

## INFLUENCE OF FIRE ON SPRUCE WOOD LIGNIN CHANGES

DANICA KAČÍKOVÁ, FRANTIŠEK KAČÍK, TATIANA BUBENÍKOVÁ  
FACULTY OF WOOD SCIENCES AND TECHNOLOGY, TECHNICAL UNIVERSITY IN ZVOLEN, SLOVAKIA

BOŽENA KOŠÍKOVÁ  
INSTITUTE OF CHEMISTRY, SLOVAK ACADEMY OF SCIENCES, BRATISLAVA, SLOVAKIA

### ABSTRACT

The paper deals with the chemical and physico-chemical changes of lignin during the degradation of spruce wood by one-sided thermal loading according to the standard temperature curve ETK in temperature range from 30 °C to 310 °C. The changes caused by thermal loading were studied with infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), gel permeation chromatography (GPC) and nitrobenzene oxidation (NBO). We observed the lignin and extractives amount increase at thermal loading. The changes of functional groups took place in lignin – amount of  $\alpha$ -C=O and  $-\text{OCH}_3$  decreased, amount of  $\beta$ -C=O increased. At lower temperatures of the thermal treatment, the lignin macromolecule is degraded, the relative molecular weights decrease, at higher temperatures the condensation reactions are predominant and the relative molecular weights increase.

**KEY WORDS:** spruce, lignin, thermal loading, infrared spectroscopy, nuclear magnetic resonance, gel permeation chromatography, nitrobenzene oxidation

### INTRODUCTION

The increased temperature influences the physical, structural and chemical properties of wood. The wood structure is very complicated, the individual compounds are bonded by the different types of bonds and thus the thermal degradation of the wood is the complex process. Thermally treated wood has various useful properties (reduced swelling and shrinkage, better resistance to fungal attack, enhanced weather resistance, darker colour is desirable in furniture production, etc.) (Sivonen et al. 2003, Nuopponen et al. 2004a). However, the mechanical properties, e.g. strength, hardness and stiffness are reduced during heat treatment. The extents of these modifications depend on the heat treatment conditions. Different types of chemical reactions (dehydration, depolymerisation, termooxidation) take place in wood by the effect of the heat. The alterations are due to the atmosphere, pressure, moisture, too. The chemical composition of wood alters also at the increased moisture (hydrothermal treatment) or at the decreased pressure (vacuum drying) at the temperatures lower 100 °C. The limiting temperature for the classification of the thermolytic

reaction of the wood polymers (hemicelluloses, cellulose, and lignin) is 300 °C (Shafizadeh, 1984, Horbaj 1997, White, Dietenberger 1999, Kačík et al. 2001, Rowel, LeVan-Green 2005).

Lignin is more stable wood component in comparison to hemicelluloses and cellulose, but increased temperature influence causes its chemical changes, too. Faix et al. (1988) divided spruce lignin's thermal decomposition into 4 phases within 100–580 °C temperature range. Cleavage of the  $\beta$ -O-4 linkages in lignin was observed in softwoods by  $^{13}\text{C}$  CPMAS NMR spectroscopy (Sivonen et al. 2002). Demethoxylation of lignin increases crosslink sites within the lignin leading to a more condensed structure (Wikberg, Manuu 2004). The condensation of lignin during heating of spruce wood has been interpreted as mainly a diphenylmethane type condensation (Funaoka et al. 1990). At lower temperature of the heating, the molecular weight of spruce wood lignin decrease, the higher temperature causes the condensation reactions predominantly (Kačík et al. 1999, 2007a)

The aim of this paper was to compare chemical and physico-chemical changes of lignin in the different thermal zones of the one-sided thermal loaded spruce wood.

## MATERIAL AND METHODS

The samples were isolated from the glued spruce board with size 500x500x100mm. The board after the conditioning (temperature 23 °C, final moisture 8%) was thermal loaded in accordance with DIN 4102, part 8. The time of the one-sided thermal load was 90 min, the standardized thermal curve ETK was used. The layer of glued board with thickness of 40 mm burned up. The thermal zones 3, 6, 9, 12, 15, 18, 21 with thicknesses 3 mm were isolated consecutively from the burn up line (denoted ETK-3, ETK-6, ETK-9, ETK-12, ETK-15, ETK-18, ETK-21) and comparing zone 60 with thickness 3 mm, from the board edge opposite to the thermal load (sample ETK-60).

