Journal of Analytical and Applied Pyrolysis 113 (2015) 123–132; http://dx.doi.org/10.1016/j.jaap.2014.11.016

Pyrolysis of wood – PVC mixtures. Formation of chloromethane from lignocellulosic materials in the presence of PVC

Zsuzsanna Czégény*, Emma Jakab, János Bozi, Marianne Blazsó

Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H1117-Budapest, Magyar Tudósok körútja 2, Hungary; tel: +36-13826510

czegeny.zsuzsanna@ttk.mta.hu; jakab.emma@ttk.mta.hu; bozi.janos@ttk.mta.hu; blazso.marianne@ttk.mta.hu

Abstract

Thermal decomposition of polyvinylchloride (PVC) – wood and wood component mixtures were examined under slow and fast heating by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and thermogravimetry/mass spectrometry(TG/MS) techniques in order to clarify the chemical interaction of biomass materials and PVC during thermal decomposition. A hardwood and a softwood (beech and pine), their lignin and two types of cellulose (Avicel and Whatman) were chosen as natural polymer components. Comparing the gaseous and liquid pyrolysis products of pure samples to those of mixtures it was found that considerably lower amount of several reactive compounds have been produced when the biomass sample was mixed with PVC. On the other hand significant amount of chloromethane appeared in the pyrolysate of wood and lignin samples mixed with PVC under fast and slow pyrolysis conditions as well, but only in traces of chlorinated organic compounds were detected from cellulose mixtures. It was concluded that the methoxy groups at phenolic rings in lignin are the methyl source of chloromethane formation, and this reaction consumed most of the HCl evolved from PVC.

Keywords: *Pyrolysis, PVC, Biomass, Chloromethane*

1. Introduction

Several types of wooden waste, like waste furniture and demolition wood may contain PVC as paint or coating. PVC-based wood flour composites are widely used in building applications like decking, doors, wall panel, etc. At the end of their life-cycle the reutilization of these materials is also an important issue and pyrolysis is a possible route of feedstock recycling. Being both PVC and biomass fiber thermally sensitive, an improved knowledge on the decomposition process of their mixture could be of interest for the users and manufacturers as well. The municipal waste is also a multicomponent mixture, containing paper, wood and plastics (including PVC), which cannot be separated economically. Conversion of biomass and waste plastics into fuel represents a feasible way for recovering the organic content of polymeric waste.

PVC contains chlorine at every second carbon atom in the polymer chain. It is well known that hydrogen chloride is eliminated from PVC at around 300 °C [1-3], and benzene is also formed during this first thermal decomposition step. The evolved hydrogen chloride often catalyses the decomposition of other synthetic polymers in plastic wastes [4-7], however, the presence of other polymers or inorganic salts also modify the dehydrochlorination step of PVC [8-11]. Significant effects of PVC have been observed on the thermal decomposition of natural polymers as well. From cellulose the amount of hydroxyl group containing volatile pyrolysis products are strongly reduced when co-pyrolysed with PVC, while that of carbonyl and unsaturated group containing ones are increased in the char. These effects and the enhanced char formation have been attributed to dehydration and charring by HCl evolved from PVC [12]. Dehydrochlorination of PVC and decomposition of hemicellulose and cellulose components of wood occur in the same temperature interval. It is known that the acid-catalyzed pyrolysis or acidic pretreatment promote the formation of levoglucosenone from cellulose, while hinder the formation of levoglucosan [13-14]. The influence of PVC on the cellulose derived products of wood was found to be analogous to that on pure cellulose. Significantly reduced HCl emission was found by Kuramochi and co-workers [15] during pyrolysis of wood or wood components when mixed with 1 wt% of PVC. It was concluded that hemicellulose fixed HCl in the char. For cellulose and hemicellulose – PVC mixtures acceptable chlorine balance has been obtained, but it was considerably incomplete for wood- and lignin – PVC mixtures. This observation was explained by assuming formation of low-molecular organic chlorides emitted in to gas. Nevertheless, the emitted gas has not been analyzed completely (only HCl has been measured). Suppressed HCl formation was found as well from municipal solid waste by Ren et al. [16] in the presence of cotton stalk.

Chlorine-containing organic pyrolysis products (1,2-dichloroethane and 1-(chloromethyl)-2-methylbenzene) were detected in the pyrolysis oils of PVC – cellulose and PVC – lignin mixtures produced in a semi-batch process [17]. Dehydrochlorination of PVC is promoted by cellulose and hemicellulose components of wood. It was supposed that the acidic products of cellulose (formic acid, acetic acid) initiate HCl elimination from PVC [18]. Evolution of methyl chloride was detected among the decomposition products of wheat straw and energy grass of high inorganic chloride ion content (0.2-0.3%) under slow heating in an inert atmosphere by TG/MS method [19].

The aim of the present work is to investigate the thermal decomposition process of wood in the presence of PVC in detail. Special attention is paid for tracing and elucidating the formation of low molecular chlorinated hydrocarbons, moreover understanding the incomplete chlorine balance in the thermal decomposition of wood-PVC mixtures.

2. Materials and Methods

2.1. Materials

Pine and beech wood, pine and beech milled wood lignin and two types of cellulose (Avicel and Whatman) were chosen as natural polymer components. Pine and beech wood samples were cryo-ground in a Retsch MM301 mill, other samples were used as received.

PVC (Vinoflex) powder was obtained from BASF and was used as received.

The composition of wood or wood component – PVC mixed samples were 3:1 by weight. The components of the mixtures were measured directly into the quarz tube (for py-GC/MS) or platinum sample pan (TG/MS) and were mixed carefully with the help of a fine needle. The wood (or wood component) was measured first in each case.

2.2. Methods

2.2.1. Thermogravimetry/mass spectrometry (TG/MS)

TG/MS measurements were performed on a modified Perkin-Elmer TGS-2 thermobalance and a HIDEN HAL 2/301 PIC quadrupole mass spectrometer. Typically 2-4 mg pure or mixed sample was placed into the platinum sample pan and heated at 20°C min^{-1} up to 900°C in a helium atmosphere. A small proportion of the evolved gas and vapor was introduced into the mass spectrometer through a glass lined metal capillary transfer line heated to 300°C. The quadrupole mass spectrometer operated at 70 eV electron energy.

2.2.2. Pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS)

Py-GC/MS measurements were carried out in a CDS Pyroprobe 2000 equipped with a platinum coil and quartz sample tube. About 0.4 mg sample was pyrolyzed at 600°C for 20 s in a quartz tube using helium carrier gas. The pyrolyzer was coupled to an Agilent 6890/5973 GC/MS instrument, the pyrolysis products were separated on an Agilent DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The pyrolysis interface and the GC injector were held at 280°C. The GC oven was programmed to hold at 40°C for 4 min and then increase to 280°C at a rate of 6°C min^{-1}. The mass spectrometer was operated in EI mode at 70 eV, in the scan range *m/z* 14-500 amu. The GC/MS total ion peak areas of decomposition products were related to the sample mass of biomass material in the mixture. Because the peaks of gaseous products are not well separated under the applied GC conditions, peaks areas of molecular or fragment ion chromatograms were used for quantitative comparison of gaseous organic compounds.

