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Micro-pyrolysis of technical lignins in a new modular rig and product analysis by GC–MS/FID and GC × GC–TOFMS/FID

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ABSTRACT

A new offline-pyrolysis rig has been designed to allow multifunctional experiments for preparative and analytical purposes. The system conditions can be set and monitored, e.g. temperature, its gradients and heat flux. Some special features include (1) high heating rates up to 120 °C/s with pyrolysis temperatures up to 850 °C at variable pyrolysis times and (2) the selection of different atmospheres during pyrolysis. A complete mass balance of products and reactants (gas, liquids and solids) by gravimetric methods and sequential chromatographic analyses was obtained.

The pyrolytic behaviour and the decomposition products of lignin-related compounds were studied under different conditions: heating rates (from 2.6 °C/s up to 120 °C/s), pyrolysis temperatures at 500 °C and 800 °C in different atmospheres (N₂, H₂, and mixtures of N₂ and acetylene). Kraft lignin, soda lignin, organosolv lignin, pyrolytic lignin from pine bio-oil, residues from biomass hydrolysis and fermentation were studied.

The obtained pyrolysis products were classified into three general groups: coke, liquid phase and gas phase (volatile organic compounds (VOC) and permanent gases). The liquid fraction was analysed by GC–MS/FID. In addition, comprehensive two-dimensional GC was applied to further characterise the liquid fraction. VOCs were semi-quantified by a modified headspace technique using GC–MS/FID analysis. The micro-pyrolysis rig proved to be an efficient and useful device for complex pyrolysis applications.

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1. Introduction

Nowadays lignin is regarded as an abundant renewable source for aromatic (phenolic) polymers. Currently, Kraft lignins generated during sulphate pulping in alkaline medium are further developed as important technical lignins and are used for various applications. Lignin primarily serves as a fuel source and only a small amount (ca. 1–2 wt.%) is employed in a wide range for specialty products, which however, amount to 1 million tons per year worldwide [1].

Other numerous lignin products and derivatives that originated from unusual plant sources or experimental pulping processes have been described [2]. In future, more lignin-enriched residues could be obtained from biomass hydrolysis and fermentation processes.

Lignins vary in structure according to their method of isolation and their plant source [3,4]. In the plant tissue hardwoods develop

a different lignin compared to softwoods and annual crops. However, the differences are minor as far as most applications are concerned. Major differences exist between lignins from the various technical processes [4,5]. Non-energetic utilization of lignins for added value products demand precise analytical methods to determine their structural and molecular properties, as well as the extended coherences of the comprehensive processes, for example the mass balance of the whole pyrolysis product stream.

Analytical pyrolysis is a well-known technique to analyse high-molecular compounds and various authors published different analytical methods to determine the composition of lignocellulosic materials [6–9]. Additionally, other analytical methods and comprehensive data for quantification of lignin depolymerisation products are reported in literature [10,11]. Primarily, these analyses focus on selected compounds or groups of compounds. Bench-scale rigs have been used extensively to analyse the complete range of pyrolysis products in one run [12–14]. These preparative methods work very well and give comprehensive process and product information, but are more complex and time consuming in comparison to small-scale analytical units. Furthermore, the preparative pyrolysis of lignins often causes problems (blockage) by means of the low softening point of the polymer [15].

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Table 1
Ash contents of lignin samples.

	Ash content (wt.%)
Kraft lignin	0.52
Soda lignin	0.09
Pyrolytic lignin	0.00
Organosolv lignin	0.00
Etek lignin	0.04
Etek lignin	1.64

Small size offline-pyrolysis systems could combine advantages of preparative rigs and avoid disadvantages of online apparatus.

Offline-pyrolysis units are well-known analytical tools, which have been used for post-pyrolytic silylation [16]. Also work with offline-pyrolysis (tetramethylammonium hydroxide) TMAH-GC-MS has been carried out [17]. Techniques and methods from previous authors have been employed for the construction of a new pyrolysis rig presented in this paper [8,18,19]. The working principle and the results will be described.

2. Materials and methods

The used lignins were as follows:

- Kraft lignin (Holmen AS, NO) produced by conventional alkaline Kraft process from softwood feedstock.
- Soda lignin (Granit, CH) produced by sulphur free alkaline process from annual crops and precipitated by the Granit process.
- Organosolv lignin (Alcell, USA) produced by the Alcell process with mixtures of ethanol/H₂O and hardwood as feedstock.
- Pyrolytic lignin (vTI, DE) precipitated from bio-oil obtained by fast pyrolysis of pine wood [20].
- Etek (Etek Etanolteknik AB, SE) lignin filtration residue from acid straw hydrolysis.
- Haak (Haak, DE) lignin-enriched residues from anaerobic biomass fermentation.

All lignins were milled to fine powder and then dried in an evacuated desiccator over phosphoric anhydride. The ash contents are reported in Table 1.