The following temperature intervals were measured in the samples used for the analyses (Tab. 1).

*Tab. 1: Temperature intervals of different zones*

Sample	ETK-3	ETK-6	ETK-9	ETK-12	ETK-15	ETK-18	ETK-21	ETK-60
°C	245-310	200-245	170-200	145-170	120-145	105-120	95-105	30

The disintegrated and sieved sawdust were extracted in a soxhlet with a mixture of ethanol and toluene (ASTM D 1107-96) (2006).

The dioxane lignins were prepared after the extraction by the ethanol-toluene mixture and hot water in accordance with Pepper at the conditions: 10g of wood meal (with dimensions less than 0.355 mm) in 200 ml mixture dioxane-water (9:1), time 5 h, temperature 80 °C. Lignin was determined according to the ASTM method D 1106-96 (2006) and extractives by the gravimetric method. Methoxyl groups in dioxane lignins were determined by gas chromatography of methanol liberated after hydrolysis with sulphuric acid (Kačík et al. 2004). Nitrobenzene oxidation (NBO) was carried out in 10 mL stainless steel vessels at temperature of 180° C, for 2 hours and products of oxidation were analysed by HPLC (Kačík et al. 1995). Gel permeation chromatography (GPC) of dioxane lignins has been carried out on a Separon Hema S-300 column in the mobile phase 0.05 M LiBr in N,N'-dimethylformamide (Kačík et al. 1992). The infrared (IR) measurements were performed with FTIR spectrometer NICOLET Magna 750 using KBr pellets.  $^{13}\text{C}$  NMR spectrum was recorded in deuterated dimethylsulfoxide at 303 K with a Bruker AM 300 NMR spectrometer operating at 74.47 MHz in the inverse gated decoupling mode. The pulse delay was 10 s, the total number of scans ranged from 10000 to 20000.

## RESULTS AND DISCUSSION

The amount of the extracted compounds by the ethanol-toluene mixture increases with the temperature increase (Tab. 2).

Tab. 2: Analysis of the thermal degraded spruce wood (in %, calculated on the dry non-extracted wood, methoxyl groups calculated on the dioxane lignin)

Sample	ETK-3	ETK-6	ETK-9	ETK-12	ETK-15	ETK-18	ETK-21	ETK-60
Extractive s	3.05	1.71	1.43	1.54	1.37	1.59	1.55	1.59
Methoxyl groups	10.9	11.9	12.1	-	-	-	-	12.4
Klason's lignin	29.75	26.46	26.76	26.44	26.71	26.77	26.81	26.75
Dioxane lignin	7.16 (24.07)	6.39 (24.15)	6.09 (22.76)	-	-	-	-	6.05 (22.62)

Note: The yields of dioxane lignins calculated on the lignin amount in the wood are in the brackets

The trend of the dioxane and Klason's lignins alterations is the same (Tab. 2). The Klason's lignin content increases at higher temperatures. This increase is due to the auto condensation of lignin and condensation reactions of the lignin with the products of the thermal degradation of the polysaccharides. Some authors found out the lignin amount increase at the thermal treatment of softwoods (Nuopponen et al. 2004b, Alén et al. 2002).

Softwoods lignins contain 11.5-15.8% of methoxyl groups (Fengel, Wegener 1984) and their amount change depends on the conditions of thermal treatment. We found out the thermal loading causes lignin demethoxylation (Tab. 2), which is in the agreement with results of other papers (Fengel and Przyklenk 1970, Kačík et al. 1999, 2007a,b, Wikberg and Manuu 2004).

From the course of dioxane lignins distribution curves obtained by the method of gel permeation chromatography (Fig. 1, Tab. 3) we can see at the lowest temperature (sample ETK-9) the lignin is preferentially degraded and the molar weight decreases. The condensation reaction takes place at the temperature increase and at the highest temperature (sample ETK-3) the lignin macromolecule is also degraded. It causes polydispersity ( $PD = M_w/M_n$ ) increase and molar weight decrease.