3. Results and Discussion

3.1 Fast pyrolysis of wood samples alone and mixed with PVC

Comparing the pyrolysis gas chromatograms (pyrograms) detected by mass spectrometry (Fig.1), considerable differences are observed due to the effect of PVC on the volatile thermal decomposition product distribution of wood samples. In Fig. 1a and Fig. 1c the pyrograms of beech and pine, besides in Fig. 1b and Fig. 1d those of the wood samples mixed with PVC are shown. The decomposition products of PVC such as HCl, benzene, toluene, naphthalene and some other aromatic compounds of negligible amounts are obviously appearing among the components of the pyrolysis products of mixtures. On the basis of the mass spectra of the GC peaks we can distinguish the compounds originating from the cellulose and the lignin components of wood, thus we may draw conclusions on the specific effect of PVC on the macromolecular parts of different chemical composition of wood.

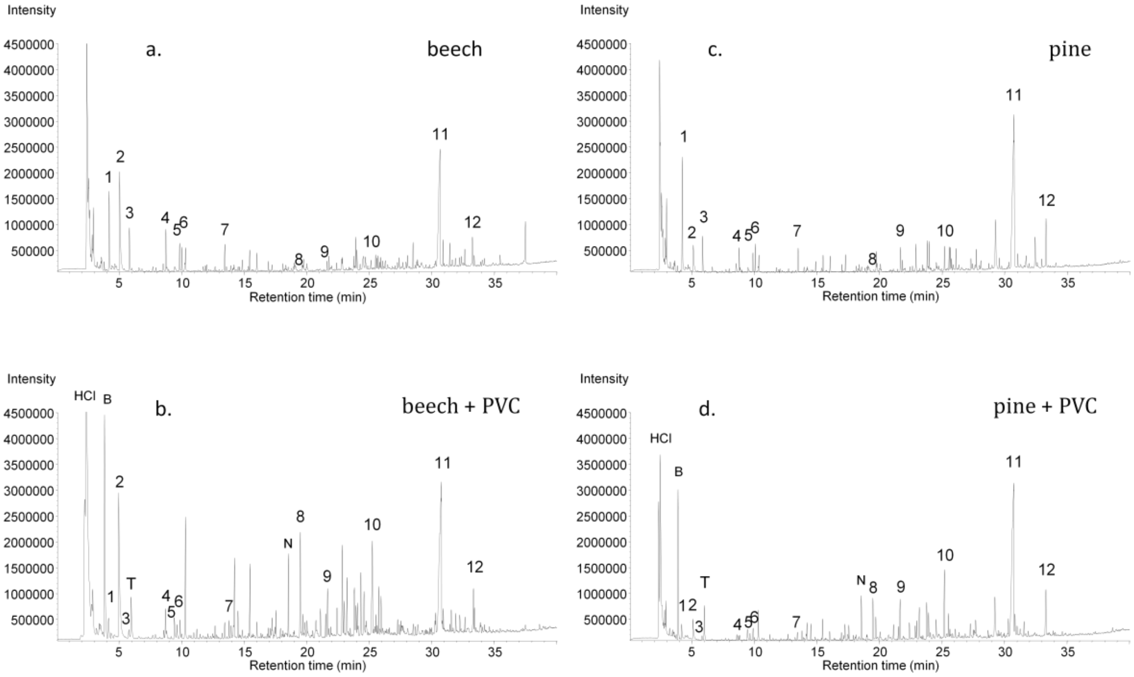


Figure 1. Total ion MS pyrograms of (a) beech, (b) beech and PVC mixture, (c) pine, and (d) pine and PVC mixture. Peak numbers correspond to those in Fig. 2. Peak labeled by letters are indicating hydrogen chloride, benzene, toluene and naphthalene (HCl, B, T, and N, resp.).

3.1.1 Cellulose derived pyrolysis products of wood and wood-PVC mixture

The main thermal decomposition products of cellulose are anhydrosugars, pyranone and furan derivatives and oxo compounds [13, 20, 21]. Relative peak areas (normalized to unit sample mass) of some volatile pyrolysis products of the cellulose component of beech and pine wood samples and of their mixtures with PVC are presented in Fig. 2. Among the significant components those have been chosen for demonstration the amount of which changed considerably when the sample was mixed with PVC. For comparison the peak areas of two cellulose samples are also included from experiments carried out under the same conditions. The effect of PVC on the formation of some products of pure cellulose differs from that of the cellulose component of wood samples.

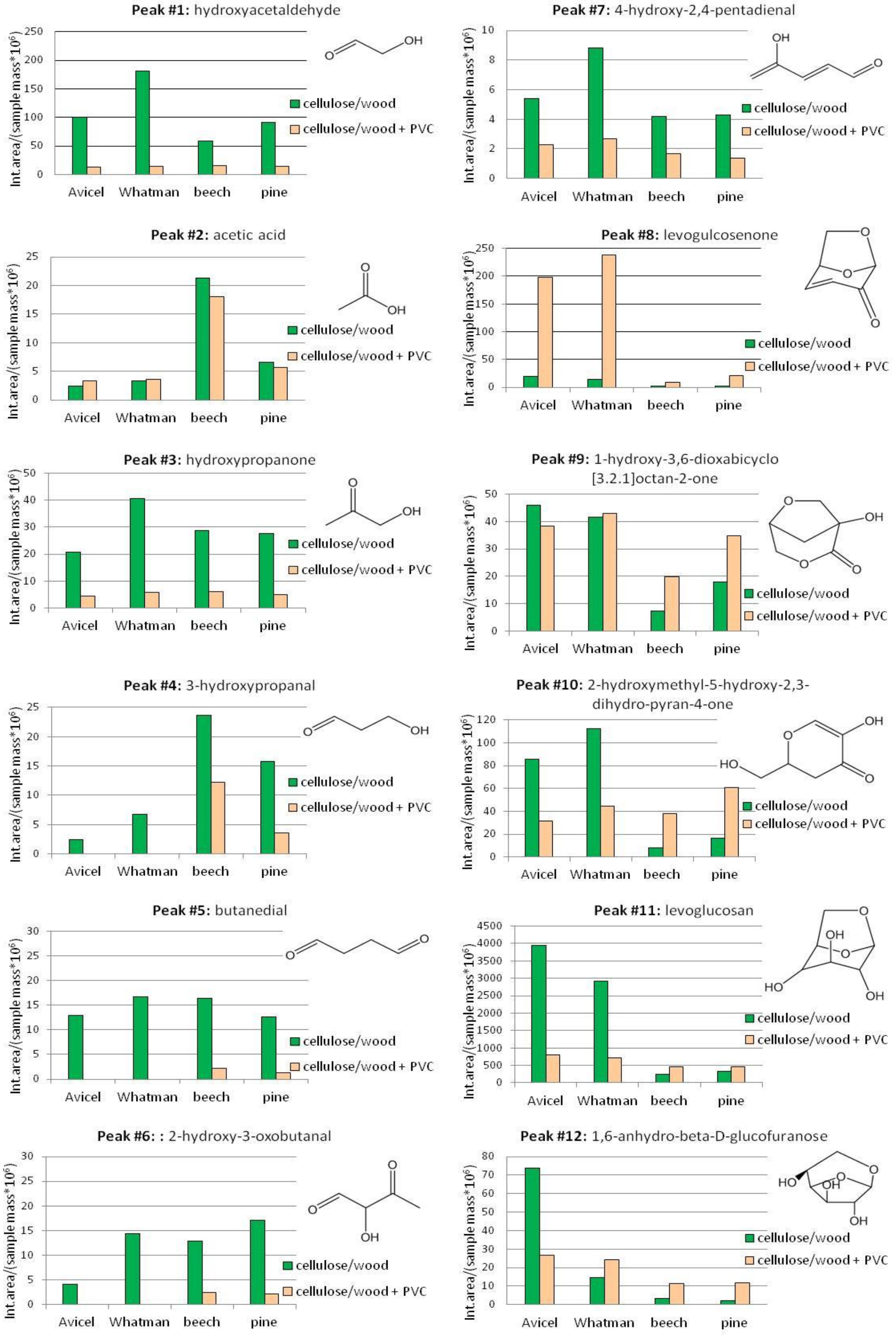


Figure 2. Relative GC/MS peak areas of selected volatile pyrolysis products of cellulose, beech and pine wood samples and of their mixtures with PVC.

