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Study on low mass thermal degradation products of milled wood lignins by thermogravimetry-mass-spectrometry

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Summary. Thermogravimetry-mass-spectrometry (TGMS) as a sophisticated analytical instrument is described for the thermal analysis of milled wood lignins from spruce (*Picea abies* L.), beech (*Fagus sylvatica* L.) and bamboo (*Bambus* sp.). The samples were heated on the thermobalance in an inert gas atmosphere (Ar) with 20 °C/min heating rate.The weight loss curves (TG) and their 1st derivatives (DTG) were recorded. The evolution of 10 low mass degradation products with m/z below 44 was monitored as a function of the temperature by means of a quadrupol mass spectrometer. Thus the intensity profiles of H_2, $CH_3^{\bullet}$, H_2O, CO, $CHO^{\bullet}$, HCHO, $CH_3O^{\bullet}$, CH_3OH, $CH_3CO^{\bullet}$ and CO_2 were recorded and interpreted in terms of lignin structure and the course of carbonization. The results are in agreement with the results of differencial scanning calorimetry (DSC) and pyrolysis-gas-chromatography mass-spectrometry (PyGCMS) of the phenolics.

Introduction

Modern concepts for wood utilization require a separation of cellulose, hemicelluloses, and lignins as the major wood components because each of them has its special potential use. Thermal degradation studies are also frequently carried out separately on the major components for the sake of simplicity, as there are several hundreds of thermal degradation products of wood detectable with modern analytical instruments. Wood behaves during thermal degradation approximately as if it were a mixture of cellulose, hemicelluloses and lignin (Eickner 1962; Stamm 1962), thus, this analytical approach is recommendable. Frequently the burning and pyrolytic behavior of lignins is in the focus of interest because lignins as by-products of pulping processes are traditionally burned together with other organic residues in order to recover inorganic cooking chemicals and to improve the energy balance of the process. Many publications deal with lignin pyrolysis. Most of them describe the GC separation of phenolic products. In the last decade PyMS and PyGCMS studies gained in importance. Besides, results of DTA and DSC analyses were also described (Arima 1973; Nassar and MacKay 1984; Reh et al. 1986). Nguyen et al. (1981 a, b) give a review on thermal analysis of lignocellulosics. PyGCMS is without doubt the most appropriate method for the identification and (semiquantitative) determination of stable lignin degradation products with molecular weights higher than 50 Daltons. The study of the low molecular weight degradation products in relation to the temperature needs, however, special equipment and implies special difficulties because the thermal degradation leading to gas products is a rapid, complex and heterogeneous process. In the recent literature there are no reports about this subject. There is a gap in our knowledge with regard to pyrolysis products from lignins in the low mass range, although gases and volatiles represent up to 30% of pyrolysis and hydrogenolysis products. This paper adresses this field of lignin thermodegradation.

The TGMS method was applied for the problem solution. In this technique a thermogravimetrical balance (TG) is coupled with a mass spectrometer (MS). The substance on the TG balance is continually purged with an inert or reactive gas. The experiments are carried out isothermally or the sample is heated with heating rates between 0.5–200 °C/min. The weight loss is recorded in dependence to the time and/or temperature. Chauvette et al. (1985) and Grandmaison et al. (1987) demonstrated recently the analytical power of TG for analysis of lignocellulosics. In a TGMS equipment the volatile substances are monitored synchronously to the time elapsed or to the temperature. Their amount can be related to the weight loss curve. For the mass spectrometrical identification it is important that the substance in question gives rise to a typical mol mass (or mass fragment). This prerequisite is fulfilled best for low molecular weight substances. TGMS provides in the first place kinetical information, but after calibration quantitative data can also be obtained. The consideration of the intensity profiles from products with low boiling points is very important for answering the following, or similar questions: Which oxygen containing substances – besides phenolics – leave the biomass heated? How is the relation of CO/CO_2? At which temperatures does the evolution of water, formaldehyde, formic and acetic acid occur? Which thermal demethoxylation characteristics display lignins? How much hydrogen can be obtained by heating lignins?