Tab. 3: Average molar weights and polydispersity (PD) of dioxane lignins after thermal loading of spruce wood

Sample	$M_w$ (g.mol <sup>-1</sup> )	$M_n$ (g.mol <sup>-1</sup> )	$M_z$ (g.mol <sup>-1</sup> )	$M_{z+1}$ (g.mol <sup>-1</sup> )	PD ( $M_w/M_n$ )
ETK-3	6 948	1 665	18 997	31 428	4.17
ETK-6	6 228	2 035	16 738	29 843	3.06
ETK-9	4 656	1 611	12 460	22 341	2.89
ETK-60	6 192	1 965	16 786	29 817	3.15

According to Adler (1977), the main product of spruce wood nitrobenzene oxidation (NBO) is vanillin and small portions of *p*-hydroxyaldehyde and syringaldehyde. In this work, vanillin and vanillic acid were the main products of NBO, *p*-hydroxybenzaldehyde yield was small (Tab. 4).

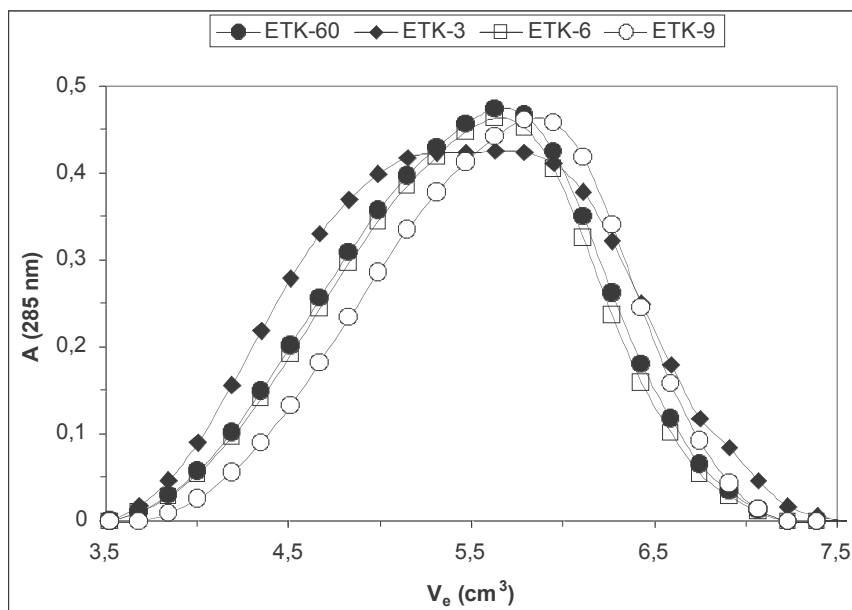


Fig. 1: Distribution curves of dioxane lignins of isolated samples after thermal loading of spruce wood in accordance with standard temperature curve ETK

Tab. 4: Products yield of dioxane lignins nitrobenzene oxidation

Sample	Vanillin (%)	Vanillic acid (%)	<i>p</i> -Hydroxybenzaldehyde (%)	Syringaldehyde (%)	Yield (%)
ETK-3	8.61	1.55	0.24	0	10.40
ETK-6	11.64	2.16	0.23	0	14.03
ETK-9	11.82	1.95	0.26	0	14.03
ETK-60	11.55	2.06	0.40	0.18	14.19

From the results we can see the decrease of NBO products yield at the temperature increase (sample ETK-3) because of condensation reactions occurrence. It is confirmed by the results of macromolecular characteristics of dioxane lignins obtained by GPC method (Tab. 3). Fuanoka et al. (1990) observed the decrease of NBO products yields, too.

The structural changes of lignin component of spruce wood during thermal loading were investigated by FTIR analysis of dioxane lignins isolated from untreated wood (sample ETK-60) as well as from the different layers of heated wood samples (ETK-3, ETK-6, ETK-9). The obtained spectra are illustrated in Fig. 2 and the quantitative analysis of the absorption bands related to aromatic vibration at  $1515\text{ cm}^{-1}$  is summarised in Tab. 5.