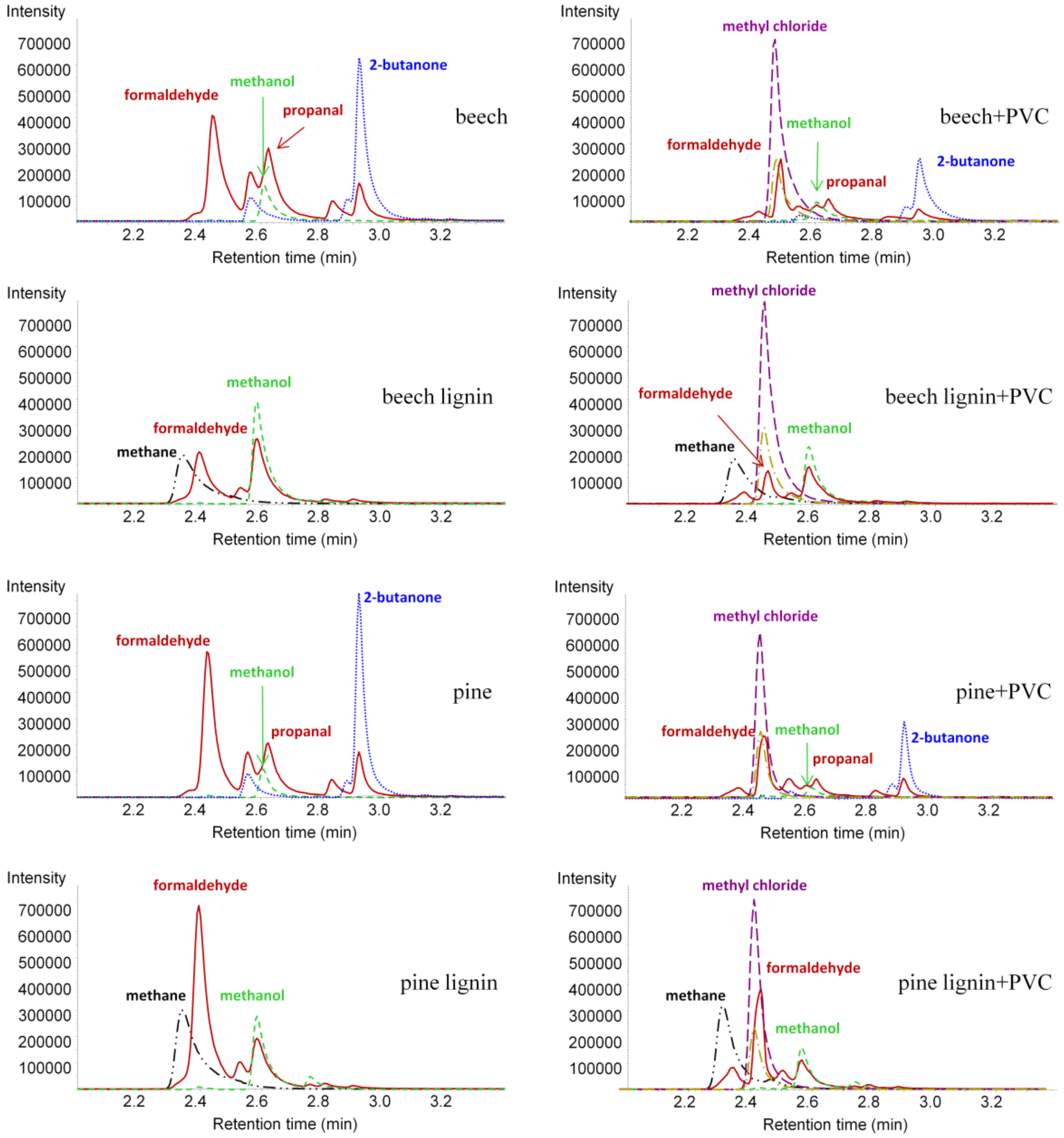


Figure 3. MS ion-chromatographic peaks of organic gaseous products evolved from wood, lignin and their PVC mixture. Methane: m/z 16 (black dot dot line); formaldehyde and propanal: m/z 29 (red solid line); methanol: m/z 31 (green dash line); 2-butanone: m/z 43 (blue dot line); chloromethane: m/z 50 and m/z 52 (purple long dash and yellow dash dot line, resp.)

The unresolved peaks of gaseous products can be compared examining the selected ion chromatograms presented in Fig. 3. The peak intensity of MS ion chromatogram monitored at *m/z* 29 for aldehyde (formaldehyde and propanal are designated), at *m/z* 43 for ketone (2-butanone is designated), and at *m/z* 31 for methanol confirm considerably lower amounts of these compounds produced from wood samples mixed with PVC than from pure wood. In the analogous selected ion chromatograms of cellulose samples (not shown in Fig. 3) the methanol peak intensity of *m/z* 31 ion is by an order of magnitude lower, than of that of wood samples. This observation and the considerable higher intensity of the methanol peak in the chromatograms of lignin pyrolysis products compared to that of the related wood shown in Fig. 3 indicate that the majority of methanol is formed from the lignin component of wood samples.

Taking into consideration the results shown in Fig. 2 and Fig. 3 decreased formation of gaseous and volatile aldehydes, ketons, methanol, and acetic acid has been found when wood samples were pyrolyzed with PVC, while increased evolution of cellulose derived cyclic and bicyclic compounds including levoglucosane has been observed. These trends of the changes correspond well to the published observations [12].