2.1. Offline-pyrolysis (Py)

Offline-Py was performed using the experimental equipment shown in Fig. 1. This system can be divided into a reaction- and a trapping section. A quartz tube reactor combined with a moveable and program controlled oven comprise the reaction system. Fast pyrolysis experiments were done by preheating the oven in the preheating zone to 500 °C or 800 °C. Next the oven was moved manually to the pyrolysis zone, where the sample was placed

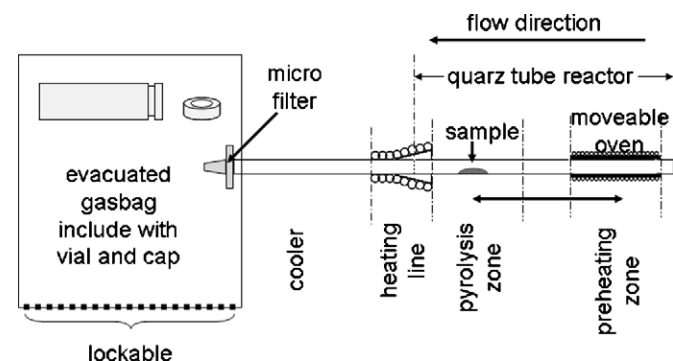


Fig. 1. Scheme of the offline-pyrolysis unit.

previously. The intermediate pyrolyses were carried out directly in the pyrolysis zone.

The trapping section consists of a quartz tube cooler, which was coupled directly to the reactor. The connection was heated to 320 °C to ensure that all volatile pyrolysates could leave the reactor and condense afterwards on the glass wall. The outlet of the cooler was equipped with a porous micro-filter (pore size 0.2 μm) to allow trapping of aerosols. All product gases (permanent and non-permanent) plus the carrier gas, accumulate in an evacuated polyethylene (PE)-gasbag in which a standard headspace vial (20 ml) with screw cap was placed. This arrangement allows sampling of an aliquot part of the volatile components by simply closing the vial inside the yet locked gasbag.

Several preliminary studies were carried out to ensure the complete trapping of all volatile compounds. It was observed that the installation of different adsorption materials such as Tenax, Carbosieve and even a 1500-mm long quartz spiral cooled to -90 °C was not successful. Therefore, these parts were renounced and instead a gasbag system installed.

At the beginning of each experiment the whole apparatus was flushed thoroughly with the respective gas (N₂, H₂, and N₂/acetylene), then the gas flow-rate was adjusted to 5 ml/min, while the oven and the heating line were tempered accordingly. During the following pyrolysis step, the flow was increased to 30 ml/min resulting in an intermediate gas velocity of 20 mm/s. After each experiment, the oven was redrawn to the preheating zone so that the pyrolysis zone (with the remaining coke) could be cooled with pressurised air. The mass balance was established by weighing the reactor, the cooler and the micro-filter with a Mettler AT 261 Delta range balance and the gas amount was calculated by difference.

2.2. GC-MS/FID analyses of the liquid phase

The products from both the cooler and the micro-filter were defined as the liquid phase and were collected by rinsing with 200–300 μl acetone. The acetone contained a known concentration of fluoranthene as internal standard for GC quantification. GC was performed using a HP 6890 from Agilent with splitless injection, injector temperature was 250 °C, volume 1 μl. Separation was carried out on a 60 m × 0.25 mm Varian (f4 1701) fused-silica column, containing 14% cyanopropyl-phenyl-methylpolysiloxane (0.25 μm film thickness). Oven programme was as follows: hold constant at 45 °C for 4 min then heat with 4 °C/min to 280 °C and hold for 20 min. Helium was used as carrier gas with a constant flow of 2 ml/min. The system was equipped with parallel FID & MS-detection. Electron impact mass spectra were obtained on a HP 5972 MS using 70 eV ionisation energy. Pyrolysis products were identified by comparison with mass spectra of authentic compounds and mass spectra in the NIST and a home-made library.

2.3. GC-MS/FID analyses of the gas phase

All products trapped in the gasbag are called gas phase. An aliquot part of these compounds was collected in a headspace GC-vial and analysed with standard HS-technique. The first step was incubation (3 min @ 80 °C), followed by sampling with a headspace syringe (injection volume 250 μl/syringe temp. 100 °C) and injection in the GC (HP 6890N). Programmed temperature vaporisation (PTV) injection was used to concentrate and also to separate the VOC phase from the permanent gasses. The injection occurs in a Tenax liner at -40 °C, the desorption of the trapped compounds was under the following conditions: hold 0.5 s, ramp 12 °C/s final temperature 260 °C.

A ZB Innowax (60 m × 0.25 mm, 0.25 μm film) GC column was used, sample introduction occurred in split mode (1:10). The carrier gas was He and the system ran in constant flow mode (2 ml/

Table 2
Pyrolysis conditions.

Experiment	Heating rate (°C/s)	Pyrolysis temperature (°C)	Atmosphere	Total pyrolysis time (s)
Reference experiment	120	800	N ₂	12
Demonstration tests				
Temperature	120	500	N ₂	12
Hydrogen	120	800	H ₂	12
Heating rate	2.7	800	N ₂	389
Atmosphere	120	800	N₂/acetylene	12

The bold values indicates the varied test conditions.

min.). The oven programme: initial temperature. 36 °C, hold 4 min, ramp 6 °C/s, final temp. 260 °C, hold 10 min.

The system was coupled with FID & MS-detectors with parallel signal outputs. Electron impact mass spectra were obtained on an Agilent 5975B inert XL MSD. Pyrolysis products were identified by comparison with the mass spectra of authentic compounds and mass spectra in the NIST-library.

A semiquantification of the gas phase was carried out by external calibration with toluene. Several blank runs with different amounts of toluene as external standard were used to establish a calibration curve. The GC peak areas of toluene gave a linear correlation. As it was found in all gas phase pyrograms, it was quantified directly with the calibration curve. All other compounds were calculated using the toluene equivalents.

