Differential Calorimetric Study of Pine and Poplar Lignins between 300 and 525 K*

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INTRODUCTION

The different morphological elements of wood contain various lignin types in more or less intricate associations with cellulose and hemicelluloses. Lignin heterogeneity is a central problem, not only in academic studies (e.g., biosynthesis or biodegradation pathways), but also in practical ones such as lignin reactivity or development of lignin byproducts.

Lignins are polydisperse, crosslinked, three-dimensional macromolecules made of phenylpropane (C_9) units. Their main structural characteristics are shown in Table I, with the usual symbols and notations commonly met in the field of lignin chemistry.[1] The practical consequence of such complexity is that one is obliged to consider lignins to be different according to the treatments required to recover them.[1-4]
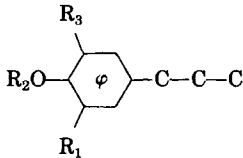
Such differences are particularly noticeable in guaiacyl–syringyl type lignins isolated from a deciduous wood (poplar) where variations of the syringyl to guaiacyl ratio or of the xylan proportions have been reported.[5] The other lignins studied were guaiacyl type, extracted from a coniferous normal wood (opposite pine wood) and guaiacyl–p-hydroxyphenyl type, coming from a coniferous reaction wood (compression pine wood).[6] Additionally, other structural differences are noteworthy, such as the quantity of condensed structures which is higher in compression wood than in opposite one,[7,8] as well as the proportion of galactose units present only in compression fractions as seen by their ^{13}C NMR signals,[9] which confirms the intricate association between lignins and galactose recently discussed by Timell.[6]

Previous differential scanning calorimetry studies (DSC) were performed by Hatakeyama et al.[10] on dioxane treated lignin, desiccated at 423 K and kept under a dry atmosphere. These authors investigated the influence of annealing temperature (380–400 K) and its duration (60–900 mn) on the glass transition temperature (T_g) and the heat capacity at T_g. Since all samples showing any trace of rehydration or degradation (as evidenced by a weight gain or loss) were systematically discarded, they found that lignin behaved like an ordinary high polymer.

The aims of this study are different from Hatakeyama's, as they investigate possible gross modifications of lignin fractions following gentle ther-

TABLE I
Lignin Fractions Characteristics

Characteristics	Usual notations and symbols
Phenylpropane structural unit	R_3 R_2O—〈 φ 〉—C—C—C R_1
Monomeric composition	Unit p-OH phenyl: $R_1 = R_3 = H$ Guaïacyl: $R_1 = OCH_3$; $R_3 = H$ Syringyl: $R_1 = R_3 = OCH_3$
Nonlignin components	+ p-OH benzoic esters (in poplar lignin) + Carbohydrate contaminants

mal treatments. Particular attention was placed upon T_g values, which proved to be a sensitive parameter for comparison.

Studies on glass transition temperature and on thermal stability of wood components may have a great technical interest as woods are subjected to thermal treatments in many processes such as drying, dimensional stabilization, thermochemical pulpings, steam explosion, production of boards or panels, and sterilization. Numerous publications concerning this subject have been reviewed recently by Fengel and Wegener.[4] However, owing to their complex structures, the main wood polymers have been characterized in relation to these thermal properties only during the last decades. Comparative studies of thermal stability of lignin fractions isolated from the same sample of wood are lacking until now. Such comparison may thus be of interest to explain differences in thermal behavior of woods, because plastification and thermal modifications of the amorphous lignins may contribute to mechanicochemical rearrangements of the semicrystalline polyosidic polymers from wood: cellulose and hemicelluloses.

EXPERIMENTAL

Samples

Lignin fractions were prepared according to a previously described extraction scheme[5] which may be summarized thus: fraction M corresponds to the dioxane–water extract of the ultraground extractive-free sawdust; fraction E is similarly extracted from the M-free residue, following its enzymatic hydrolysis with commercial cellulase; fraction R is obtained from the M- and E-free residue, after a last ultragrinding step.[5] Extractions yields are shown in Table II.