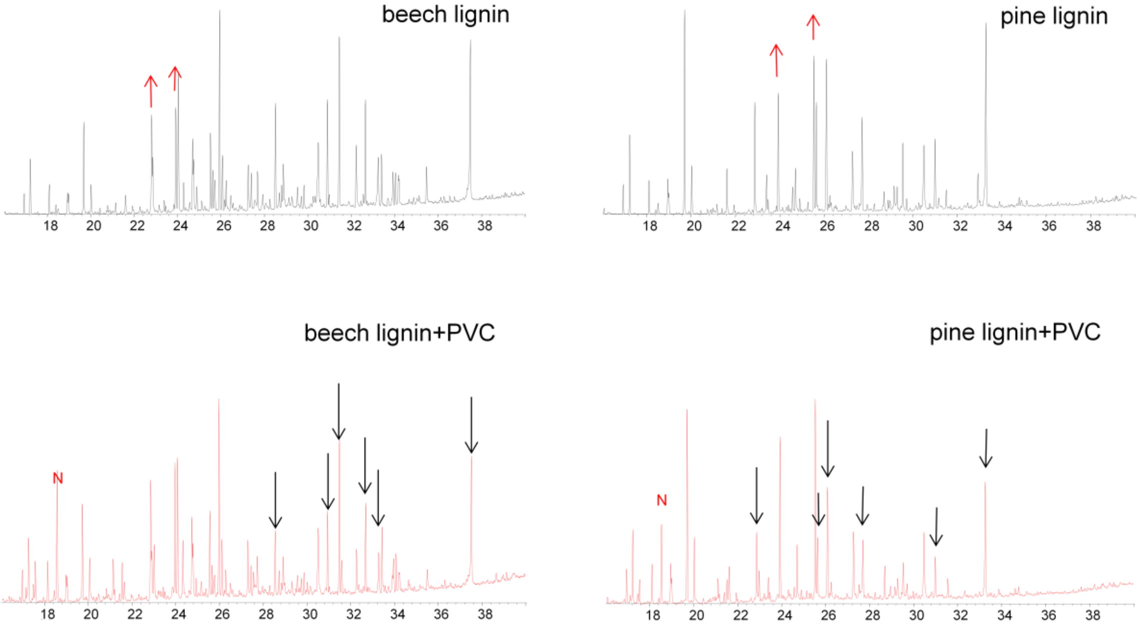


Figure 4. Total ion MS pyrograms of beech lignin, beech lignin and PVC mixture, pine lignin, and pine lignin and PVC mixture. N designates naphthalene (product from PVC), black down and red up arrows point to peaks of decreased and increased area due to the effect of PVC, respectively. The identity of the indicated peaks is given in the text (part 3.1.2).

3.1.2 Lignin derived pyrolysis products of wood and wood-PVC mixture

Beech and pine lignin have been investigated parallel with beech and pine wood samples for easily distinguishing the pyrolysis products of the lignin component from those of cellulose and other components. The main gaseous organic compounds evolved from lignin are methane, formaldehyde, propanal and methanol demonstrated in Fig. 3. The MS ion pyrogram (monitored at *m/z* 16) shows that methane is a not negligible component among the gaseous pyrolsis products of lignin, although it is only an insignificant product of wood samples. Comparing the MS ion pyrograms of lignin samples to those of lignin mixed with PVC the intensity of methane peak is similar, while that of methanol and aldehyde peaks are considerably lower, moreover a new significant peak of chloromethane (monitored at *m/z* 50 and 52) appears in the pyrograms of lignins mixed with PVC.

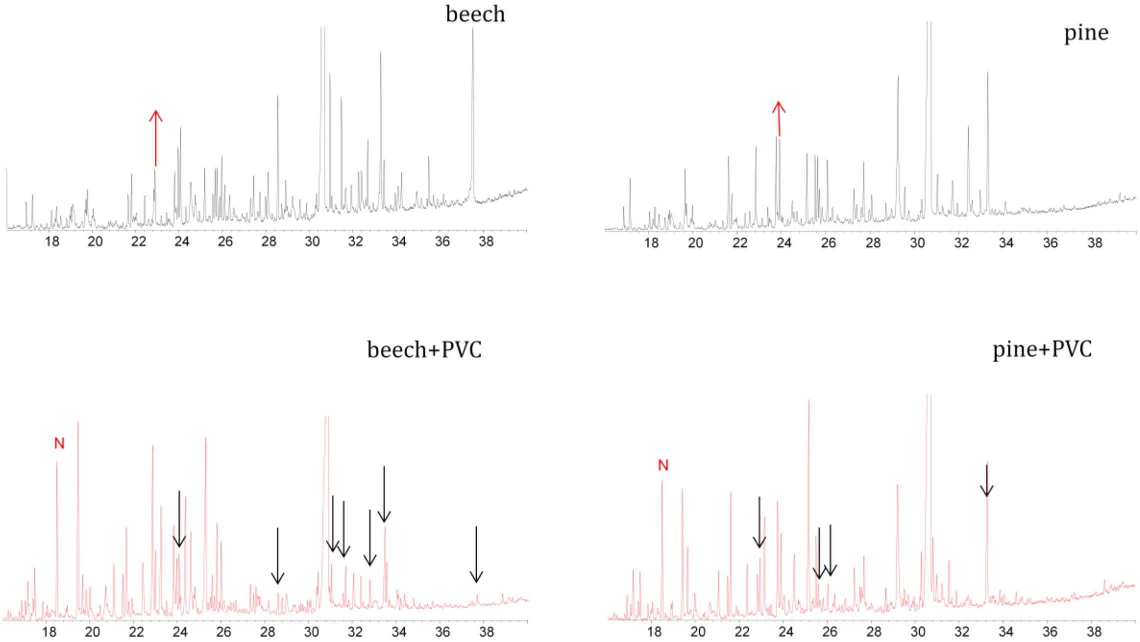


Figure 5. Total ion MS pyrograms of beech, beech and PVC mixture, pine, and pine and PVC mixture. N designates naphthalene (product from PVC), black down and red up arrows point to peaks of decreased and increased area due to the effect of PVC, respectively. The identity of the indicated peaks is given in the text (part 3.1.2).

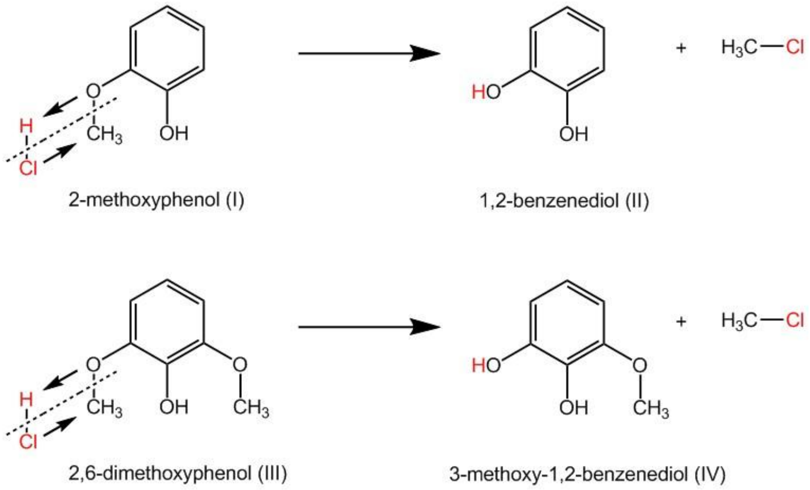
The major volatile decomposition products of lignin are mostly phenol derivatives. These compounds were identified among the pyrolysis products of both lignin and wood samples. Significant changes have been observed in the quantity of lignin products when the samples were mixed with PVC. Total ion pyrograms of lignin and lignin-PVC mixture are compared in Fig. 4. The peaks indicated by red and black arrows point the product compounds of increased and decreased yields, respectively, when the sample has been pyrolysed mixed with PVC. Two red arrow indicated peaks have been identified as 3-methoxy-1,2-benzenediol and 1,2-benzenediol in the pyrogram of beech lignin, and 1,2-benzenediol and 4-methyl-1,2-benzenediol in that of pine lignin. The increased yield of benzenediols among the pyrolysis products reveals that methoxy groups of both guaiacol and siringol moieties in lignins are partly converted to hydroxyl groups. Furthermore the black arrow indicated peaks in Fig. 4 have been identified as 1,3-dimethoxyphenols with 4-C$_2$-ene, 4-C$_3$-ene, 4-C$_1$-al, 4-C$_3$-one groups, and 4-hydroxy-3-methoxy- and 4-hydroxy-1,3-dimethoxycinnamaldehyde in the pyrogram of beech lignin (listed according to increasing GC retention time). In the pyrogram of pine lignin the black arrow indicated peaks are 3-methoxyphenols analogously substituted at the 4th position as the above listed 1,3-dimethoxyphenols. We may summarize these results that from lignin samples mixed with PVC lower amount of phenols with olefin, aldehyde and keton groups have been formed under pyrolysis. The same intensity changes of lignin pyrolysis products are observed in Fig. 5 but obscured to some extent for a few peaks by the products of cellulose and other wood components. These results demonstrate that the above recorded observations for lignins are valid for the wood samples as well.