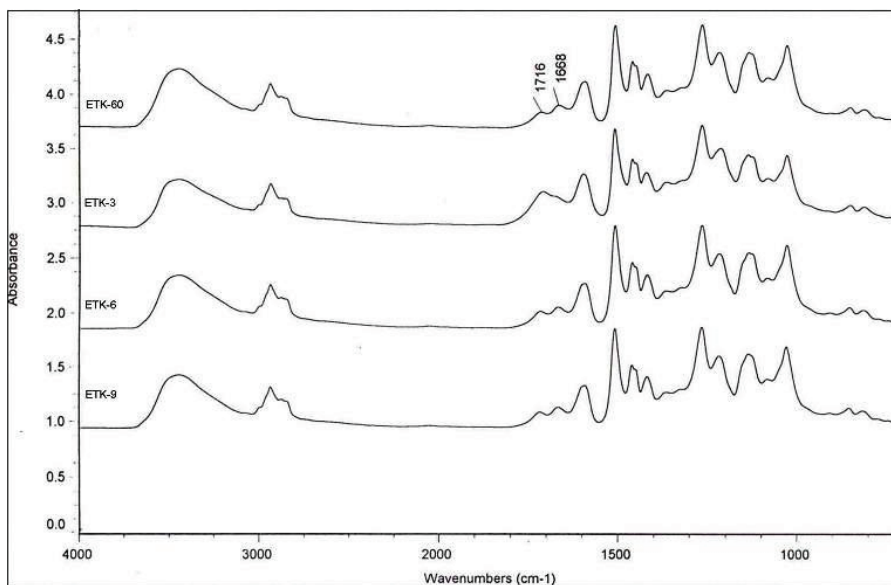


Fig. 2: Infrared spectra of dioxane lignins before and after the thermal loading of spruce wood

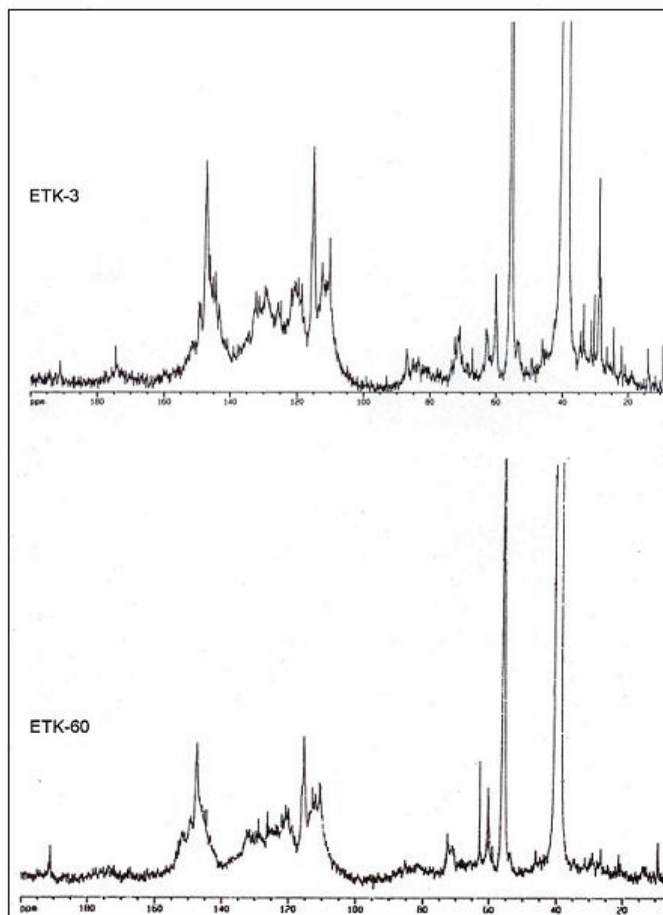
Tab.5: Infrared absorption of dioxane lignins isolated from spruce wood before and after thermal loading related to the aromatic vibrations at 1515  $\text{cm}^{-1}$

