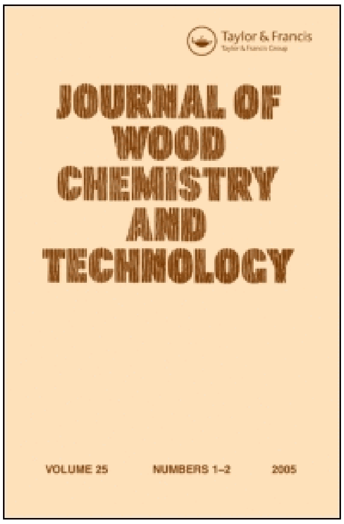

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Evolution of Extractive Composition During Thermal Treatment of Jack Pine

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Abstract: The thermal treatment of wood has many benefits such as better dimensional stability and attractive dark color and does not use toxic chemicals. The resistance against biological decay can be improved when wood is not in contact with ground. On the other hand, after thermal transformation, wood becomes more fragile. The changes of the wood properties are related to the modification of the wood composition. During the thermal treatment, the evaporation of the moisture content is not the only event. Volatile extractives are evacuated from the wood, while new products and by-products of different chemical reactions appear. The comparison of the extracts obtained from untreated and treated wood can help to identify thermo-chemical reactions, taking place during the heat treatment. This article presents the analysis by Gas Chromatography–Mass Spectroscopy (GC-MS), High Performance Liquid Chromatography (HPLC), and Thin Layer Chromatography (TLC) of polar and non-polar extracts of untreated and heat-treated North American Jack pine (*Pinus banksiana*). The study of the impact of maximum heat treatment temperature on the composition of the Jack pine extracts showed that the major part of extractives leaves the wood under 200°C whereas most of the new products appear only above 200°C. While the extractives of the untreated Jack pine are dominated by non-polar components, the thermo-transformation seems to generate mainly polar compounds. However, presence of water vapor increases the portion of polar extractives in wood. Interestingly, an important decrease of concentration of phenolic compounds (such as pinosylvin, pinosylvin monomethyl ether, and pinobanksin) in Jack pine wood was observed between 160–200°C. On the other hand, 4-hydroxy-methylfurfural and vanillin have been identified as compounds generated by the heat treatment above 200°C. The identification of other by-products will be presented in a later paper.

Keywords: Extractives, GC-MS, HPLC analysis, Jack pine, thermal treatment, TLC

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INTRODUCTION

Wood heat-treated at high temperature (between 150–240°C) and in inert atmosphere becomes more and more hydrophobic and resists better to biological attack when thermo-transformed wood is not in contact with ground.[1] Contrary to traditional preservation methods involving the use of biocides, the heat treatment avoids the use of toxic chemicals, improves significantly the dimensional stability,[2–4] and gives an attractive dark color to the wood. Unfortunately, heat-treated wood looses its elasticity and becomes more fragile.[5–14] Hardness of wood can increase or decrease depending on wood species and treatment conditions.[13,14] Due to the increasing hydrophobicity, the wood also becomes more difficult to glue.[15]

All these changes are related to the modification of the chemical composition of the wood. At low temperature range (under 130°C), moisture content is evaporated and volatiles start to migrate out of the wood. At higher temperatures, chemical reactions such as depolymerization of hemicelluloses by hydrolysis,[16,17] ramification of lignin,[5,17–22] and oxidation take place. As amorphous hemicelluloses content decreases, the crystallization degree of wood polymers increases.[23–27] The cleavage of acetyl side groups has been also reported.[28–30] The decrease of the number of hydroxyl groups accessible to the water was also observed.[28] However, very little work has been done on the chemical modifications of extractives. This is an important aspect of heat-treatment because polymer degradation could generate new extractives. These extractives could be implicated in the resistance improvement of the wood or prove to be toxic by-products.

Although the production of secondary metabolites in plants is often low (less than 1% dry weight), the produced compounds generally have an important role in the interaction of the plant with its environment.[31] An acetone extract of Jack pine knotwood mainly constituted of Pinosylvin (PS), pinosylvin monomethyl ether (PSM), pinocembrin, and pinobanksin has shown *in vitro* antibacterial activity.[32] Also, PS and PSM are often considered to protect the natural wood substrate and decrease the rate of decay.[33–35] These results suggest that secondary metabolites play an important role in the resistance of natural wood to decay. Fatty acids,[36] sugars,[37] a phenylpropane,[38] monoterpenes,[39] diterpenes, and resin acids,[36] have also been identified in Jack pine. The analysis of the variations in the composition of the extractives occurring during heat treatment can improve our knowledge on the importance of secondary metabolites in the improvement of decay resistance and the thermo-chemical reactions taking place in the wood due to this treatment.