Milled wood lignins (MWL's) from spruce, beech and bamboo were investigated. These samples represent a wide variety of lignin types, the so-called G, GS, and HGS lignins, and are well described in the literature. (The abbreviations H, G, and S refer to the presence of 4-*h*ydroxy-phenylpropane, *g*uaiacylpropane and *s*yringylpropane units in the lignin macromolecule.) These lignins were already characterized by PyGCMS (Faix et al. 1987a, b). To complete the thermoanalytical characterization differencial scanning calorimetry (DSC) curves were additionally recorded.

Material and methods

Milled wood lignins (MWL) were isolated by the standard procedure described by Björkman (1956). Elemental analysis data, calorific values, C_{900} formula and the composition of the lignins from the basic units with H, G and S structure are presented in Table 1. The calorific values were calculated by Dulong's formula (Boocock and Mackay 1980) and the basic units by means of IR spectroscopical data as described by Faix (1987).

ATGMS instrument developed by the Hungarian Academy of Sciences, Budapest was used (Székely et al. 1980; Várhegyi et al. 1986). Here, only the most important data are compiled. TG: a reconstructed Perkin-Elmer TGS-2 with microprocessor controller system no. 4. Weight max.: 5 g; in our experiments: Spruce MWL 3.25 mg, beech MWL 2.92 mg, bamboo MWL 2.05 mg. Sensitivity: 0.5 µg. Vol. of the bal-

Table 1. Analytical data of three MWL's

Sample	Elementary analysis				Calorific value (1)	C_{900} formula				Basic units Mol-% (2)			Yield of phenolics (3)
	%C	%H	%O	%OMe	KJ/kg	C	H	O	OMe	H	G	S	%
Fagus sylvatica beech MWL, I	61.09	5.97	32.94	22.04	23,333	900	779	277	146	0	54	46	18.4(4)
Bambus sp. bamboo MWL, II	62.54	5.69	31.76	16.60	23,630	900	778	279	103	20	67	13	13.2
Picea abies spruce MWL, III	62.79	5.88	31.32	15.79	24,069	900	821	276	97	3	97	0	16.2

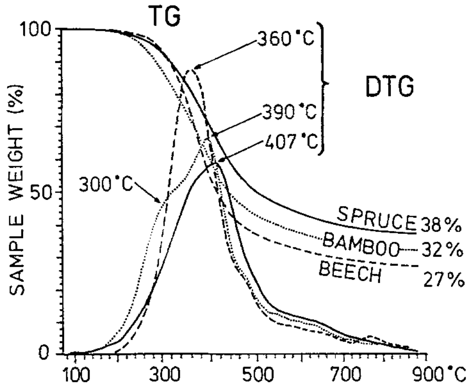
Structural details about the MWL's are published: I: Nimz (1974); II: Shimada (1972); Nakamura, Higuchi (1976); III: Freudenberg (1968); (1) according to Dulong's formula as quoted by Boocock and Mackay (1980); (2) according to Faix (1987); (3) according to PyGCMS studies of Faix et al. (1987 a, b); (4) Photoionization MS of this lignin was described by Genuit et al. (1987)

ance chamber: 60 ml. Purge gas velocity: 50–350 ml/min; in our experiments: Ar 140 ml/min. Temp. range: 20–900 °C. Temp. accuracy: 5 °C. Heating rate: 0.3–200 °C/min; in our experiments: 20 °C/min. Coupling with a mass spectrometer: in two steps by means of a heated glass lined capillary (l = 800 mm, 0.3 mm I.D.) and a pre-chamber with 1.3 mbar pressure. MS: Balzers QMG 511 quadrupol mass spectrometer, mass range 1–511 m/z. Electron energy: 70 eV.

The MWL's were characterized additionally by DSC. For the better comparability the same heating program was applied as in the case of TGMS analyses. (Nassar and MacKay 1984 pointed out, that the heating rate severely influences the DSC – and other thermoanalytical – data.) A Mettler TA 3000 with a DSC 20 standard cell controlled by a TC 10A processor was used. Temp. range: 20 to 600 °C. Flushing gas: N_2, 70 ml/min. 3 to 5 mg of a sample were heated in a standard aluminium vessel. Each experiment was repeated at least twice. The results are depicted in Fig. 2.