3.1.3 Formation of chloromethane from lignocellulosic materials mixed with PVC under fast heating

The chlorine content of PVC is released mainly as hydrogen chloride under pyrolysis. Among the pyrolysis products o f wood – PVC mixtures the only significant chlorine-containing organic compound is chloromethane (methyl chloride). Some chlorobenzene is also detected in the pyrograms, which is presumably the minor pyrolysis product of PVC. Chloromethane is eluted together with other gaseous products under the first, inefficiently separated gas chromatographic peak of the pyrograms. Fig. 3 demonstrate that chloromethane is one of the main organic gaseous products of wood – PVC and lignin – PVC mixtures. The relative amounts of chloromethane produced under fast pyrolysis from pure PVC and PVC-containing mixtures are displayed in Fig. 6a. The data represent the amount of chloromethane related to that of benzene, calculated dividing the peak area of chloromethane in the ion pyrogram at *m/z* 50 by that of benzene at *m/z* 78 monitored for benzene molecular ion. Since benzene is the main organic pyrolysis product of PVC, its mass chromatographic peak area is expected to be a suitable data of reference. Similarly relating the peak area of chlorobenzene at *m/z* 112 ion chromatogram to that of benzene at *m/z* 78 roughly the same value is obtained for all the samples as for pure PVC shown in Fig. 6b. This result confirms that the source of chlorobenzene is exclusively the PVC component in the mixed samples. As the bar diagram in Fig.6a shows, the yield of chloromethane from the PVC mixtures is nearly one order of magnitude higher than from PVC. In our earlier study [22] a very similar effect was observed, when significantly increased formation of bromomethane was found pyrolyzing brominated epoxy flame retardant – wood and lignin mixtures. Analogously, the yields of both bromomethane and chloromethane are higher from beech than from pine wood mixtures and higher from beech lignin- than from pine lignin-containing samples. As the hardwood lignin contains more methoxy groups bonded to the phenolic rings than softwood lignin, it is highly probable that those metoxy groups are the methyl sources of the produced chloromethane.

Reactions leading to chloromethane are proposed in Scheme 1, supposing methyl group cleavage from methoxy substituent of guaiacol or syringol (moieties of lignin) by hydrogen chloride evolved from PVC under pyrolysis. Since all the attacked and the product molecules in these reactions are also formed during fast pyrolysis of wood and lignin samples in the absence of PVC, we may estimate the relative importance of the chloromethane producing reactions comparing the ratio of GC peak areas of compounds

II/I and IV/III. Table 1 shows that the ratios obtained for each samples mixed with PVC are significantly higher than those for the corresponding samples alone. This result means that the amount of methoxyphenol decreased or/and that of benzenediol increased as a consequence of the methoxy group cleavage according to Scheme 1. The increased amount of 1,2-benzenediol and 3-methoxy-1,2-benzenediol is already noticed above (in part 3.1.2 and in Fig. 4).



Scheme 1. Proposed formation of methyl chloride by the interaction of a methoxy group at a phenolic moiety of lignin with an HCl molecule evolved from PVC copyrolysed with wood or lignin sample

Table 1. Molecular ion peak area ratios of the product and the reacting compound in the pyrolysate of wood and lignin samples.

	Peak area ratio of compounds[a]			
	II/I		**IV/III**	
Sample	*Average*	*St.dev*	*Average*	*St.dev*
Pine	3.05	0.06	[b]	
Pine + PVC	4.26	0.69	[b]	
Pine lignin	3.08	0.77	[b]	
Pine lignin + PVC	4.46	0.65	[b]	
Beech	[c]		0.38	0.14
Beech + PVC	[c]		0.64	0.11
Beech lignin	2.60	0.75	0.58	0.03
Beech lignin+ PVC	3.69	0.30	0.68	0.01

[a] Compound Roman numbers defined in Scheme 1

[b] Compounds **III** and **IV** are absent in the pyrolysate of pine and pine lignin samples

[c] Values of too high deviation because of the small peak of compound **I** in the pyrolysate of beech sample are not included in this table

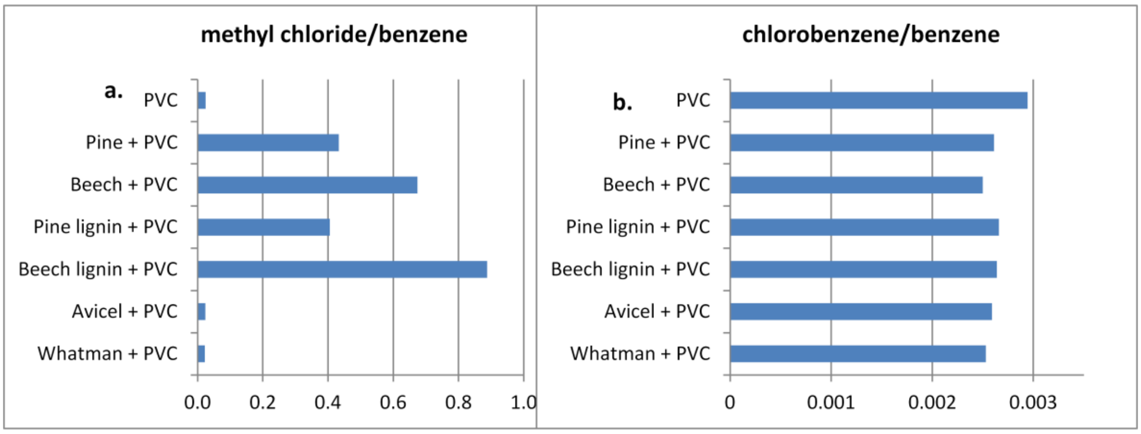


Figure 6. Relative peak areas of chloromethane (a) and chlorobenzene (b) evolved from wood samples, wood lignins and cellulose samples mixed with PVC

3.2. Slow rate pyrolysis of wood and wood-PVC mixture

The overall course of thermal decomposition of wood is significantly influenced when PVC is mixed with the sample. Fig.7 is constructed for comparing the measured thermogravimetric curves of the mixtures to calculated ones obtained by summing the mass change of the original sample and that of PVC measured under the same experimental conditions. The experimental and calculated curves are expected to exhibit dissimilar course when interaction occurs between the components of the mixture altering thermal decomposition. Fig. 7 reveals that considerable interaction occurs between wood samples and PVC, while lignins and PVC practically decompose similarly in mixture and separately. Thus we may expect that other components of wood are responsible for the interaction of wood and PVC, possibly cellulose. The TG and DTG curves of two cellulose samples mixed with PVC demonstrate in Fig. 7 that the measured curve of cellulose reaches its maximum at a lower temperature than the calculated one, and similarly the maxima of the first peak of the measured curve of wood samples is located at a lower temperature than that of calculated one. Thus we may suppose that hydrogen chloride evolved from PVC is promoting cellulose thermal decomposition that occurs also in cellulose component of wood samples mixed with PVC.