Thermal Treatment

These experiments were performed in a Differential Scanning Calorimeter (Perkin-Elmer DSC-2C) equipped with a dry glove box and a cooling device, which allowed the use of the fastest cooling rate of this apparatus (320 K mn^{-1}).

TABLE II
Extractions Yields[a] of Different Lignin Fractions

Fractions[b]	M	E	R	Total
Samples				
Poplar, Populus trichocarpa ev. Fridzi Pauley (16% Klason lignin)	34	46	18	98
Pine, Pinus maritima Opposite wood (29% Klason lignin)	16	23	31	70
Compression wood (36% Klason lignin)	15	18	27	60

[a]Yields are expressed as weight percentages of total lignin (Klason determination) in the extractive free wood sawdust.
[b]See text for fraction definition.

Lignin fractions were kept in an evacuated desiccator for 2 weeks at least. Samples were then pelleted under hand pressure in a glove box filled with dry nitrogen and encapsulated in large or small DSC pans. The latter, which are normally tight, were pierced just before heating in order to allow vapors to escape.

A rigourous experimental procedure was devised so as to obtain results from samples not polluted by atmospheric water, or by the products resulting from previous pyrolysis. The pans were wrapped in pieces of aluminum foil of known weight, in which the volatile products condensed. After each heat treatment the pan was carefully wiped, the foil replaced, and then both were quickly weighed. This technique minimizes the possibility of water vapor to enter the system during the weighing operations, as shown by the absence of the corresponding peak around 320 K. However in spite of these precautions, it proved impossible to prevent some volatile products settling on the surface of the DSC measuring heads and also on the sample holder enclosure block. It was found essential to make use of the guard ring insert accessory which facilitates daily cleaning. It must be emphasized that all experiments were run using dry nitrogen as the carrier gas.

All samples were subjected to identical thermal cycles: from a base temperature of 295 K, two successive heatings up to 473 K, a heating up to 525 K with a 3 mn stay, two heatings up to 525 K. Heating to 473 K was performed at 10 K mn^{-1}, heating to 525 K at 20 K mn^{-1} whereas the cooling rate was always 320 K mn^{-1}. These temperature programs are labelled 1–5 (cf. Table III).

The DSC signals were processed by the 3600 Thermal Analysis Data Station (Perkin-Elmer) to give values for T_g, which were evaluated at the midpoint of the glass–liquid transformation. Unless stated, the temperature reported is the mean value of two samples. The standard deviation may be calculated and is systematically given. A typical example of a DSC trace for the 1st, 2nd, 3rd, and 5th heating cycles is shown in Figure 1, and will be discussed later.

TABLE III
Relative Weight Loss (%) of Lignin Fractions as a Function of Successive Heating Cycles or Treatments

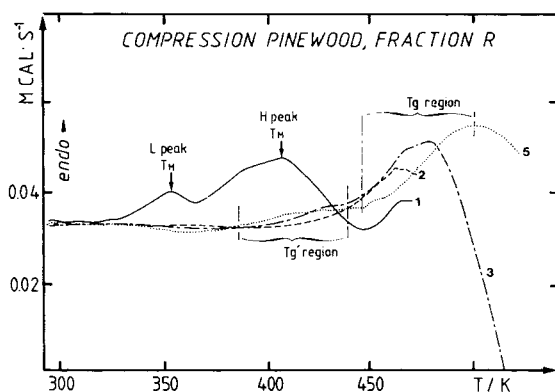| Treatment sequence	Limiting temperature (K)	Wood	Lignin fraction					
			M		E		R	
			Weight loss (%)	Standard deviation (%)	Weight loss (%)	Standard deviation (%)	Weight loss (%)	Standard deviation (%)
1	473	Pine compression	3.3	1.4	4.2	0.4	3.0	0.1
2	473		0.3	0	0.6	0	0.6	0.2
3	525 (3 mn)		7.2	1.0	9.6	0.4	9.2	0.3
4	525		1.3	1.1	0.9	1.1	0.4	0.2
5	525		0.2	—	0.6	0.4	0.4	0.3
1	473	Pine opposite	5.2	1.4	3.8	0.6	2.8	0.6
2	473		0.5	0.1	0.8	0.4	0.7	0
3	525 (3 mn)		6.6	0.1	8.4	0	8.4	0.3
4	525		0.6	0.2	—	—	0.3	0.4
5	525		—	—	—	—	—	—
1	473	Poplar	2.3	0.9	2.1	0.7	2.4	1.4
2	473		0.3	0.4	0.4	0.1	0.7	0.1
3	525 (3 mn)		6.8	0.3	8.4	0.8	8.2	0.1
4	525		1.2	0	1.2	0.2	1.2	0.2
5	525		0.4	0.3	0.9	0.1	0.7	0.2