2.4. Two-dimensional GC and time of flight mass spectrometry for analysis of the liquid phase

GC × GC–TOFMS analysis was performed using a HP 6890N GC with auto sampler HP 7683 (Agilent Technologies, Palo Alto, CA, USA) connected to a Pegasus III TOF/MS from LECO Instruments, St. Joseph, MI, USA. Cryofocussing was applied by liquid nitrogen and a dual jet modulator (Zoex, Houston, TX, USA); modulation time 10 s. The first dimension chromatographic separation was performed by the apolar column VF-5MS (5% phenyl in polydimethylsiloxane; PDMS), 30 m × 0.25 mm I.D. and 0.25 μm film thickness. The second dimension column was a VF-17MS situated in a dual internal oven and coated with phenyl (50%); 2 m long × 0.1 mm I.D. and 0.2 μm film thickness. Both columns are from Varian (Middelburg, The Netherlands).

Table 3
Summary and quantitative effects of all pyrolysis experiments (wt.% based on dry lignin).

Experiment	Kraft lignin	Soda lignin	Pyrolytic lignin	Organosolv lignin	Etek lignin	Haak lignin
Results from the reference experiment						
Gas	23.7	18.1	13.2	29.0	14.6	16.6
Liquid (GC-detectable)	35.8 (6.0)	43.1 (12.5)	61.0 (6.5)	43.6 (7.1)	65.7 (12.9)	46.1 (6.8)
Coke	40.5	26.2	25.8	27.4	19.6	37.3
Effects of pyrolysis temperature (500 °C)						
Gas	20.3	n. a.	4.8	n. a.	n. a.	6.9
Liquid (GC-detectable)	41.6 (8.5)	n. a.	63.2 (n. a.)	n. a.	n. a.	50.6 (n. a.)
Coke	38.0	n. a.	32.0	n. a.	n. a.	42.6
Effects of hydrogen						
Gas	37.5	16.7	n. a.	31.2	34.1	n. a.
Liquid (GC-detectable)	35.1 (7.4)	74.5 (8.1)	n. a.	48.7 (7.8)	61.2 (16.4)	n. a.
Coke	27.4	8.8	n. a.	20.1	4.7	n. a.
Effects of intermediate conditions (heating rate)						
Gas	24.8	n. a.	29.0	22.6	20.1	21.8
Liquid (GC-detectable)	30.9 (8.7)	n. a.	46.0 (7.6)	45.8 (9.3)	57.4 (16.9)	40.5 (6.1)
Coke	44.3	n. a.	25.0	31.6	22.5	37.7
Effects of atmosphere						
			n. a.			

n. a., not analysed.

Temperature programming was performed at a starting temperature of 40 °C of the GC oven during 5 min and a rate of 3 °C/min to a final temperature of 300 °C. The dual column was programmed 10 °C ahead of the GC oven gradient. The carrier gas (helium 99.999%) flow rate was 1 ml/min; split injection of 1 μl sample solution (split ratio 1:500) at an injection temperature of 275 °C.

The net 2D-retention time of *n*-decane (~0.6 s) was used as a reference and after loading each chromatographic data file in the worksheet, the 2D-retention time of decane was set to 0.600 s. Data acquisition (100 spectra/s; *m/z* 50–500 Da), identification by apex peakfinder algorithm and mass spectral deconvolution as well as integration of the trace-ion signal was done by the ChromaTOF software of the Pegasus system. The deconvoluted spectra were compared with the NIST software library for compound identification.

3. Results and discussion

All listed lignins were analysed in a reference experiment (see Table 2). Semiquantitative VOC phase analyses were carried out only for this reference experiment. A temperature of 800 °C was chosen to ensure that all reactions were finished [21].

Another intention of this work is to demonstrate the diversity of this pyrolysis rig. As per Table 2, some additional experiments under different conditions were accomplished. To insure compact breakdown it was decided to limit the scope of further work, insofar the demonstration tests as presented in Table 3 were carried out. Their selection range was guided by the attached importance of the lignins or was influenced by the results obtained from the reference experiments.

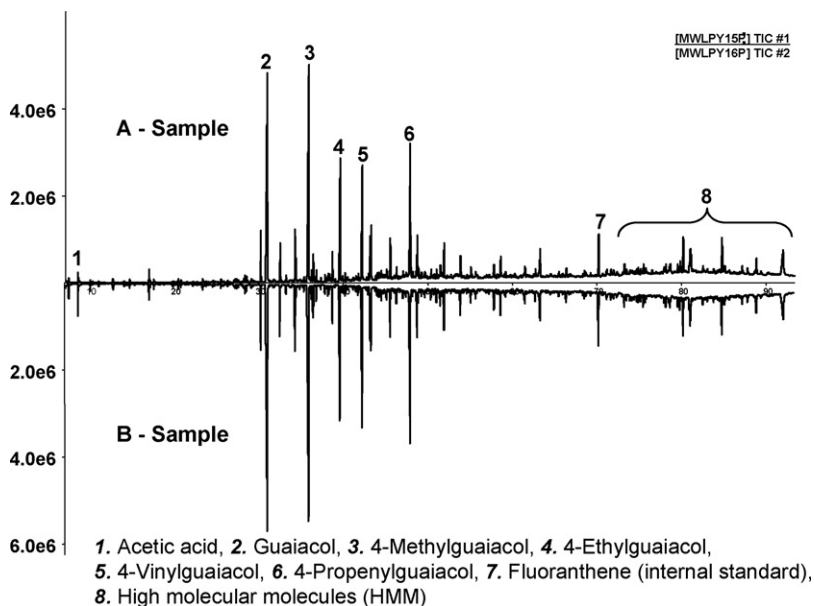


Fig. 2. GC-MS overlay of two liquid phase pyrograms from Pyrolytic lignin.