A few articles can be found in the literature, presenting Gas Chromatography–Mass Spectroscopy (GC-MS) and ^{13}C Nuclear Magnetic Resonance (NMR) analysis of different thermally treated European pine woods extracts[1,28,39] in humid gas at the temperature range of 190–250°C. Those papers mention the formation of different polycyclic hydrocarbon derivatives from lignin and long aliphatic saturated hydrocarbon chains. Closed reactors are often used to treat the wood at high temperature in laboratory scale.[40,41] Contrary to industrial furnaces, these systems do not allow volatiles to escape and they accumulate considerably. For example, the excessive decrease of pH due to the building up of acid content can promote hydrolysis. Poncsak et al.[13] and Kocaefe et al.[14,42] solved this problem by using a thermo-gravimetric system in which the humid and inert gas stream flushed out the extractives from the wood.

The aim of this work was to investigate the impact of the heat treatment conditions (maximal temperature, heating rate, gas humidity) on the composition of extractives obtained from North American Jack pine, when the wood is exposed to a continuous hot inert gas stream. Extracts obtained with hexane, dichloromethane, and methanol from treated and untreated wood (Table 2) were weighed and analyzed with Thin Layer Chromatography (TLC), High Performance Liquid Chromatography (HPLC) and combined GC-MS.

MATERIALS AND METHODS

Preparation of Wood Samples

Canadian Jack pine (*Pinus banksiana*), coming from a local sawmill, was cut into small samples with dimensions of 20 cm × 3.5 cm × 3.5 cm, and pre-dried in air at room temperature until wood moisture content of 6–10% was reached. Some of the specimens were used as untreated references, while the others were heat-treated in a thermo-gravimetric furnace. Wood samples were treated using a constant heating rate of 20°C/h up to different maximum temperatures (160°C, 200°C, 220°C, 230°C) (Table 1). The test with the maximum temperature of 220°C was repeated without injection of additional water vapor in the furnace (low humidity, Table 1), and with a slower heating rate of 10°C/h (Table 1). A gas mixture, containing 80% nitrogen and 20% carbon dioxide, was circulated continuously through the furnace in order to assure inert atmosphere similar to that of the industrial furnace. Above 100°C, 100 g/m^3 water vapor was added to the gas mixture. As soon as the maximum temperature was reached, wood was cooled down with fine water-spray. Due to the relatively small dimensions of the specimens, the average cooling rate was as high as 10°C/minute. A more detailed description of the thermo-gravimetric system is presented by Poncsak et al.[13]

Both the heat-treated and the untreated wood samples were ground in a Fritsch D-55743 mill grinder and then sieved in order to produce a wood powder with particle size range of 150–250 μm.

Chemicals

Cinnamyl alcohol was obtained from Fluka (Oakville, ON, Canada). Eugenol was purchased from Aldrich (Oakville, ON, Canada). Trans-cinnamaldehyde

Table 1. Identification of hexane, dichloromethane, and methanol extracts obtained from wood heat treated with different operational parameters

ID	Solvent	Maximal temperature (°C)	Heating rate (°C/h)	Gas humidity (g/m^3)
HUT	Hexane		Untreated wood	
H160	Hexane	160	20	100
H200	Hexane	200	20	100
H220	Hexane	220	20	100
H230	Hexane	230	20	100
HLH	Hexane	220	20	10
H10C/h	Hexane	220	10	100
DUT	CH_2Cl_2		Untreated wood	
D160	CH_2Cl_2	160	20	100
D200	CH_2Cl_2	200	20	100
D220	CH_2Cl_2	220	20	100
D230	CH_2Cl_2	230	20	100
DLH	CH_2Cl_2	220	20	10
D10C/h	CH_2Cl_2	220	10	100
MUT	MeOH		Untreated wood	
M160	MeOH	160	20	100
M200	MeOH	200	20	100
M220	MeOH	220	20	100
M230	MeOH	230	20	100
MLH	MeOH	220	20	10
M10C/h	MeOH	220	10	100

was purchased from PFALTZ and Bauer Inc. (Waterbury, CT, USA). Vanillin was obtained from Alfa Aesar (Ward Hill, MA, USA). Furfural and hydroxymethylfurfural were purchased from TCI America (Portland, OR, USA). Pimaric acid, isopimaric acid, sandaracopimaric acid, levopimaric acid, dehydroabietic acid, and abietic acid were purchased from Helix Biotech (Richmond, B.C., Canada). Pinosylvin, pinosylvin monomethyl ether, and pinobanksin were obtained using a method developed in previous work of Simard et al. on *Pinus resinosa*.[43]