Results and discussion

Figure 1 is a plot of the weight loss of the three samples vs. the temperature of decomposition (TG curve). As this Figure demonstrates, spruce MWL left 38%, bamboo MWL 32% and beech MWL 27% charcoal residue when heated in an inert Ar atmosphere at a heating rate of 20 °C/min to 900 °C. The first weight loss begins between 180 and 200 °C. The highest weight loss rates can be observed between 360 and 407 °C. An important help to notice sample specific differences is the first derivative (DTG) of the weight loss curve. These are drawn in Fig. 1, too. The DTG curves complete the implications of the TG curves and demonstrate unequivocally that thermal weight loss behaviour of the lignins is different. Bamboo MWL decomposes up to 300 °C at the highest rates. Beginning from this temperature beech MWL shows the highest and spruce MWL the lowest decomposition rates. The maxima of the



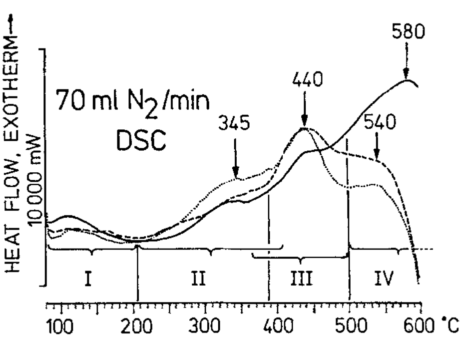


Fig. 1

Fig. 2

Fig. 1 and 2. Thermogravimetry (TG), differencial thermogravimetry (DTG), and differencial scanning calorimetry (DSC) curves of MWL's from spruce, bamboo and beech. Heating rate: 20 °C/min

DTG indicate different temperatures for the highest velocity of degradation: 360 °C (beech), 390 °C (bamboo), and 407 °C (spruce). From then on the degradation rates slow down. An additional shoulder on the DTG curve of bamboo MWL at 300 °C demonstrates that from this point on other kinds of degradation mechanisms have the preponderance.

The DSC curves in Fig. 2 display substance specific peculiarities. The graphics can be subdivided roughly in four sections: the first one between 100 an 200 °C is weakly endotherm. Adsorbed gases and traces of water are lost; in magnified sections of this range glass transitions between 150 and 170 °C can be observed. The exothermic reactions between 200 and 400 °C in section II have weak maxima at 345 °C or a shoulder (beech). In this low temperature range the reactions of bamboo are more exothermic than those of beech and spruce. In section III with maxima around 440 °C bamboo and beech MWL's display a maximal heat flow in similar order of magnitude, whereas spruce MWL develops a maximum of energy release in section IV at 580 °C. In this range beech and especially bamboo MWL already show decreasing heat flow curves with shoulders around 540 °C. Summarizing the similar tendencies of DSC and TG analysis it can be stated: bamboo and beech MWL develop more exothermic heat flow at lower temperatures and display higher weight losses than spruce MWL. The latter needs higher temperatures for a profound degradation.

The oxygen content of the lignins has certainly an influence on their thermodegradation characteristics; Chow (1972) stated that the pyrolysis of wood at low temperatures is likely to be controlled by an oxydative step. Beech and bamboo MWL contain 1.1 to 1.6% more oxygen than spruce MWL. This fact, however, can only partly explain the higher degradation rates in the low temperature range.

Our knowledge on the structure of the lignins investigated permits a rough interpretation of these results. The presence of thermolabile ester linkages in bamboo MWL may explain the rapid decomposition at lower temperatures. The lower temperature maximum of 47 °C for the highest decomposition rate for beech MWL in comparison to spruce MWL can be interpreted by the presence of syringyl units in the former. Syringyl as well as the guiacyl units are built into the lignin macromolecule mainly by alkyl-aryl ether linkages (β-0-4 bonds). In beech lignin 60–65% and in spruce lignin 50–55% β-0-4 linkages are likely (Freudenberg 1968; Nimz 1974). However, it is a well known fact, that β-0-4 linkages between syringyl units are easier to split than those between guiacyl units.

Domburg et al. (1974) investigated the thermal stability of the β-ether bonds in lignins and its models and also came to the conclusions: alkyl-aryl ether bond stability is higher in coniferous lignins than in decideous ones. The influence of the side-chain structure on the thermal stability was also stressed by these authors.