Hence, most of the experiments were done with Kraft lignin as it is actually the most relevant lignin source. Overall, the Etek lignin gives the broadest variety and the highest amount of monomer compounds. Therefore it was studied in more detail. Particularly the pyrolysis in nitrogen/acetylene atmosphere was only done with this feedstock. The results for this experiment are not listed in Table 3. With regard to the reactive atmosphere it is evident, that, the mass balance is incomparable to the others.

Other lignin types were used representative to demonstrate the effects of the related pyrolysis method.

During the experiments adjustable transport gas flew through the closed system. This allowed quick removal of pyrolysis products from the hot reactor zone into a cold trap and a gas absorption trap. Solid products remained in the reactor. All pyrolysis products were classified in three general groups: charcoal, liquid phase and gas phase and were analysed by chromatographic techniques. Gas chromatography (GC) fitted with mass spectrometric (MS) detector was used to characterise gas and liquid fractions.

3.1. Analyses of the reference experiment

In general, the system performed good reproducibility for the qualitative analyses of the liquid phase monomers as well as of the VOC phase (see Figs. 2 and 3). Quantitative analysis of liquid monomers showed deviations up to 3% rel. For the VOC phase this calculation was not carried out because these measurements were only semiquantitative.

The complete mass balance of all reference experiments is depicted in Fig. 4 and represents four repetitions from each lignin. A characteristic decay pattern can be observed. The amount of the coke residue ranges from 20 wt.% for Etek lignin to 40 wt.% for Haak and Kraft lignin. The amount of liquid phase is in the range of 36 wt.% (Kraft lignin) to 66 wt.% (Etek). The yield of the gas phase is between 13 wt.% (pyrolytic lignin) and 29 wt.% (organosolv lignin).

Some of the lignins showed high scattering (up to 25%) around their average values probably due to the inhomogeneity of the

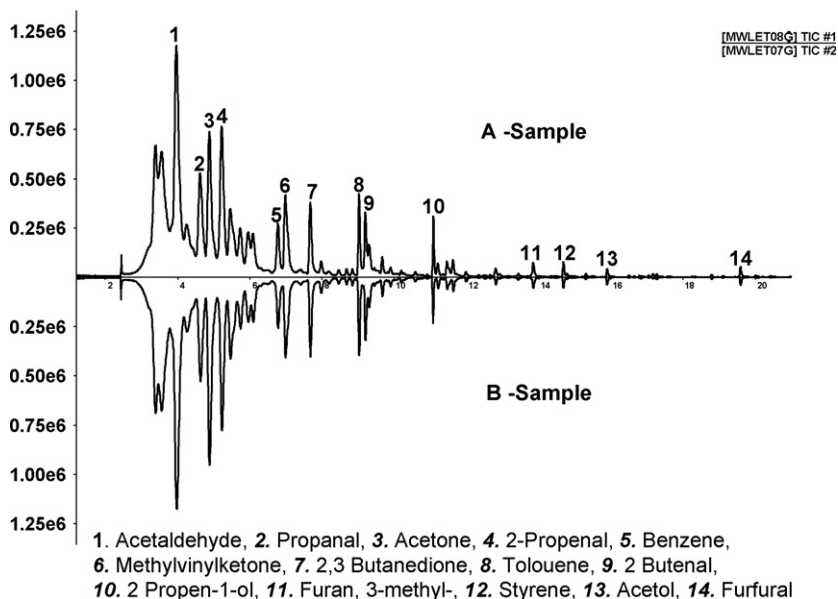


Fig. 3. GC-MS overlay of two VOC-phase pyrograms from Etek-lignin.

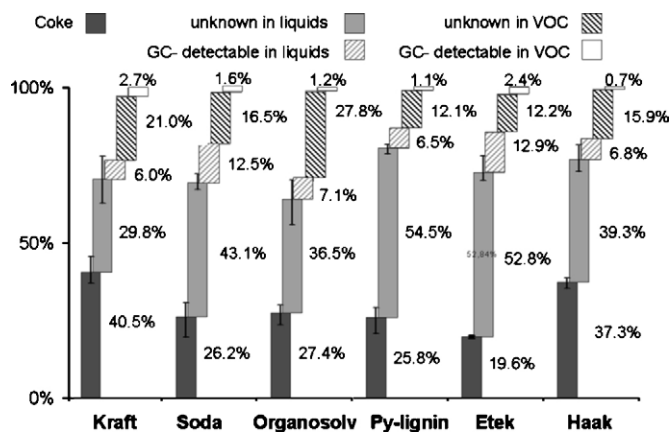


Fig. 4. Mass balance from the reference experiments (wt.% based on sample as is).

natural feedstock. Furthermore, it seems that the cokes (especially from Kraft lignin) reacted aggressively with the quartz tube, resulting in a small loss of wall material. However, these effects may have less influence on the output weight. The essential reason for these deviations is unreliable weighing. Because of the strong swelling of lignin during heating [15] in the small reactor the sample amount was reduced to 3 mg to avoid uncontrolled expansions. This was proven to be the lower sample weight limit of the system. Comparative experiments with intermediate pyrolysis conditions, which were carried out with a sample weight around 15 mg, gave much more less deviation (ca. 3%).

The quantification of the obtained liquid phase gave good reproducibility. Fig. 5 shows the result for all lignins. For the sake of clarity pyrolysates have been sorted according to their chemical groups. Compounds which represent unimportant fractions (acids, aldehydes, ketones, furans, pyrans, etc.) are summarized in the category “others”.