Soxhlet Extraction

Treated and untreated wood powder samples (50 g each) were successively extracted with hexane, dichloromethane, and methanol using a Soxhlet apparatus to obtain extractible fractions with increasing polarity. Identification of extracts is shown in Table 1. Each extraction was carried out for 24 h using 700 ml solvent. After the extractions, the solvent was evaporated and the extracts were kept cold in screw cap vials.

Extracts Composition Analysis

The weight of each dried extract was measured using a Metler Toledo AB204 analytical balance (precision ± 0.1 mg). TLC, HPLC, and GC-MS were used to analyze the components extracted after the thermal treatment. TLC was performed on silica gel 60 F254 glass plate (250 μm layer thickness, Silicycle, Québec, Canada). A mixture of 40:1 $CHCl_3$-MeOH was used as eluant for both hexane and CH_2Cl_2 extracts whereas 25:1 $CHCl_3$-MeOH was used for MeOH extracts. TLC plates were first visualized under UV light (254 and 365 nm) and then sprayed with 5% H_2SO_4 followed by 1% vanillin in ethanol and heated at 110°C for 5 min.[44]

Prior to GC-MS analysis, approximately 1 mg of both hexane and MeOH extracts were esterified using diazomethane as described by Schlenk and Gellerman.[45] MeOH extracts were derivatizated using BSTFA (Pierce chemical). Approximately 1 mg of each MeOH extract was dissolved in 1 ml of BSTFA and heated for 30 min at 45°C. GC-MS analysis was performed using an Agilent technologies (Delaware, USA) 6890N Network GC System equipped with an automatic split-splitless injector, Agilent technologies 7863 series autosampler, and a Mass Selective Detector model Agilent technologies 5973 Network. A DB-5MS column from J&W scientific was used (30 m length, 0.25 mm i.d., 0.25 μm film thickness) and He carrier gas was circulated at a flow-rate of 1 ml/min. The chromatographic conditions are shown in Table 2. The injector temperature was set at 250°C. The column temperature was initially kept at 100°C for 2 min and then increased to 280°C at a rate of 3°C min^{-1} where it was held for 10 min. The detector temperature was set at 280°C.

Reversed phase HPLC analysis was performed using an Agilent technologies (Delaware, USA) 1100 series HPLC system with UV detector using an Inertsil ODS C18 column (6.0 × 250 mm, GL Siences Inc., Tokyo, Japan). Detection wavelength was set at 300 nm and the flow rate was 1 ml/min. A linear gradient elution of A (H_2O) and B (MeOH) was used starting with 90% A and 10% B to reach 100% B at 40 min. The system was then held at 100% B for 10 min.

RESULTS AND DISCUSSION

Yields of Extractions

Since three solvents were used for the extractions, three extracts were obtained from untreated wood and other 18 extracts were obtained from the wood heat

Table 2. Compounds assessed by GC-MS extracts of treated and untreated Jack pine

	Relative composition (%)					
	Hexane extracts		CH_2Cl_2 extracts		MeOH extracts	
Compounds	Untreated	Heat treated*	Untreated	Heat treated*	Untreated	Heat treated*
Methyl pimarate	5.4	5.7	0.7	2.9	—	—
Methyl sandaracopimarate	1.4	1.4	0.2	0.9	—	—
Methyl isopimarate	6.7	7.3	0.7	2.4	—	—
Methyl palustrate	15,4	4.1	—	—	—	—
Methyl dehydroabietate	20.3	30.5	4.2	25.8	—	—
Methyl abietate	16.5	21.9	1.8	17.6	—	—
Pinosylvin	—	—	3.7	3.4	7.6	—
Pinosylvin monomethyl ether	—	—	25.2	3.4	11.7	0.9
Pinosylvin dimethyl ether	—	—	1.4	1.6	—	—
Pinobanksin	—	—	—	—	23.9	—
Vanillin	—	—	—	—	—	6.7
Unidentified compounds	34.3	29.1	62.1	42.0	56.8	92.4

*Maximal (final) temperature of treatment was 230°C.

treated using six different conditions (Table 1). All the extracts obtained with methanol were fine granular powder, while the other extracts seemed more like gums, probably due to their resin content. In general, increasing the heat treatment temperature increased the rigidity of the gums. In all cases, higher maximum temperature resulted in darker color extracts. When the Jack pine was treated, the color of the hexane extracts changed from orange to brown. All the other extracts, separated with both dichloromethane and methanol, were brown, but they became very dark when the maximum heat treatment temperature of the wood exceeded 200°C.