Fig. 1. Thermograms of successive heatings of a compression pinewood fraction R: (1, 2, 3, 5) order of heatings; peak L = low temperature peak; peak H = high temperature peak; T_M = temperature of the maximum of a peak; T_g, T_g' = glass transition temperatures.

The results were systematically analyzed using Student's t test.[11] †

Results

As Hatakeyama had reported low temperature anomalies in NMR experiments,[12] the samples were examined between 100 and 290 K, but no transition was detected.

Weight Loss During Successive Heatings

Although data for weight loss after heating are not usually associated with DSC analysis, the results obtained here are interesting and hence reported. It appears from the examination of Figures 2(a) that all lignin samples behaved according to the same general pattern: Large weight losses occurred only after the first heating to 473 or 525 K. The analysis of results contained in Table III showed clearly that there was no significant difference between samples M, E, and R, whatever the origin of the wood. It must be noted that the third heating of all M samples caused a smaller weight loss than in R or E ones.

Thermal Analysis

In all cases studied, the first heating is marked by one or two endothermic peaks followed by a rise in enthalpy, characteristic of a glass transition

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† If X_1, S_1, n_1 and X_2, S_2, n_2 are respectively the mean values, the standard deviations, and the sizes of samples 1 and 2, it can be defined a variable t, such that $t = (X_1 - X_2)/[\sigma(1/n_1 + 1/n_2)^{1/2}]$, where $\sigma = \{(n_1 S_1^2 + n_2 S_2^2)/(n_1 + n_2 - 2)\}^{1/2}$. The distribution of t is a Student's distribution with $df = (n_1 + n_2 - 2)$ degrees of freedom. On the basis of a two tail test at 0.05 level of significance, the null hypothesis (all samples compared are similar) is to be rejected (result not "probably significant") if t falls outside the range $t_{-0.975}$ to $t_{+0.975}$, which, for $df = 2(n_1 = n_2 = 2)$, is -4.303 to $+4.303$. To get a "really significant," answer t has to lie between $+$ and $- 9.925$ ($t_{-0.995}$ to $t_{0.995}$).
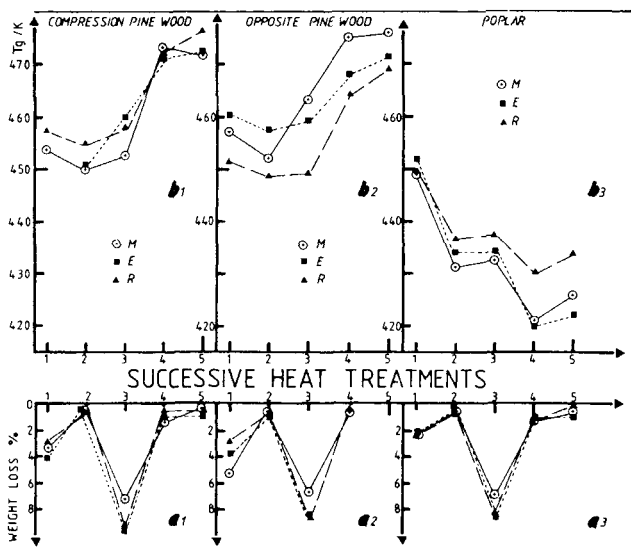
Fig. 2.   Weight loss (a) and evolution of T_g (b) of different lignin fractions as a function of heating cycle; ($\oplus$) M; ($\square$) E; ($\blacktriangle$) R.