Apart from Etek- and Haak-lignins, the liquid monomers contain mainly aromatics such as phenols and methoxyphenols (guaiacols). Some others, such as soda-, organosolv- and Haak-lignin, have also dimethoxyphenols (syringols) as they are derived from annual plants and hardwoods. Soda lignin gave the highest amount of aromatic monomers; followed by organosolv-, Kraft- and pyrolytic-lignin. The lowest yield was obtained from Etek- and Haak-lignin but accompanied with high amounts of levoglucosan, hydroxyacetaldehyde (Etek), ketones and organic acids (Haak) due to larger amounts of residues from carbohydrates. It was observed that each lignin gave a typical product distribution. The GC-detectable amounts ranged only between 10 and 20 wt.% based on the overall liquid phase. The rest can be attributed to higher

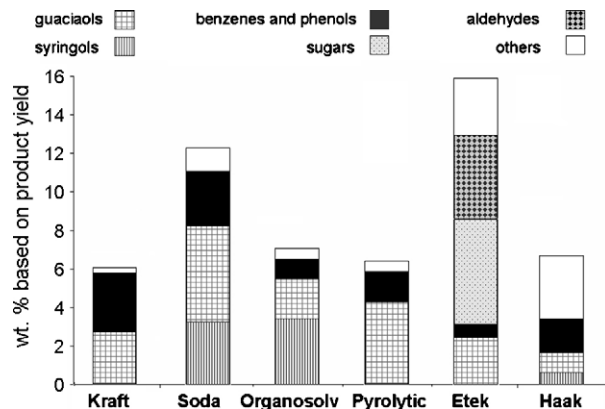


Fig. 5. Quantification by GC-FID of the liquid phase products (reference experiment).

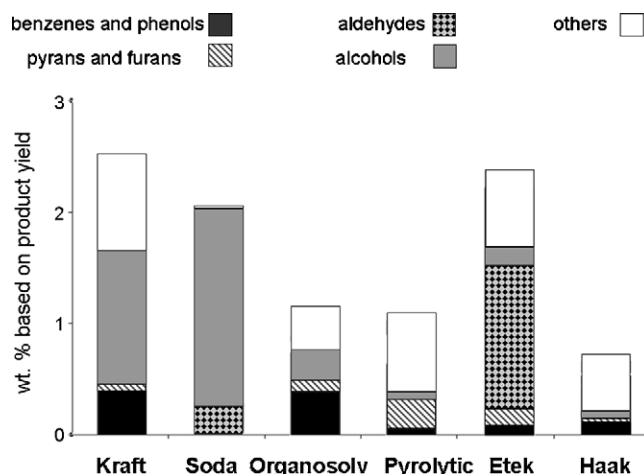


Fig. 6. Quantification by GC-FID of the VOC phase products (reference experiment).

molecular weight components, polar constituents and also some reaction water.

The semiquantitative results from the VOCs are depicted in Fig. 6. Due to their low boiling points not only aromatics, such as benzene, toluene or styrene were detected, but also quite substantial amounts of furans, aldehydes and alcohols. The term “others” indicates ketones, small chain alkanes, alkenes and also some special substances, depend on the type of lignin. For example Kraft lignin yielded several sulphur containing compounds, such as thiophene, methyl disulfide, and 2-methylthiophene.

Assuming that the used quantification method gives acceptable values, the VOCs part of the overall gas phase ranges between 3 and 10 wt.%. This is not surprising, because the permanent gases (CO, CO₂, H₂O, CH₄, etc.) were not trapped in the liner of the GC due to the applied method.

Detailed information of pyrolysates from lignin was already published [8]. For more extensive identification of components in liquid or gas samples also hyphenated or two-dimensional techniques can be used, as shown by an example of GC × GC-TOF/MS analyses.

3.2. Influences of heating rate and pyrolysis temperature

Heat transfer is restricted by the mechanical structure of the sample. Therefore, intermediate pyrolysis allows for a synchronised heating, but fast pyrolysis gives a temperature gradient inside the sample. Various influences on the pyrolytic decomposition and the reactions kinetics can be assumed. This can be studied in Fig. 7 with the example of Kraft lignin. Fast pyrolysis at 800 °C shows intensive decomposition. The amount of guaiacols was low and their degradation to phenols and benzenes increased. Lower pyrolysis temperature as well as intermediate conditions gave more guaiacols and overall larger fractions of monomers. Additionally, some catechols were found in the intermediate pyrolysis.

In Table 3 the mass balances of the performed experiments are presented. Low-temperature pyrolysis (500 °C) gave less gas phase products, a tendency to higher amounts of coke and also higher yields of liquids. Apart from one exception (organosolv) all intermediate experiments gave lower liquid yields, more gases and a slight increase of coke. The amount of GC-detectable monomers is in any case higher under intermediate conditions.

3.3. Influences of various atmospheres

3.3.1. Hydrogen atmosphere

Some pyrolysis experiments were carried out in hydrogen atmosphere. Variations in the mass balance are presented in

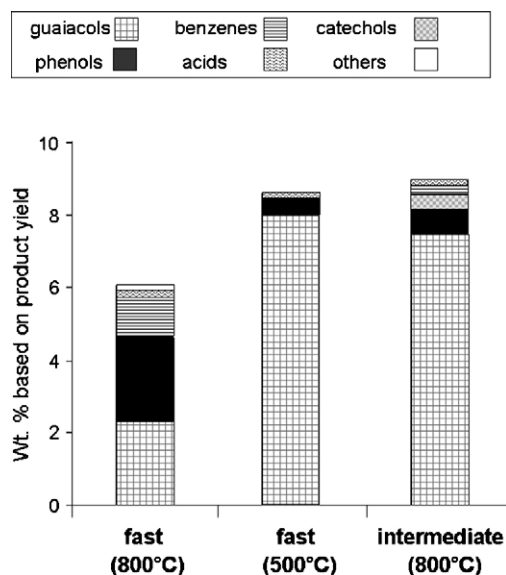


Fig. 7. Comparison of the influences from various pyrolysis conditions on obtained monomer compounds produced from Kraft lignin.