The dried wood powder was weighed before and after all extraction steps to determine the weight loss of the wood samples due to the extraction ($\Delta\ m_w$). The difference between m_e (the mass of each dried extract) and $\Delta\ m_w$, caused by the lost of material due to the manipulation of the extract, has never exceeded 4%. Figure 1 shows extraction yield (ratio of the weight of the extract to the initial weight of the wood powder) as a function of the maximum heat treatment temperature for the three solvents used. Yields obtained for untreated wood are presented at 25°C (room temperature). The untreated wood seems to contain the biggest portion of extractives, especially non-polar components (hexane extract). As the wood is heated up to intermediate temperatures (160–200°C),

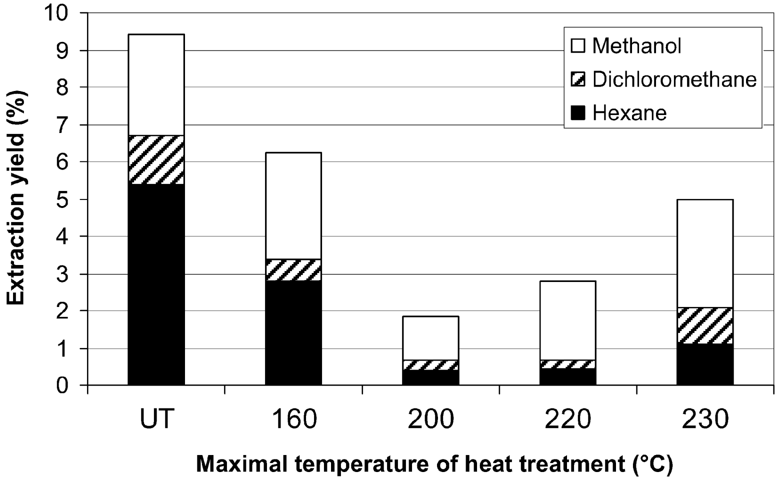

Figure 1. Yield of the extracts obtained from thermally treated Jack pine, using different maximal temperatures. Solvents of extraction were hexane, dichloromethane, and methanol (UT is used for untreated wood).

the weight of the extractives decreases gradually until a minimum is reached around 200°C. The results show that the weight decrease of non-polar extracts is the most important, while the quantity of the polar extract remains almost constant until 160°C and decreases only around 200°C. This general decreasing tendency is probably caused by the volatilization of different extractives from the wood due to heat.

The yield of the methanol extract increases significantly above 200°C. Some increase in the quantity of dichloromethane and methanol extracts can be also observed above 220°C. However, contrarily to the untreated wood, the samples heated above 200°C contain mainly polar extractives. This fact suggests the formation of new polar compounds during the degradation of biopolymers.

The impact of the heating rate and the gas humidity on the extract formation was also investigated at the maximum temperature of 220°C (Figure 2). When the heating rate was decreased from 20 to 10°C/h, the weight of extracts increased slightly for all solvents. However, only the change of the polar extract, obtained with methanol, is important. In fact, at lower heating rate, more polar by-products might form due to the longer period of heat treatment. At low humidity content, the extracts seem to be clammier. The presence of additional humidity, injected to the gas phase (100 kg/m^3 instead of 5–10 kg/m^3), increased the quantity of the polar (methanol) extract. According to the literature, moisture promotes the hydrolysis of the hemicelluloses, producing small polar compounds.[11,16,46] Gas humidity had only a small impact on the