3.2.1. Formation of chloromethane under slow heating

Evolution of chloromethane from samples mixed with PVC under slow heating was monitored by TG/MS measurements. It is known that thermal decomposition of PVC starts with dehydrochlorination accompanied by evolution of benzene in a same temperature range [3]. In our TG-MS experiment of PVC decomposition displayed in Fig. 8a hydrogen chloride ion curve starts and reaches the maximum at higher temperature than benzene, because the detection of the highly polar hydrogen chloride

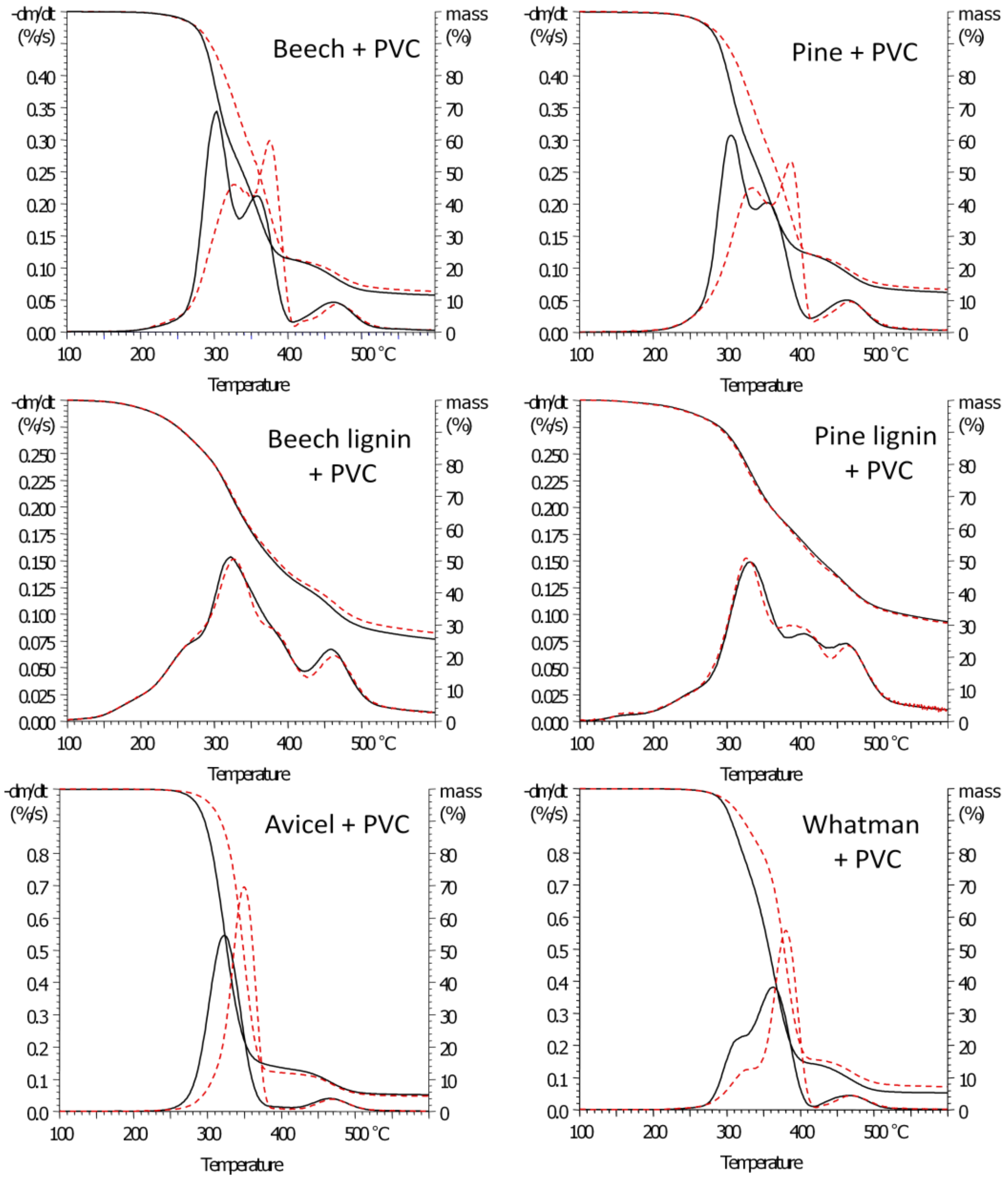


Figure 7. TG and DTG curves of the samples mixed with PVC (black solid lines) and sum of the superposed curves of the of the original sample and PVC (red dot lines)

is delayed unfortunately due to the adsorption on the wall of the approximately 1 m long transfer line between the TG furnace and MS ion source. But it is much more important to recognize the striking difference between the relative size of hydrogen chloride and benzene peak comparing volatile products of PVC sample in Fig. 8a to those of beech lignin mixed with PVC in Fig. 8b. The observed huge deviation suggests that only a part of the hydrogen chloride produced by dehydrochlorination of PVC evaporates from the wood lignin sample mixed with PVC. This experimental result will be explained below.

The ion curves at m/z 50 and 52 of PVC in Fig. 8a are fragment ion curves of benzene proved by their parallel shape with the curve of benzene molecular ion at *m/z* 78.

The TG, DTG and selected ion intensity curves of beech lignin mixed with PVC are presented in Fig. 8b. The *m/z* 50 and 52 ion curves are considerably higher, much wider and have different shape, moreover the relative intensity of the two curves is also largely changed compared to the curves in Fig 8a obtained for PVC.

In order to visualize the evolution of chloromethane in the course of TG-MS experiments the evolution curves of the molecular ions at *m/z* 50 and 52 were corrected by subtracting of the ion intensities corresponding to benzene fragment ions from the measured intensities. The intensity of *m/z* 50 and 52 benzene fragment ions were calculated from that of *m/z* 78 (molecular ion of benzene) multiplying by a factor representing the 50/78 or 52/78 ion ratio in the mass spectrum of benzene. These factors were obtained from the ion intensity values of pure PVC obtained under the same experimental conditions.