PyGCMS studies on G and GS lignins as well as on different model compounds at different temperatures corroborate: syringol and syringaldehyde and other S phenolics are found in higher quantities among the low temperature pyrolysis products than the corresponding degradation products from guaiacylpropanes (Faix et al. 1988). Guaiacol type phenols easily undergo ionic condensation and under pyrolytic conditions mainly radical coupling reactions on the aromatic ring in orto or meta position to the phenolic OH groups. Such condensation products remain in the high boiling tar fraction or in the solid coal residue. The consequences are: lower yields on monomeric phenolics and higher coal residues in the case of G lignins. From this point of view it is not surprising that the amount of coal residue from bamboo MWL with a S content of 13% is between those of beech (46% S) and spruce (0% S) MWL's. The higher degradability of bamboo MWL at the onset of pyrolysis can be explained by the rupture of thermolabile ester and ether bonds, including those of syringylpropane units. The process slows down during the degradation of G and H units, which show a higher tendency for condensation reactions.

The question arises whether these sample specific degradation patterns are also visible considering the degradation products with low molecular weights.

To answer this question the intensities of 10 ions with masses below 44 m/z are plotted in Figs. 3–11 vs. the degradation temperature. In Table 2 the integrals of the same products are listed in the order of increasing m/z masses. It should be born in mind, however, that in this study more than 100 ions were monitored simultaneously during the thermal degradation. The consideration of these ions such as the quantitative evaluation was beyond the scope of this paper. The data in these Figures and in Table 2 can only be used for comparisons of the three lignins in question. Quantitative data are not yet available. The identification of these ions is based on literature data (e.g. Cornu, Massot 1966) and on chemical consideration of the lignin structure. In a few cases other minor compounds may also have contributed to the intensity of a m/z values reported in the Figures and Tables. E.g. in the following ion pairs with identical masses the product first mentioned is more important for the interpretation of lignin degradation than the second one: $CO/C_2H_4^{\bullet}$, $CHO/C_2H_5^{\bullet}$ and $CH_3CO^{\bullet}/C_3H_7^{\bullet}$. Moreover, one should be aware of the fact that thermal splitting and splitting in the ion source cannot be differentiated by the method used in this work.

Figure 3 demonstrates that the evolution of hydrogen occurs in two steps. The maxima of the first dehydrogenation at low temperature are between 440 and 480 °C. These show highest intensities between 15 to 20 on the arbitrary intensity scale. The origins are probably hydrogen atoms from –OH, –OOH groups, and side chains. Clear-cut minima at 540 °C and steeply increasing H_2 intensities above this tempera-

Table 2. Low mass thermal degradation products of MWL's and their integral values (arbitrary units) as determined by TGMS (Figs. 2–11)

m/z		Formula of probable fragments	Integral values		
			beech MWL	bamboo MWL	spruce MWL
1	2	H_2	23,175	20,775	22,103
2	15	$CH_3^{\bullet}$	1,550	2,450	2,170
3	18	H_2O	3,750	4,500	4,750
4	28	CO	1,025	1,450	1,870
5	29	$CHO^{\bullet}$	1,025	1,300	975
6	30	HCHO	245	425	300
7	31	$CH_3O^{\bullet}$	450	450	237
8	32	CH_3OH	275	140	88
9	43	$CH_3CO^{\bullet}$	18	20	10
10	44	CO_2 and/or CH_3CHO	1,250	1,325	900