(Fig. 1). The second heating shows only the glass transition. These features are considered separately.

Low Temperature Endothermic Peaks

One or two peaks are clearly visible on the thermograms corresponding to the first heating but their areas cannot be easily separated (Fig. 1). It is usual in DSC studies to take the departure from base line (the onset temperature) as the temperature of a transition, but in the present case it was found to be unreproducible. Hence, only the maximum peak temperatures T_M were considered. The results are included in Table IV.

Poplar exhibits a single peak between 300 and 450 K which coresponds to the high temperature peak (H) observed on pine thermograms together with a low temperature one (L). The temperature maxima of the latter lie between 340 and 356 K and do not vary significantly. The temperature maxima of the H peak differ significantly according to the fractionation method: in all cases $T_M < T_R < T_E$. When the species are compared, the T_M of pine samples are probably the same and differ from those of poplar, which are always lower.

In all samples, the presence of peak H may be due to some solvent evaporation, if the corresponding enthalpy variations ΔH are related to the total weight loss occuring during first heating. These values are somewhat unreproducible, and hence no correlation could be made. It may be noted, however, that this enthalpy is generally much lower than the water vaporization enthalpy (509.5 cal g^{-1}),[13] but higher than the dioxane one (94.3 cal g^{-1}).[13] These two solvents, used for lignin preparation, are potentially present within the samples and their close boiling points (373.15 and 374.8 K, respectively) are in the neighborhood of the observed H peak. The conclusion

TABLE IV
Maximum Temperature (K) and Enthalpy Variation of Endothermic Peaks Following First Heating of Lignin Fractions

Wood	Lignin fraction	Low temperature peak (L)		High temperature peak (H)		Total peak enthalpy	
		T_M (K)	Standard Deviation (K)	T_M (K)	Standard Deviation (K)	ΔH (cal g^{-1})	Standard Deviation (cal g^{-1})
Pine compression	M	347.0	4.2	392.5	0.4	313	230
	E	392.5	0.7	417.3	5.0	156	3
	R	354.0	0	404.9	2.8	240	79
Pine opposite	M	340.0	9.2	387.8	6.2	221	154
	E	339	15.6	414.2	1.6	208	76
	R	345	4.2	402.9	3.3	147	38
Poplar	M	—	—	334.5	0.3	396	83
	E	—	—	398.5	6.8	245	27
	R	—	—	393.5	0.4	450	213

that peak H is due to solvent evaporation is substantiated by two observations. It was found in a sample of opposite pine wood (fraction M), fortuitously rehydrated after the 2nd heating, that no first peak was observed and ΔH was 506 cal g^{-1}. The second observation occurred in a rehydrated pyrolysed compression pine fraction R, where ΔH amounted to 534 cal g^{-1}.

As the different samples had been lyophilized, these results emphasize the experimental difficulty in obtaining lignin samples perfectly free from traces of moisture or of solvent used during the extraction step. Occurrence of dioxane in some lignin preparations has been also observed by ^{13}C NMR spectroscopy.[9] The dependence of solvent retention upon wood origin remains unexplained as well as the nature of peak L.

Glass Transition

The results are given in Table V and reported in Figure 2(b); the error bars have been omitted for purposes of clarity.

PINE LIGNIN FRACTIONS

As seen in Figures 2(b1) and 2(b2), there is a common general trend in T_g variation with successive heat treatments, but only the increase of T_g observed during the 4th one (i.e., after a previous 3 mn stay at 525 K) is really significant. It was seen, however, on a single sample than upon further heating T_g increased from 471 to 475 (6th) and 481 K (7th heating) associated with small weight losses (0.7 and 0.3%).

When corresponding fractions subjected to similar heat treatments are statistically compared, it may be shown that M samples are very similar, while E ones are possibly different and R fractions are surely different from each other: the difference of T_g is significant only in this last case.

A small thermal effect was encountered in practically all pine lignins between 390 and 410 K, but is was not possible to decide whether it was attributable to a small endothermic peak or to a glass transition (T'_g), which seems more likely (see Fig. 1). In the latter case it will follow more or less the trend observed for the high temperature T_g with a larger uncertainty.