Table 3 by comparison with the related reference experiments. Significant decrease of coke can be observed for each lignin. The extent of conversion can be shown clearly with Etek lignin. In comparison to the reference experiment the decrease of coke is approximately 75%. This effect is also evident for other lignins. Soda lignin follows with approx. 60%, as well as organosolv- and Kraft-lignin with approx. 30%. Consequently, increasing of the liquid or gas phases can be observed, accompanied with higher amounts of GC-detectable monomers in the liquid product. For each lignin the degradation is characteristic: organosolv- and soda-lignin showed a significant increase of the liquid phase of about 20% and a gas phase without significant variations. Etek- and Kraft-lignin gave higher values for the liquid and the gas phase.

As shown in Fig. 8 qualitative and quantitative variations in the liquid phase exist. Kraft lignin gives significant rearrangements from benzenes and phenols to guaiacols. Additionally, influences can be observed by comparing VOCs from Etek lignin pyrolysed in

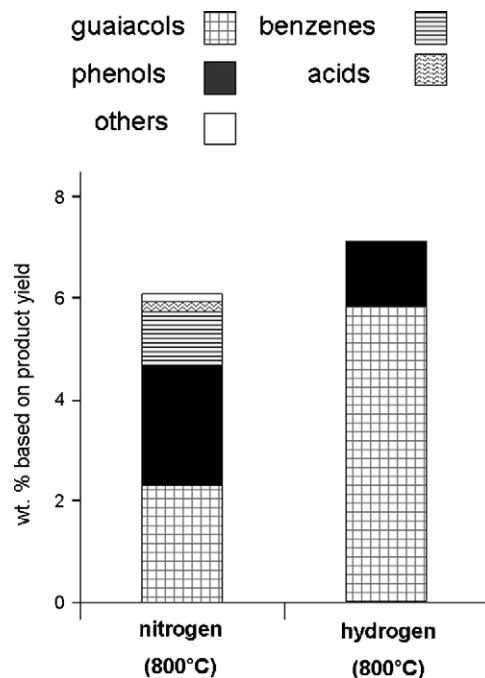


Fig. 8. Influences of hydrogen atmosphere on obtained monomer compounds produced from Kraft lignin.

hydrogen. An overlay of the related pyrograms is shown in Fig. 9. The lower relative peak area for the pyrolysates obtained under hydrogen is evident. Therefore, their quantitative amount should be small and higher amounts of permanent gases can be assumed. With the exception of some small peaks in the fraction obtained under hydrogen atmosphere, qualitative reproducibility of the peaks is satisfactory. Additionally, methylene chloride (DCM) and chloroform were detected in the hydrogen pyrogram of the Etek lignin. Under the influence of hydrogen these compounds were also detectable in the gas phase of soda lignin.

From literature [22], approx. 0.5 wt.% of chlorine can be assumed for annual plant feedstocks, which have been used in the Etek and soda process. Also the release of chlorine-based

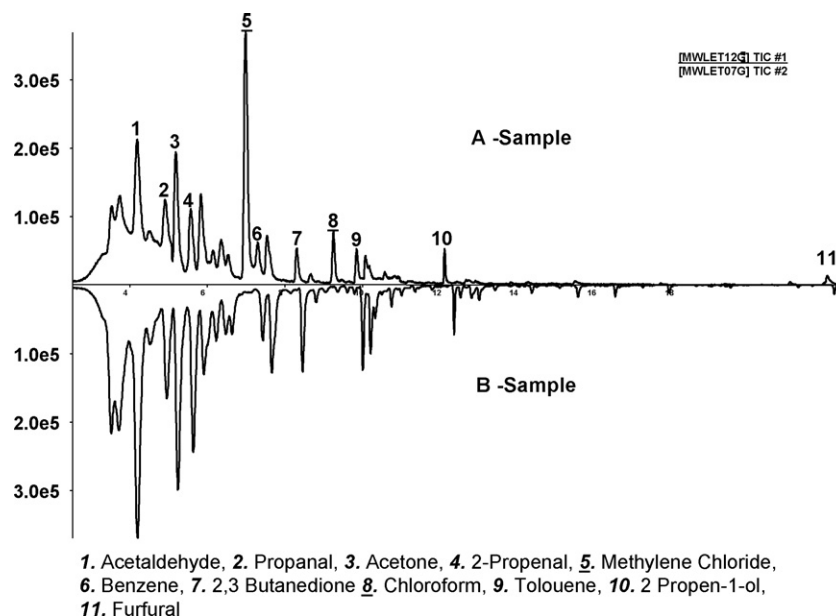


Fig. 9. GC-MS overlay of pyrograms obtained under different atmospheres.