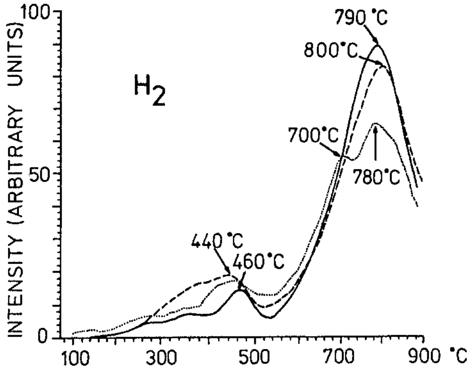


Fig. 3

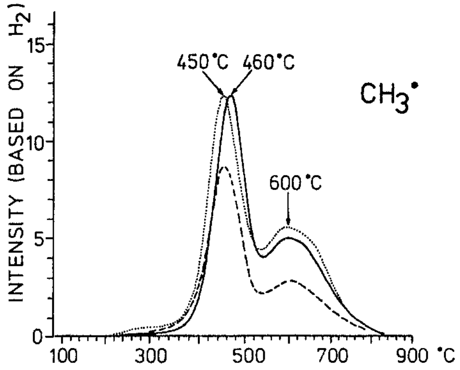


Fig. 4

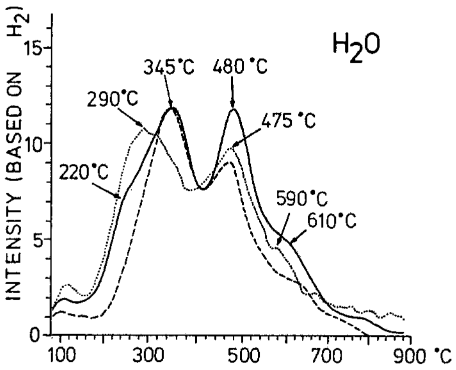


Fig. 5

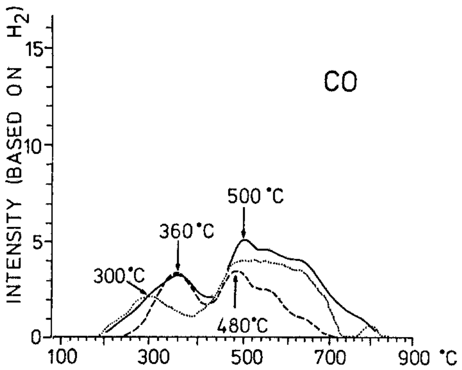


Fig. 6

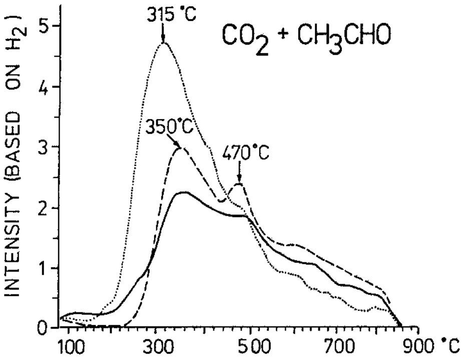


Fig. 7

Figs. 3–7. Intensity of low mass thermal degradation products from MWL's plotted vs. the degradation temperature. —— spruce MWL; ---- beech MWL; ..... bamboo MWL ture indicate the start of dehydrogenation of aromatic rings. This point is also the onset of real carbonization, i.e. the last step of pyrolysis giving rise to charcoal residues deprived of hydrogen, after the majority of oxygen having been removed in previous deoxygenation steps. The temperature maximum of this process is at 780–800 °C and intensities between 65 (bamboo) and 85–90 (spruce and beech) can be observed. Bamboo shows also a maximum at 700 °C. Here are also sample specific differences; beech and bamboo evolve more H_2 than spruce in the low temperature range.

The temperature dependence of the formation of $CH_3^{\bullet}$ radicals, which are most likely the EI ionisation products of methane, also display two maxima: the first one with high intensities between 450 (beech and bamboo) and 460 °C (spruce), and a second one at 600 °C with lower intensities. Figure 4 and the corresponding integral values in Table 2 reveal that beech MWL develops less methane (and methyl radicals) than the other two samples. Thermal fragmentation of the side chains to $CH_4/CH_3^{\bullet}$ is probably the main source of this product below 500 °C. This assumption is in agreement with the observation that the evolution of sidechain-less methoxyphenols (not shown here) occurs in the same temperature region. Demethylation of the methoxyl groups can also contribute to a small extent to the intensities in this temperature range. Beginning with 500 °C the rupture of aromatic rings starts, which also gives rise to methyl radicals. The evolution of hydrogen also begins at this temperature indicating the initiation of profound degradation and rearrangement reactions.

Very informative is the intensity profile of water splitting-off reactions in Fig. 5 because water-removing probably leads to condensation products, i.e. to new carbon to carbon linkages. Four intensity maxima or shoulders can be observed: around 290 °C (bamboo, spruce), 345 °C (spruce, beech), 475 to 480 °C (all samples) and 590 to 610 °C (low intensity shoulders of all samples). Spruce MWL released the most reaction water (Table 2). This sample also lost more water in the temperature range around 480 °C than the others. It can be concluded that dehydratation reactions start earlier in the case of lignins rich in guaiacylpropan and 4-hydroxyphenylpropan units. This may be the first sign of the higher yields of carbonized residues at the end of the process (e.g. spruce and bamboo MWL).