POPLAR LIGNIN FRACTIONS

The effect of heat treatments upon lignin samples starts with a general decrease of T_g: even the first step at 473 K has a dramatic influence, as does the short stay at 525 K [see Fig. 2(b3)]. The following excursions to 525 K seem to increase T_g. An additional heating with a 10 mn stay at 525 K performed on a single R sample confirmed this tendency: T_g rose from 428.5 to 437.8 K and was accompanied by a signifcant weight loss of 7%.

Although there is the same general trend for the three fractions, the R one is significantly more resistant to thermal treatment than the other two.

It may be seen (Fig 3) that fraction M and R react to high temperature not only by an increase in T_g but also by the formation of a new compound whose melting (?) point is around 506 K. The enthalpy variation associated with this peak is more intense in fraction M, and $\Delta H = 1.4$ cal g^{-1} of

TABLE V
Glass Transition Temperatures of Lignin Fractions as a Function of Successive Heating Cycles

| Treatment sequence	Wood	Limiting temperature (K)	Lignin fractions					
			M		E		R	
			T_{g_M} (K)	Standard deviation (K)	T_{g_M} (K)	Standard deviation (K)	T_{g_M} (K)	Standard deviation (K)
1	Pine compression	473	453.7	—	—	—	457.6	1.7
2		473	450.0	4.6	451	4.2	454.8	9.3
3		525 (3 mn)	452.7	2.8	459.8	16.3	457.9	1.7
4		525	473.0	4.9	470.9	1.4	472.3	0.1
5		525	471.7	7.5	472.3	3.4	476.4	4.5
1	Pine opposite	473	457.0	2.8	460.4	0.3	451.2	3.2
2		473	451.8	4.0	457.4	0.1	448.6	0.8
3		525 (3 mn)	463.1	1.6	459.2	2.2	448.9	5.1
4		525	475.1	3.5	468.1	3.0	464.1	0.5
5		525	476.1	1.0	471.5	—	469.2	1.1
1	Poplar	473	449.3	0.2	452.2	1.8	449.2	0.3
2		473	431.3	0.1	434.2	0.1	436.7	0.3
3		525 (3 mn)	432.6	0.5	434.0	0.1	437.2	0.6
4		525	420.9	4.2	420.4	2.5	430.3	3.3
5		525	425.9	5.5	422.2	1.9	433.9	0
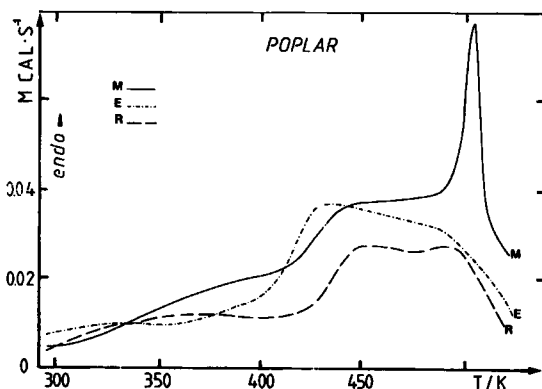
Fig. 3. Thermogram of the 5th heating of poplar lignin fractions: (—)M; (– · –) E; (---) R.

pyrolyzed lignin. It must be noted that this ΔH does not rise after the second heating to 525 K.

DISCUSSION

Thermal softening of lignin, which marks its glass transition, was first reported by Goring[14] at temperatures around 400–500 K depending on origin. In previous DTA studies it was often difficult to detect a T_g, it being masked by the large peak corresponding to water evaporation which extends from 330 to 480 K.[15]

T_g values observed in the present study are in general agreement with published values concerning dry lignins: Hatakeyama et al.[10] report values around 400–420 K for dioxane lignin, Back and Salmen[16] quote results between 400 K and 460 K for lignins of different origins, whereas Irvine[17] reported 410 K for a sample of milled wood lignin Eucalyptus regnans and Glasser et al.[18] found 440 K for Kraft pine lignin. This demonstrates the paramount importance of recovery methods on the definition and therefore the properties of a lignin sample.