Sample	1716 $\text{cm}^{-1}$	1666 $\text{cm}^{-1}$	1595 $\text{cm}^{-1}$	1280 $\text{cm}^{-1}$	1220 $\text{cm}^{-1}$	1030 $\text{cm}^{-1}$
ETK-3	0.378	0.050	0.521	1.033	0.795	0.712
ETK-6	0.171	0.201	0.430	0.980	0.724	0.779
ETK-9	0.158	0.211	0.434	1.021	0.713	0.781
ETK-60	0.151	0.215	0.456	0.987	0.714	0.785

The observed intensity decrease of the  $\alpha$ -C=O band at 1666  $\text{cm}^{-1}$  and the simultaneous increase of the  $\beta$ -C=O band at 1716  $\text{cm}^{-1}$  in the IR spectra of the thermally modified lignins can be explained by thermal cleavage of  $\beta$ -arylether groups and subsequent guaiacylglycerol side-chain -C=O rearrangement from  $\alpha$ - to  $\beta$ - as was observed during acidolysis in methanol (Polčín et al. 1963) as well as in dioxane (Košíková et al. 1973). According to Funaoka et al. (1990) conjugated carbonyl groups are reactive sites with phenyl nuclei. Therefore, one of the factors which caused the disappearance of  $\alpha$ -C=O band might be their condensation with adjacent phenyl nuclei. Besides of this the significant decrease in the 1666  $\text{cm}^{-1}$  absorption band under wood thermal treatment can be accounted for by oxidation  $\alpha$ -C=O groups into carboxyl groups followed by the elimination of side chain. The comparison of the FTIR spectra of the sample isolated from untreated and thermally treated spruce wood shows that the absorption at 1716  $\text{cm}^{-1}$  increased significantly in treated wood. This band corresponding to unconjugated carbonyl and/or carboxyl groups probably is generated upon thermal cleavage of  $\beta$ -arylether groups at the temperature 270 °C (Domburg et al. 1974).

Moreover, the structural changes of lignin in thermal process were examined by  $^{13}\text{C}$  NMR analysis. The comparison of the spectra of lignins ETK-60 and ETK-3 (Fig. 3) indicates an

appearance of several new signals isolated from heated wood. Based on the literature data (Robert 1992) the signal at  $\delta$  174 ppm correspond to unconjugated C=O in aliphatic carboxylic groups. The signals between  $\delta$  34 and 22 ppm originate most probably from methylene carbons.



*Fig. 3: NMR spectra of dioxane lignins before and after the thermal loading of spruce wood*

The obtained results indicate that depolymerisation of lignin during heating of wood is accompanied by oxidative modification and condensation of side chains. Similar observations have been reported previously at thermally modified pine (Sivonen et al. 2002) and spruce (Wikberg, Maunu 2004) wood, respectively. A competition between depolymerization and condensation reactions was observed at thermal modification of pine and beech wood (Weiland, Guyonnet 2003).

## CONCLUSION

The backwash of thermal degradation of the one-sided thermal load of spruce wood according to the standard temperature curve ETK is the increase of the lignin and extractives amount. The thermal loading causes the alterations functional groups amount in lignin – the decrease of  $\alpha$ -C=O and  $-\text{OCH}_3$  groups and increase of  $\beta$ -C=O groups. At the lower temperatures the lignin depolymerisation is dominant, at the higher temperatures the condensation takes place.

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DANICA KAČÍKOVÁ  
FACULTY OF WOOD SCIENCES AND TECHNOLOGY  
TECHNICAL UNIVERSITY IN ZVOLEN  
T.G.MASARYKA 24  
960 53 ZVOLEN  
SLOVAKIA  
E-mail: kacikova@vsld.tuzvo.sk

FRANTIŠEK KAČÍK  
FACULTY OF WOOD SCIENCES AND TECHNOLOGY  
TECHNICAL UNIVERSITY IN ZVOLEN  
SLOVAKIA

BOŽENA KOŠÍKOVÁ  
INSTITUTE OF CHEMISTRY  
SLOVAK ACADEMY OF SCIENCES  
BRATISLAVA  
SLOVAKIA

TATIANA BUBENÍKOVÁ  
FACULTY OF WOOD SCIENCES AND TECHNOLOGY  
TECHNICAL UNIVERSITY IN ZVOLEN  
SLOVAKIA

