualitative and quantitative analysis of residual lignin in pulp. Although the quantification by a GC/FID-system bears the advantage of a higher reproducibility and better proportionality the GC/MS-system was preferred for this study, as it allows to distinguish between overlapping peaks especially occurring when pulp is to be analysed.

## 2. Experimental

### 2.1. Sample preparation

Milled Wood Lignin was prepared from spruce (*Picea abies*) according to Björkman [16]. Sixty to 100 µg of MWL was weighed into the sample cups with an accuracy of 1 µg. For the pyrolysis combined with in situ methylation 2, 4, 8 or 10 µl of 10% aqueous solution of TMAH (by dilution of 25% aqueous solution (merck-Suchardt)) was used. Alternatively, 4 µl of 25% solution of TMAH (solution in H<sub>2</sub>O or Methanol (Aldrich)) was applied. The reagent was added to the sample by a microsyringe making sure the sample was covered by the solution (hardly possible in case of 2 µl). In case of TMAH pentahydrate (Aldrich) as the methylating agent the crystals were added to the sample and their weights recorded in order to determine the ratio of TMAH to sample. Because of the inhomogeneous size of the crystals the variation of the ratio was fairly high.

### 2.2. Pyrolysis-gas chromatography/mass spectrometry

The pyrolysis system consisted of a Frontier Lab Micro furnace Double-shot Pyrolyzer (Py-2020iD) equipped with an Autosampler (AS-1020 E). Depending on the pyrolysis temperature (310, 360, 410, 510, 610 and 710 °C) the interface was kept at a temperature of 280 or 300 °C and was purged with a continuous helium flow for 15 s prior to pyrolysis. After pyrolysis the products were transferred (split 1:50) into the capillary column (ZB-1701 (Phenomenex) 60 m × 0.25 mm, 0.25 µm) via the directly connected GC-injector. The gas chromatography (Agilent 6890) was performed with helium as the carrier gas at a flow rate of 1 ml/min. The oven programme started off with 4 min of isothermal condition at 45 °C, then was raised at a rate of 3 °C/min to 280 °C and was finally kept at this temperature for 15 min. For mass spectral detection an Agilent 5973N MSD was used with an electron impact ionisation energy of 70 eV. The scan range was 35–400 *m/z*. If not stated otherwise duplet analyses were performed and averaged for display in tables and illustrations. Identification of the products was carried out by library search (NIST02) and comparison with literature sources [7,17]. For quantitative analysis, peak areas were related to the sample weight, and

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