It is well known that water plasticizes lignin: 2% water is able to decrease the T_g by at least 60 K, or even more, [16,17] when comparing the first heating of samples containing a given amount of humidity. The decrease of T_g reported here after the first heating to 473 K may not, therefore, be only due to a water loss but perhaps also to the onset of lignin degradation which may be clearly seen on a spruce sulfuric acid processed lignin[15] or on Bjorkman cypress lignin.[19]

The effect of water on treated lignin is rather spectacular: a 0.6% water intake increased T_g by 9 K (fraction M, opposite pine); a pyrolyzed lignin rehydrated up to saturation showed a T_g increase of 14 K (fraction M, compression pine).

It can be tentatively concluded that: (i) water acts not only as a simple diluent but may also react with some sample component to modify the lignin structure, and (ii) the resulting new compound has a higher glass transition temperature. Hydrogen bonding may be associated in this process. Owing

to the technical interests in hydrated lignins, it would be useful to start a large scale study of these preliminary findings.

The overall result of this work is that a moderate pyrolysis to 525 K produces an increase of T_g in pine lignins, whereas it has the opposite effect in poplar ones. This could originate from the well established property that softwood lignins—particularly from compression wood—have more condensed structures than hardwood ones.

A study published by Brezny et al.,[20] dealing with moderate thermolysis of lignin model compounds analyzed by chromatography and mass spectrometry, has shown that chemical modification of lignin, such as etherification of free phenolic groups, may drastically change their thermal sensitivity. Condensation reaction with formaldehyde may produce similar effects.

The formation of formaldehyde has been confirmed unequivocally among the products of pyrolysis of pine lignin at temperatures higher than 470 K, by Fenner and Lephardt[21]; fragmentation may occur at the terminal hydroxymethylene groups ($—CH_2OH$) present in the phenylpropane units.

When guaiacylpropane is the single monomer unit (predominant in pine lignin), it degrades into phenylalkyl products, formaldehyde, and other volatile compounds. Formaldehyde so produced may induce new condensation of the remaining lignin by reacting with the 5 carbon of the guaiacyl cycle and the formation of 5,5'-diphenyl–methane bridges. This type of reaction is well established during the reactions between lignins and formaldehyde.[22]

It has been recently shown that, during the initial stages of heat treatment, condensation reactions prevail over the degradation ones in guaiacyl lignin (pine), whereas the reverse is true in guaiacyl–syringyl lignins (aspen).[23]

When syringyl propane units are also present (mainly in R and E fractions of poplar), the additional methoxyl group may prevent (by preexisting substitution) the condensation with formaldehyde and the reticulation of lignin. Thus, degradation products may plasticize the remaining lignin in a first step and lower its T_g. The next thermolysis will increase formaldehyde yield and induce reticulation of the condensate, explaining the increase in T_g observed in subsequent heat treatments.

In concordance with this hypothesis, one may recall the observations of Wayman and Chua,[24] who observed that, during heating of wood with steam at high pressure and high temperature (468 K), there was an increase of the syringyl to guaiacyl monomer ratio in poplar lignin fractions. The significant increase of this ratio, reported after 5 min of treatment, was partly explained by a preferential condensation of guaiacyl units. This phenomena was followed by a decrease of the monomer ratio.

Additional experiments are required to test these points, by chemical or physicochemical detection of reaction intermediates, particularly, formaldehyde and condensation products.

Nonlignin components (carbohydrates contaminants, parahydroxybenzoic esters of poplar samples) may also play an important role as shown by the difference in behavior between fractions R of pine and poplar. However, the structural differences between opposite and compression samples, as described in the Introduction, were not able to induce significantly different DSC responses.

CONCLUSION

The DSC study of pine and poplar lignins has shown that, as long as careful experimental procedures are followed, one finds interesting differences of thermal behavior which may be characteristic of lignin origin. This work has shown the constraints of such studies, in particular the lack of characterization or representativity of the samples, even when they have been carefully prepared according to well-defined methods. Further studies would benefit from the inclusion of model compounds studied in parallel with actual samples.

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