Thermal splitting of CO_2 and CO belongs to the reactions which diminish the oxygen content of the charcoal residue (Figs. 6 and 7). The relative amounts of these gases are in the same order of magnitude in the case of beech and bamboo MWL's, whereas spruce MWL forms more CO than CO_2 (Table 2). Both gases are split off from bamboo MWL at lower temperatures (maxima at 300 and 315 °C) than from the other two lignins (with maxima at 360 and 350 °C). This is the consequence of the thermal degradation of the numerous carboxyl, carbonyl, and ester groups in bamboo MWL. The carbon monoxide development shows an anew increase after a minimum at 430 °C with a maximum at 480 to 500 °C. Contrary to the CO evolution, the carbon dioxide development in the high temperature range beginning from 450 °C is in general less intense than in the low temperature range.

HCHO in Fig. 8 and its main fragment ion $CHO^{\bullet}$ in Fig. 9 have of course the same origin. Therefore, it is not surprising that both curves in these Figures are very similar with their two maxima at 310 to 350 °C and 425 to 450 °C. Again, bamboo gives rise to more formaldehyde than the other samples. This observation is in agreement with the CO and CO_2 evolution. $-CH_2OH$ groups in gamma positions on

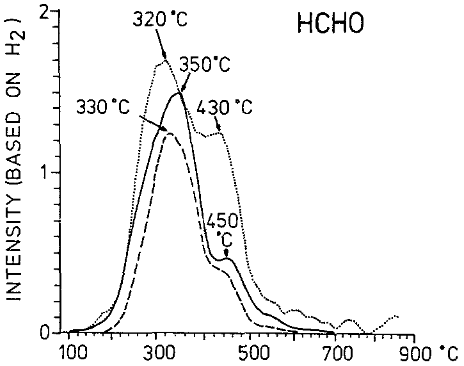


Fig. 8

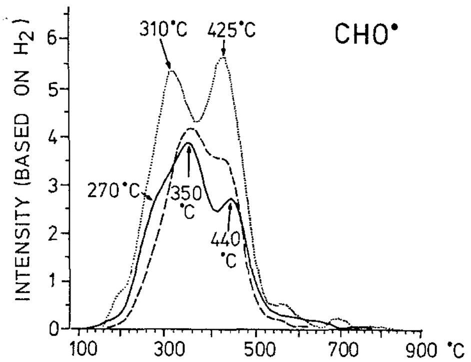


Fig. 9

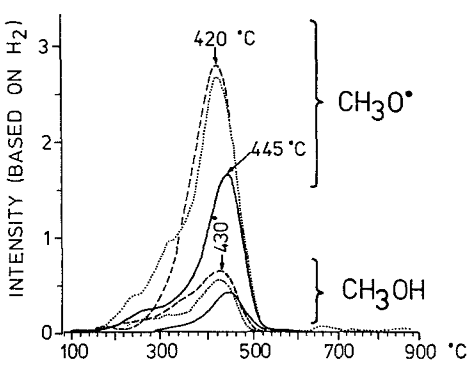


Fig. 10

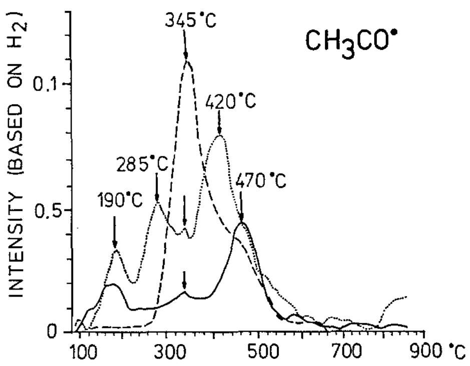


Fig. 11

Figs. 8–11. Intensity of low mass thermal degradation products from MWL's plotted vs. the degradation temperature. —— spruce MWL; ---- beech MWL; ..... bamboo MWL

the side-chain and ester and carboxylic acid groups in the same position are the most probable sources of formaldehyde.