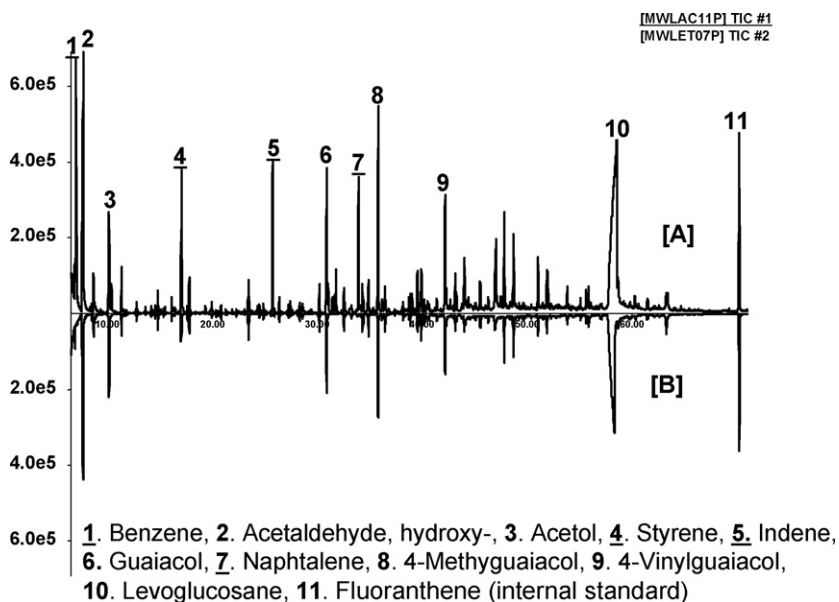


Fig. 10. GC-MS overlay of pyrograms obtained under different atmospheres (N_2/C_2H_2).

compounds (HCl) in combustion processes is well known and the behaviour of gaseous chlorine in biomass thermal utilisation has been studied [22]. Indications for formation of DCM and chloroform in biomass pyrolysis processes were not found in literature.

3.3.2. Nitrogen/acetylene mixed atmosphere

Acetylene is believed to be a precursor of polycyclic aromatic hydrocarbons (PAHs) and soot in the pyrolysis and combustion of various hydrocarbons [23,24]. The first experiment on the pyrolysis of acetylene was performed by Berthelot in 1866 cited in [24]. Since then, various devices have been used to study this reaction. The reaction mechanism at temperatures above 1500 K is classified as a free radical process, while that below 1500 K remain a subject of controversy. Free radical mechanisms were proposed because of observations of auto-acceleration and the inhibition of

this reaction by nitric oxide, a known scavenger of free radicals [24]. Acetylene is also an important reactive intermediate in the fast pyrolysis of cellulose char [25].

The question remains whether there exist effects between the lignins and acetylene intermediate pyrolysis products. First a simple preliminary pyrolysis (fast pyrolysis at 800 °C) of pure acetylene was carried out. A main reaction, which was indicated by means of visible aerosols, started at 700 °C. Benzene and toluene were detected as main compounds in the VOC phase, while aromatics, such as styrene, indene, naphthalene and PAH compounds were detected in the liquid phase.

Consequently, some experiments with Etek lignin were performed with an admixture of acetylene (10 vol.%) in the carrier gas (N_2). The top pyrogram (A) in Fig. 10 shows the GC-MS/FID results of the liquid phase. For the sake of comparison the

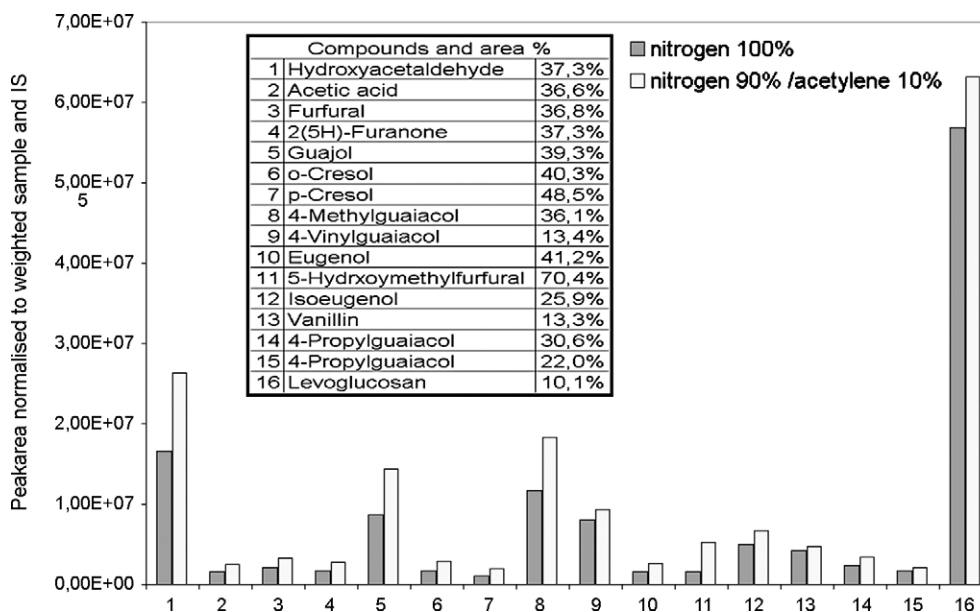


Fig. 11. Normalised abundance from selected peaks.