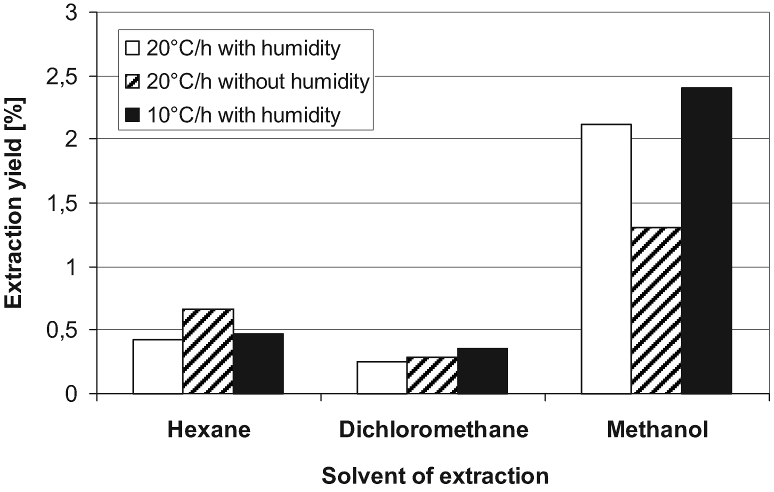

Figure 2. Yield of extracts obtained from thermally treated Jack pine, using different heating rates (10 and 20°C/h), gas humidity (10 and 100 g water/m^3 gas) at a maximum heat treatment temperature of 220°C.

amount of dichloromethane extract and increased only very slightly the amount of non-polar (hexane) extracts.

Chemical Analysis

Chemical changes of heat-treated wood extractives were investigated using TLC and GC-MS analysis. TLC of hexane extracts obtained from wood treated with increasing maximum temperatures showed only minor chemical transformations. Namely, the extracts obtained from wood treated at maximum temperatures of 200°C (H200) and 220°C (H220) showed lower intensities of resin acids spots on TLC than the extracts obtained from untreated wood (HNT) and wood treated at 160°C (H160). As expected, the resin acid concentration decreases with higher final temperature of treatment (effect of volatilization and/or degradation). However, wood treated at 230°C had a slightly higher resin acid content than H200 and H220. The GC-MS analysis confirmed this observation. These results follow a similar trend as the extraction yield obtained (Figure 1). Six resin acids have been identified with respect to their mass spectra and retention time with commercial standard (Table 3). Abietic acid and dehydroabietic acid are the major compounds in both treated and untreated wood extracts.

The most noticeable trend observed with the CH_2Cl_2 extract is the diminution of PSM after the treatment. According to TLC analysis, PSM is a major

Table 3. Compounds assessed by GC-MS extracts of treated and untreated Jack pine

	Relative composition (%)					
	Hexane extracts		CH_2Cl_2 extracts		MeOH extracts	
Compounds	Untreated	Heat treated*	Untreated	Heat treated*	Untreated	Heat treated*
Methyl pimarate	5.4	5.7	0.7	2.9	—	—
Methyl sandaracopimarate	1.4	1.4	0.2	0.9	—	—
Methyl isopimarate	6.7	7.3	0.7	2.4	—	—
Methyl palustrate	15,4	4.1	—	—	—	—
Methyl dehydroabietate	20.3	30.5	4.2	25.8	—	—
Methyl abietate	16.5	21.9	1.8	17.6	—	—
Pinosylvin	—	—	3.7	3.4	7.6	—
Pinosylvin monomethyl ether	—	—	25.2	3.4	11.7	0.9
Pinosylvin dimethyl ether	—	—	1.4	1.6	—	—
Pinobanksin	—	—	—	—	23.9	—
Vanillin	—	—	—	—	—	6.7
Unidentified compounds	34.3	29.1	62.1	42.0	56.8	92.4

*Maximal (final) temperature of treatment was 230°C

compound in the CH_2Cl_2 extract (DNT) of untreated wood while only traces have been detected in the heat-treated wood extracts. The GC-MS analysis of the CH_2Cl_2 extract (at final temperature, 230°C) of heat-treated wood reveals that abietic acid and dehydroabietic acid are the major compounds (Table 2). This result is explained by the diminution of the major compound PS with the heat treatment. Resin acids, which are minor compounds in the untreated wood extract, become more important as PS decreases. The diminution of PS is an interesting result because this compound is often considered as protector of the natural wood substrate because it decreases the rate of decay.[33–36] The yield increase between the 200°C and the 230°C final temperature of treatment (Figure 1) cannot be explained by the composition analysis of the CH_2Cl_2 extract.