Figure 10 shows the course of the thermal splitting of methanol by presenting the intensities of m/z 32 and m/z 31 ($CH_3O^{\bullet}$) fragments. The maxima of the $CH_3O^{\bullet}$ ions are at 420 (beech and bamboo) and 445 °C (spruce) and those of CH_3OH very close by at 430 (beech and bamboo) and 450 °C (spruce), respectively. The temperature profile of bamboo lignin shows an onset of $CH_3O^{\bullet}$ development with higher intensities between 200 and 300 °C than in the case of spruce and beech lignins. This can be related to the presence of thermolabile functional groups in bamboo MWL which gives rise to $CH_3O^{\bullet}$ more easily than the aromatic OCH_3 groups. Nevertheless, the aromatic methoxyl groups are the main source of $CH_3O^{\bullet}$ fragments besides $-CH_2OH$ groups in gamma position. For a quantitative consideration it should be born in mind that $CH_3O^{\bullet}$ is the main ionization fragment of methanol but this ion is also a general fragment of many other compounds such as higher alcohols, esters and ethers. It is understandable that the intensities of these fragments in Fig. 10 are approx. in the same proportion as the fragment intensities of m/z 31 to m/z 32 in the mass spectrum of methanol. Summing up the integrals of the masses 31 and 32 in Table 2 one gets values for beech, bamboo and spruce (725, 590 and 325) whose ratios (2.2/1.8/1) only reflect roughly the "true" methoxyl ratios (1.5/1.06/1). The reasons for this discrepancy are obvious after the discussion above.

The fragments with m/z 43 ($CH_3CO^{\bullet}$) reveal very different intensity profiles (Fig. 11). This ion is likely to be formed in the ion source from various acetyl compounds (e.g. acetic acid, acetone, methyl acetate). The identification of the main original compounds is not possible due to the low intensity of molecule masses. The intensity profile demonstrates that 5 distinct maxima are possible: at 190, 285, 345, 420 and 470 °C. Bamboo MWL shows 3 higher maxima at 190, 285 and 420 °C, with increasing intensities in the same order. Beech MWL has essentially one broad and high maximum around 345 °C, whereas spruce MWL display maxima at 190 and 470 °C. The last one has double intensity to the former. Again, spruce MWL has its highest maximum in the high temperature range.

Table 3 summarizes the results of TGMS analysis described above for the low temperature range below 500 °C. In general spruce MWL show maxima at higher temperatures than beech or bamboo MWL's. The degradation profiles of bamboo MWL display maxima at lower temperatures than those of beech and spruce MWL.

Conclusions

The results in this paper show that TGMS could play an important role for the thermoanalytical characterization of lignocellulosics. By analyzing the MWL's of bamboo, beech and spruce it is demonstrated to which extent different TGMS results can be expected for characterizing lignins. These lignins have very different structures and therefore clear sample specific differences can be observed by means of TGMS analyses with regard to weight loss rates, final weights of charcoal and the intensity

Table 3. Temperature maxima (°C) of DTG curves and intensity profiles of MS fragments by TGMS experiments from MWL's in the low temperature range

m/z	Formula of probable fragments	Temperature max. below 500 °C		
		bamboo MWL	beech MWL	spruce MWL
DTG		300+390	360	407
2	H_2	440	440	460
15	$CH_3^{\bullet}$	450	450	460
18	H_2O	290	290+345	345
28	CO	300	360	360
29	$CHO^{\bullet}$	315	350	350
30	HCHO	420	330	350
31	$CH_3O^{\bullet}$	420	420	445
32	CH_3OH	430	430	450
44	CO_2 and/or CH_3CHO	315	350	350

profiles of 10 degradation products with low masses. Bamboo MWL displays higher weight loss rates at lower temperatures than the other two lignins. Spruce MWL has its maximal weight loss velocity at the highest temperatures. The knowledge on the intensity profiles of the degradation products with low masses is very valuable for the better understanding of thermochemical degradation processes. E.g. the beginning of H_2O splitting-off rections indicate the start of condensation reactions; thermolabile carboxyl, carbonyl and ester groups give rise to evolution of CO_2 at lower temperatures; the total amount of methanol and $CH_3O^{\bullet}$ ions is in relation to the amount of methoxyl groups; the charcoal formation is accompanied by an increased H_2 splitting-off reaction; the rupture of aromatic rings can be recognized on the development of $CH_3^{\bullet}$ ions in the higher temperature range. The TGMS data complete the results of DSC analyses and those of PyGCMS studies on the phenolic degradation products in an ideal manner. The continuation of these studies with additional parameters – such as other lignin samples, different heating rates, using reactive gases instead of inert gas etc. – is to be recommended.

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