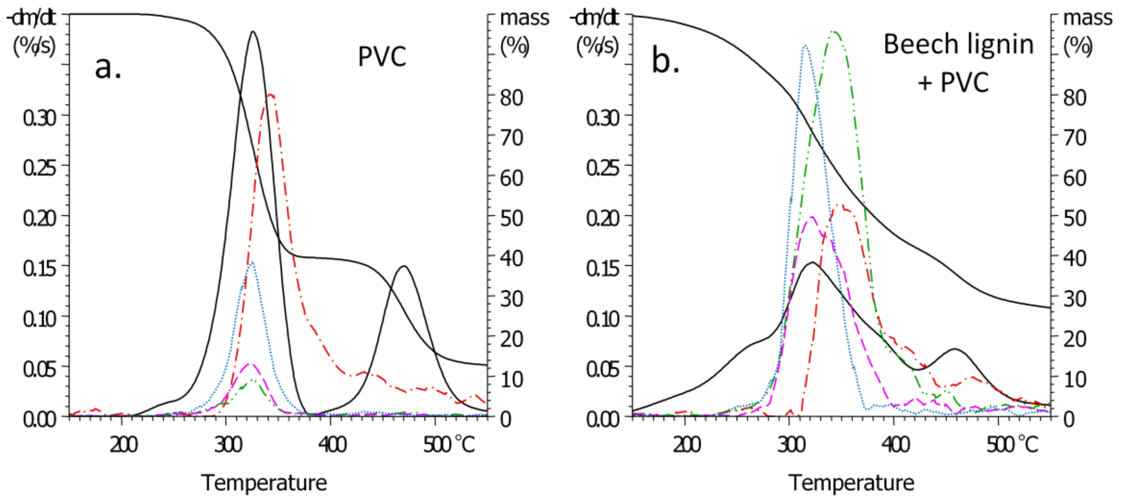


Figure 8. TG, DTG (black solid line) and selected ion curves of PVC (a), and of the mixture of beech lignin and PVC (b). Hydrogen chloride is monitored at *m/z* 36 (red dash dot line), benzene at *m/z* 78 (blue dot line), chloromethane at *m/z* 50 and 52 (green dash dot dot and purple dash lines, resp.).

$$I(m/z\ 50_{\mathrm{MeCl}}) = I(m/z\ 50_{\mathrm{total}}) - I(m/z\ 50_{\mathrm{benzene}}) \qquad (1)$$

where $I(m/z\ 50_{\mathrm{benzene}}) = f_{50} * I(m/z\ 78)$

and $f_{50} = I(m/z\ 50_{\mathrm{PVC}})^{\mathrm{max}} / I(m/z\ 78_{\mathrm{PVC}})^{\mathrm{max}} = 0.25$

$$I(m/z\ 52_{\mathrm{MeCl}}) = I(m/z\ 52_{\mathrm{total}}) - I(m/z\ 52_{\mathrm{benzene}}) \qquad (2)$$

where $I(m/z\ 52_{\mathrm{benzene}}) = f_{52} * I(m/z\ 78)$

and $f_{52} = I(m/z\ 52_{\mathrm{PVC}})^{\mathrm{max}} / I(m/z\ 78_{\mathrm{PVC}})^{\mathrm{max}} = 0.35$

The corrected ion curves according to equations (1) and (2) are shown in Fig. 9 for the mixed samples. In all cases the 50 and 52 ion curves are similarly shaped and keep the intensity ratio of 3:1 in the whole temperature range. These facts confirm that the corrected *m/z* 50 and 52 curves exhibit the evolution of methyl chloride molecular ions properly, since the intensity ratio of *m/z* 50 and 52 ions complies with that of natural isotope of chlorine atom at *m/z* 35 and 37 (3:1).

As the corrected *m/z* 50 and 52 ion curves show in Fig. 9, the evolution of methyl chloride starts already at around 280°C parallel with benzene and hydrogen chloride evolution, but reaches its maximum at a higher temperature, at about 350-360°C in all mixed samples. The temperature range of chloromethane evolution is rather wide, about 150°C in wood-PVC and 130°C in lignin-PVC mixtures. It is also clearly visible in Fig. 9 that considerably more hydrogen chloride is volatilized from pine and pine lignin - PVC than from beech and beech lignin – PVC mixtures. However, the extent of evolution of hydrogen chloride from pine and pine lignin - PVC mixtures is only about the half of that from PVC considering the TG-MS ion curves in Fig. 8a. It seems that a significant part of chlorine content of PVC is retained in the wood or lignin sample after dehydrochlorination of PVC (as in chloride or other chemical form), and evolves as methyl chloride at higher temperature.

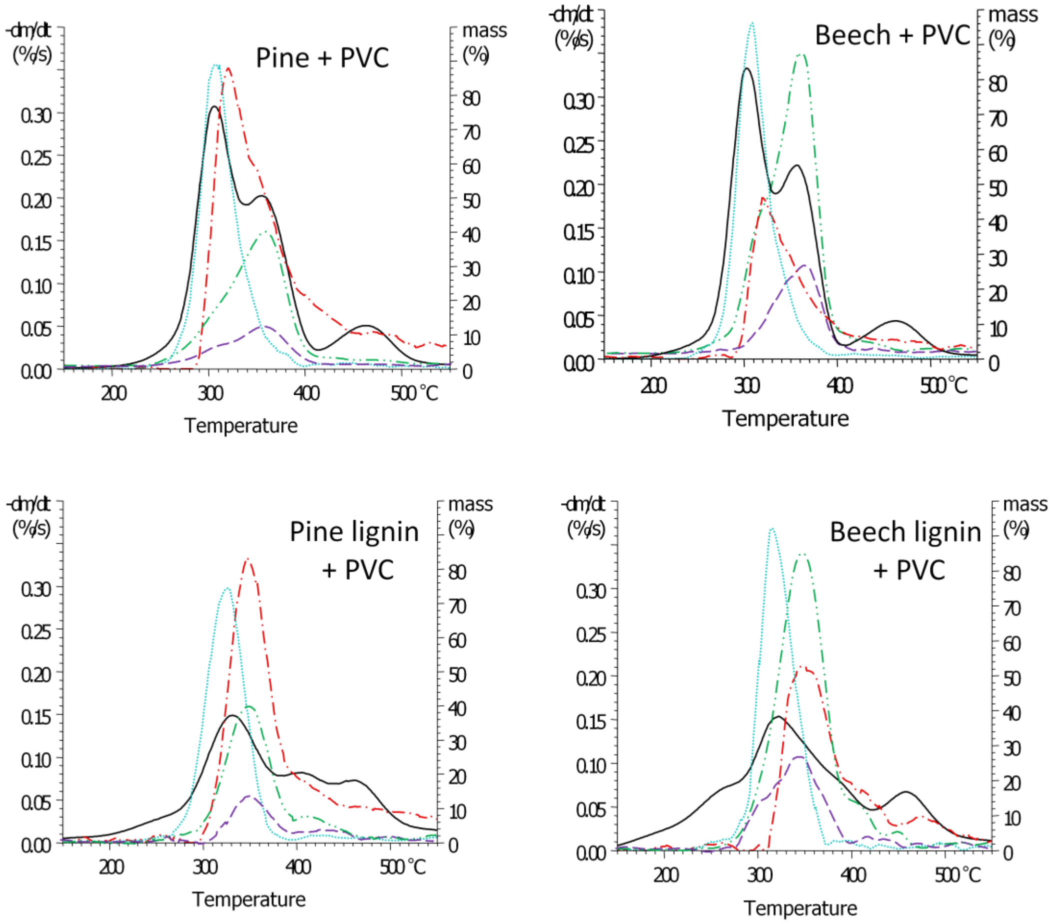


Figure 9. DTG (black solid line) and selected ion curves of wood-PVC and lignin-PVC mixtures. Hydrogen chloride is monitored at *m/z* 36 (red dash dot line), benzene at *m/z* 78 (blue dot line) and corrected chloromethane at *m/z* 50 and 52 (green dash dot dot and purple dash lines, resp.).

Sivalingam and Madras [10] found a similar effect in case of PVC – polycarbonate mixture. They found that up to 5% of chlorine remains in the polymer mixture after dehydrochlorination. In our case only about 30-50 % of the expected HCl is emitted from the mixed samples.