TLC analysis of MeOH extracts of wood treated at different final temperatures showed major chemical modifications compared to the untreated wood extract. Similarly to the CH_2Cl_2 extract, major compounds of the untreated

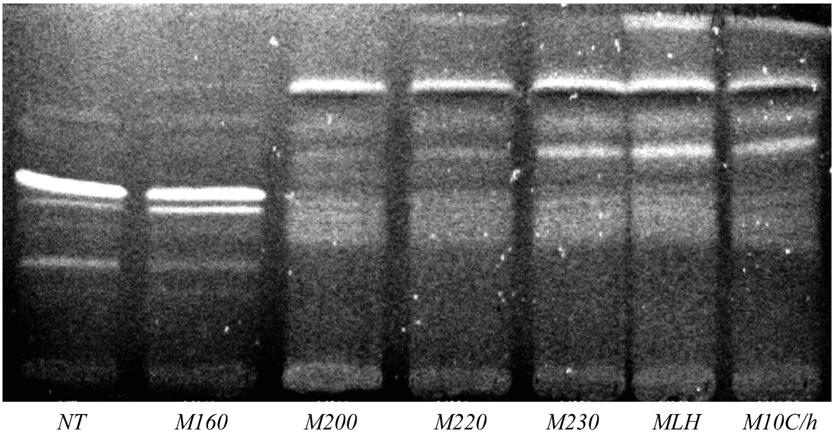

Figure 3. TLC analysis of MeOH extracts with different final temperature, heating rate, and gas humidity. Identifications of the extracts on the figure correspond to those in Table 1.

extract (PS, PSM, and pinobanksin) disappeared almost completely at a final treatment temperatures of 200°C and above (200, 220, and 230°C). This result explained the yield decrease observed with the M200 extract. Because the MeOH extraction yield increased again above 200°C, analysis of the results of this work suggested that the degradation of wood polymers created new by-products at final treatment temperature of 220 and 230°C. In an attempt to identify some of the compounds formed during the heat treatment, different possible lignin, cellulose, and hemi cellulose degradation products have been used as standards for TLC, GC-MS, and HPLC analysis. According to Sjöström,[47] degradation of pentose led to furfural and degradation of hexose led to 4-hydroxymethylfurfural (HMF). Only HMF has been weakly detected in the methanol heat-treated extract using TLC. This result has been confirmed by HPLC analysis by comparing the time retention with the commercial standard. Vanillin has also been identified as a new compound that appeared with the heat treatment by GC-MS analysis (Table 2). Cinnamylacohol, eugenol, and trans-cinnamaldehyde, which might be lignin degradation by-products, have not been detected by TLC. Although vanillin and HMF have not been quantified, it seems unlikely that these two compounds are responsible for the yield increase observed (Figure 1) because they have been weakly detected in the extract. Major compounds detected by TLC analysis of methanol extracts of heat-treated wood (Figure 3) could not be identified in this work. An isolation process would need to be developed in order to identify these compounds.

CONCLUSIONS

After the analysis of the yield and the composition of hexane, dichloromethane, and methanol extracts of untreated and heat treated American Jack pine, the following conclusions can be drawn:

- Non-polar components (especially resin-acids) represent the major part of the extractives in untreated Jack pine. They evaporate or degrade gradually during thermal treatment. The majority of the non-polar components are eliminated around 200°C.
- Six resin acids have been identified in the non-polar extractives of Jack pine. Abietic acid and dehydroabietic acid were the major compounds in the non-polar extracts of both heat-treated and untreated wood samples.
- Polar components are in minority among the untreated Jack pine extractives. They are almost not affected by heat under 160°C. The polar extraction yield decreases moderately between 160–200°C, which corresponds to the decrease of PS, PSM, and pinobanksin. The quantity of the polar compounds increases again at higher temperature, probably due to formation of polar degradation products. They become dominant among the extractives of Jack pine heat-treated above 200°C. 4-hydroxymethylfurfural and vanillin has been identified as new compounds appeared with the heat treatment. However, they cannot be responsible for the totality of the increase of yield of polar extractives. Hence, further work is necessary to identify other thermal degradation products.
- The Jack pine treated at maximum temperature of 200°C gave the smallest extraction yield. At this temperature, most of the volatiles are already removed, while the formation of by-products produced during the degradation of wood polymer components does not seem to be very important.
- Higher gas humidity and lower heating rate (longer heat treatment) seem to increase the yield of polar components, while they have no important impact on the evacuation of non-polar compounds.
- PS and PSM are known as natural protecting agents against fungi. However, they almost disappeared from the extracts obtained from wood treated above 200°C, thus they cannot play any role in the increase of the decay resistance of the heat-treated wood.

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