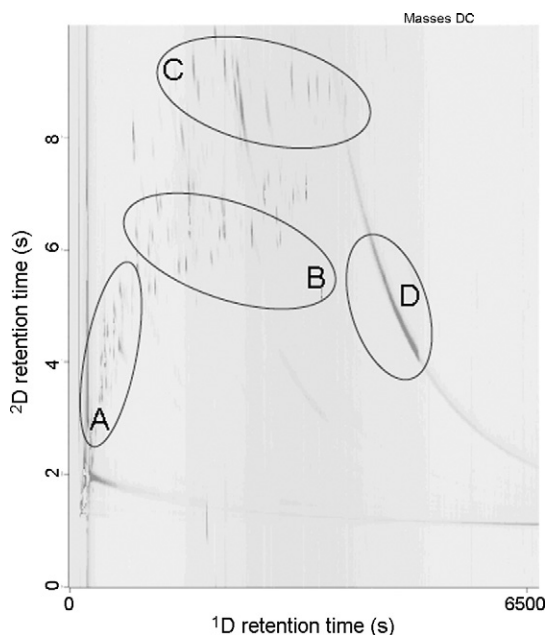


Fig. 12. Contour plot of the liquid pyrolysis fraction of Etek lignin with group type retention time fields A (aldehydes/ketones), B (phenolics), C (guaiacols and syringols), and D (sugars).

pyrogram (B) below demonstrates the liquid phase from Etek lignin in pure nitrogen atmosphere. With the exception of some aromatics (styrene, indene, naphthalene, etc.), the results concur qualitatively. Obviously, the acetylene admixture has some quantitative effects.

From the pyrograms some compounds were selected. Fig. 11 shows peak areas of these selected compounds (GC–MS/FID) normalised to the sample weight and the area of the internal standard. The deviation is presented in the associated table of Fig. 11.

The peak area of the pyrolysates obtained in the admixed acetylene atmosphere increased by 40%. A possible explanation could be the scavange of free radicals in pyrolysates from both lignin- and acetylene-preventing recombination reactions between the lignin-derived products. Thus, effects between the radicals were detectable with the modular pyrolysis rig giving options to further study reaction mechanisms.

3.4. Qualification with GC × GC

When dealing with complex samples, it is often impossible to separate all of them using any single separation dimension. This has driven the development of techniques that rely on multiple dimensions. The relative new method of comprehensive two-dimensional chromatography [26,27] and time of flight mass spectrometry (GC × GC–TOFMS) was used for additional screening of some pyrolytic liquid fractions to identify unknown components. The sample components are separated in a two-dimensional retention time area (contour plot) by GC × GC and some 25% additional components could be identified by this technique based on their mass spectra.

A special feature of the GC × GC contour plot is found in the overview of structured data. Homologue components are collected in specific retention time area of the contour plot based on boiling point separation on the x-axis and polarity separation on the y-axis. In this way, the contour plot provides a quick overview of the group type of components in a sample [28]. In Figs. 12 and 13 the contour plots of, respectively, a pyrolytic lignin and Etek lignin are shown. By the group type

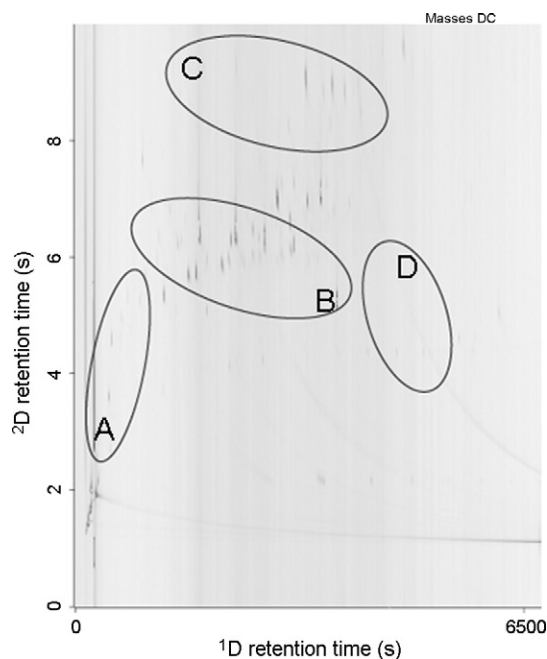


Fig. 13. Contour plot of the liquid pyrolysis fraction of pyrolytic lignin with group type retention time fields A (aldehydes/ketones), B (phenolics), C (guaiacols and syringols), and D (sugars).

classification of A (aldehydes and ketones), B (phenolics), C (guaiacols and syringols) and D (anhydrosugar, levoglucosan) it can be seen that Etek lignin (Fig. 12) is rich in aldehydes/ketones and guaiacols/syringols, while the pyrolytic lignin (Fig. 13) lacks of sugars/levoglucosan. These results correspond to the data obtained in Fig. 5.

Finally, it can be stated that the micro-offline pyrolysis rig as defined in this study offers various options of combined research. By using several analytical techniques it was demonstrated that the entire pyrolysate fractions could be studied.

4. Conclusions

This work presents a new offline micro-pyrolysis method and apparatus to provide samples for complete analysis of all reaction products. The experimental set up is made of customarily available products and offers a low-cost alternative. The modular pyrolysis rig proved to be a versatile instrument for slow, intermediate and fast pyrolysis. It serves to obtain representative samples of the gas, liquid and solid pyrolysate fractions for quantitative and qualitative analysis of products. From the series of experiments the following conclusions can be drawn:

- Approximately 17 wt.% of the pyrolysate can be quantified by GC.
- Influence of hydrogen and acetylene is significant.
- Influence of the heating rate and temperature is measurable.
- Accessory pyrolysis components can be analysed.

The 2D GC method provides contour plots to allow for fast screening of different functional groups. Still parallel detection of mass spectrometry and flame ionisation detection is favourable for quantification.

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