Considering the relative intensities of ion curves in Fig. 9, more abundant formation of chloromethane was observed from beech or beech lignin – PVC mixtures than from pine or pine lignin – PVC mixtures, and also more from beech lignin – PVC than from beech – PVC mixtures. Similar results have been obtained under fast pyrolysis presented above (in 3.1.3). Based on these results we may conclude that chlorination of methoxy groups occurs in the lignin component of wood resulting in chloromethane, according to the reactions suggested in Scheme 1. The attack of chlorine radical or a negatively charged chlorine atom of HCl at the positively charged carbon of the methoxy substituent could lead to chloromethane and hydroxyl substituent of the phenol ring not only from guaiacol and syringol, but from any larger moleculecule containing these moieties. Considering that evolution of chloromethane starts at around 250°C at which temperature the thermal decomposition of lignin only just begins, it is possible that HCl may chemisorbed around the methoxy groups already within the lignin macromolecular network, and the cleavage of methoxy group and evolution of methyl chloride occur progressively at higher temperatures.

The amount of chloromethane formed under slow heating from cellulose – PVC mixtures was under the detection limit of TG/MS technique.

4. Conclusions

The presented Py-GC/MS and TG/MS results provide new information on the modified decomposition routes of lignocellulosic materials in the presence of PVC. The cellulose content in wood is decomposing at lower temperature when wood sample is mixed with PVC, moreover the organic pyrolysis products of both cellulose and lignin components are less reactive as the production of compounds with olefin and oxygenated functional groups (aldehyde, keton, acid) are considerably suppressed. Significant amount of chloromethane evolves from PVC – wood mixtures under both fast and slow heating. At the same time proportionally less hydrogen chloride is emitted from the samples that could cause an incomplete chlorine balance if the evolved chloromethane is not taken into account. Observing that methoxy groups of both guaiacol and syringol moieties in lignins are partly converted to hydroxyl groups, it can be concluded that methoxy groups bonded to the phenolic rings in the structure of lignin are detached by hydrogen chloride producing chloromethane.

Acknowledgements

The authors gratefully thank to M.J. Antal, O. Faix and J. Puls for supplying the samples studied in this work. This study was supported by the Hungarian National Research Fund (OTKA nos. K83770 and K81959) and "Bolyai János" research fellowship. We also thank the two referees for their constructive comments.

References

1. T. Hjertberg, E:M. Sörvik, Degradation and Stabilization of PVC, in: E.D. Oven, Ed., Elsevier, London, New York, 1984, Chapter 2
2. B. Iván, T. Kelen, F. Tüdős, Degradation and Stabilization of Polymers, in: H.H.G. Jellinek, Ed., Elsevier Science, Oxford, New York, 1989, Vol. 2, p. 483.
3. I.C. McNeil, L. Memetea, W.J. Cole, A study of the products of PVC thermal degradation, Polym. Deg. Stab. 49 (1995) 181-191
4. W.H. Starns, D. Edelson, Mechanistic Aspects of the Behavior of Molybdenum(VI) Oxide as a Fire-Retardant Additive for Poly(vinyl chloride). An Interpretive Review, Macromolecules 12 (1979) 797.
5. M. Day, J.D. Cooney, C. Touchette-Barrette, S.E. Sheehan, Pyrolysis of mixed plastics used in the electronics industry, J. Anal. Appl. Pyrolysis 52 (1999) 199–224.
6. Zs. Czégény, M. Blazsó, Thermal decomposition of polyamides in the presence of poly(vinyl chloride), J. Anal. Appl. Pyrol. 58–59 (2001) 95–104.
7. K. Kulesza, K. German, Chlorinated pyrolysis products of co-pyrolysis of poly(vinyl chloride) and poly(ethylene terephthalate), J. Anal. Appl. Pyrolysis 67 (2003) 123–134.
8. Zs. Czégény, E. Jakab, M. Blazsó, Thermal decomposition of polymer mixtures containing PVC, Macromol. Mater. Eng. 287 (2002) 277-284
9. T. Karayildirim, J. Yanik, M. Yuksel, M. Saglam, C. Vasile, H. Bockhorn, The effect of some fillers on PVC degradation, J. Anal. Appl. Pyrolysis 75 (2006) 112–119
10. G. Sivalingam, G. Madras, Effect of Metal Oxides/Chlorides on the Thermal Degradation of Poly(vinyl chloride), Poly(bisphenol A carbonate), and Their Blends, Ind. Eng. Chem. Res. 43/24 (2004) 7716-7722
11. M. Blazsó, E. Jakab, Effect of metals, metal oxides, and carboxylates on the thermal decomposition processes of poly(vinyl chloride), J. Anal. Appl. Pyrolysis 49 (1999) 125–143
12. Y. Matsuzawa, M. Ayabe, J. Nishino, Acceleration of cellulose co-pyrolysis with polymer, Polym. Deg. Stab. 71 (2001) 435-444
13. F. Shafizadeh, Introduction to pyrolysis of biomass (Review), J. Anal. Appl. Pyrolysis 3 (1982) 283-305
14. G. Dobele, D. Meier, O. Faix, S. Radtke, G. Rossinskaja, G. Telysheva, 2001. Volatile products of catalytic flash pyrolysis of celluloses, J. Anal. Appl. Pyrolysis 58-59 (2001) 453-463

15. H. Kuramochi, D. Nakajima, S. Goto, K. Sugita, W. Wu, K. Kawamoto, HCl emission during co-pyrolysis of demolition wood with a small amount of PVC film and the effect of wood constituents on HCl emission reduction, Fuel 87 (2008) 3155-3157
16. Q. Ren, C. Zhao, X. Wu, C. Liang, X. Chen, J. Shen, G. Tang, Z. Wang, TG–FTIR study on co-pyrolysis of municipal solid waste with biomass, Biores.Techn. 100 (2009) 4054–4057
17. K. Vasile, M. Brebu, H. Darie, G. Cazacu, Effect of some environmentally degradable materials on the pyrolysis of plastics II: influence of cellulose and lignin on the pyrolysis of complex mixtures, J. Mater. Cycles Waste Manag. 12 147–153
18. Y. Fang, Q. Wang, X. Bai, W. Wang, P.A. Cooper, Thermal and burning properties of wood flour-poly(vinyl chloride) composite, J. Therm. Anal. Calorimetry 109 (2012)1577–1585
19. Z. Sebestyén, F. Lezsovits, E. Jakab, G. Várhegyi, Correlation between heating values and thermogravimetric data of sewage sludge, herbaceous crops and wood samples, J. Therm. Anal. Calorimetry 110 (2012) 1501-1509
20. O. Faix, I. Fortmann, J. Bremer, D. Meier, Thermal degradation products of wood. Gas chromatographic separation and mass spectrometric characterization of polysaccharide derived products, Holz als Roh- und Werkstoff 49 (1991) 213-219.
22. Z. Czégény, E. Jakab, M. Blazsó, Pyrolysis of wood, cellulose, lignin–brominated epoxy oligomer flame retardant mixtures. J. Anal. Appl. Pyrolysis 103 (2013) 52–59
21. S. Wang, X. Guo, T. Liang, Y. Zhou, Z. Luo, Mechanism research on cellulose pyrolysis by Py-GC/MS and subsequent density functional theory studies, Bioresource Technology 104 (2012) 722–728