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# THERMAL DEGRADATION OF SULPHURIC ACID LIGNINS OF HARD WOOD

G. E. DOMBURG and V. N. SERGEEVA

*Institute of Wood Chemistry, Academy of Sciences of the Latvian SSR, Riga*

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The process of thermal degradation of lignins of hard wood (birch, aspen, oak), obtained under the wood treatment with 66% sulphuric acid in the form of acid-insoluble and soluble fractions, has been investigated by thermal methods. Activation energy values of lignin pyrolysis have been determined at the stage of increasing rate of weight loss. It has been established that the difference in their thermal properties is conditioned by the structural changes in the process of isolation from wood. It has been suggested that acid-soluble lignins have a higher density than acid-insoluble ones. Sulphuric acid lignins of birch, in particular acid-soluble lignin, are assumed to possess a more homogeneous structure than sulphuric acid lignins of other species

Lignin, which goes into acid solution during wood treatment with concentrated acids and is precipitated by water from the acid solution, has been little investigated. Some time ago even its carbohydrate character was under consideration. However, at present the aromatic nature of this lignin is fully proved, but there is very little information in the literature on the structure of acid-soluble lignins.

As is known, the thermal properties of polymer materials are directly related to their stereochemistry and even slight changes of atomic arrangement in the basic and side chains of a macromolecule affect its thermal stability, mechanism and kinetics of degradation. We have used this thesis for establishing whether there are differences in the structures in acid-soluble lignins and lignins insoluble in sulphuric acid. A derivatographic technique was used in the present work, as this is one of the most sensitive methods for indicating structural changes in a substance, lignin in particular, as was shown in our recent investigation [1]. The kinetics of lignin degradation was studied at the definite stages of the process on the basis of DTA data.

Various kinds of hard woods were used to yield lignin preparations, since they provide a considerable yield of acid-soluble lignin as compared with coniferous woods.

## Experimental

Lignin preparations were obtained by treatment of sawdust (birch, aspen, oak), previously extracted with alcohol and water, with 66% sulphuric acid (48 hours, room temperature). Lignin insoluble in sulphuric acid solution was filtered out of the undiluted hydrolysate ("acid-insoluble"). Lignin, which was in acid solution and went into the filtrate, was precipitated by water ("acid-soluble" lignin). The characteristics of lignin preparations are given in Table 1.

Table 1

Characteristics of sulphuric acid lignins (based on abs.-dry substance, %)

| Wood species | Lignin preparation | Yield from wood | Elementary composition | | Content of methoxy groups | Content of general acid groups | Yield of aromatic aldehydes after nitrobenzene oxidation | Concentration of free radicals, $g^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | | | | |
| Birch | acid-insoluble | 9.3 | 61.70 | 5.39 | 20.63 | 6.96 | 0.11 | $1.04 \cdot 10^{17}$ |
| | acid-soluble | 6.6 | 61.53 | 6.10 | 21.87 | 7.00 | 0.07 | $1.35 \cdot 10^{17}$ |
| Aspen | acid-insoluble | 12.1 | 62.35 | 4.82 | 20.35 | 5.65 | 2.06 | $1.75 \cdot 10^{17}$ |
| | acid-soluble | 3.3 | 64.32 | 5.13 | 21.21 | 5.75 | 0.45 | $2.90 \cdot 10^{17}$ |
| Oak | acid-insoluble | 12.4 | 66.80 | 5.32 | 20.41 | 6.28 | 1.51 | $2.85 \cdot 10^{17}$ |
| | acid-soluble | 5.8 | 65.56 | 7.35 | 21.29 | 7.38 | 0.11 | $1.95 \cdot 10^{17}$ |

The measurements were carried out with a Paulik – Paulik – Erdey MOM derivatograph [2]. Some of the derivatograms were taken of samples placed in a crucible without a lid, where the vapour – gas mixture produced during thermal decomposition was removed by passing air through the system, and some of samples in a crucible with a lid, i.e. in an atmosphere of vapours and gases produced by heating. The heating rate was 12°/min up to 600°, the weight of sample being 100 to 200 mg.

The activation energy ($E$) for the thermal degradation of lignins was calculated from the results of the derivatographic measurements by the Horowitz – Metzger [3] method using the formula:

$$E = \frac{\ln \ln \dfrac{w_0 - w_t^f}{w_t - w_t^f} RT_s^2}{\Theta}$$

where $w_0$ = initial weight of sample, g
$w_t$ = weight of sample at the given temperature $T$, g
$w_t^f$ = final weight of sample after pyrolysis, g
$R$ = gas constant

$T_s$ = pyrolysis temperature (°K) at which

$$\frac{w_s - w_t^f}{w_0 - w_t^f} = C_s$$

where $w_s$ = weight of sample remaining at this temperature
$C_s$ = 0.368 – concentration at maximum slope when the reaction is known to be of the first order

$$\Theta = T - T_s,\ ^\circ\mathrm{C}$$

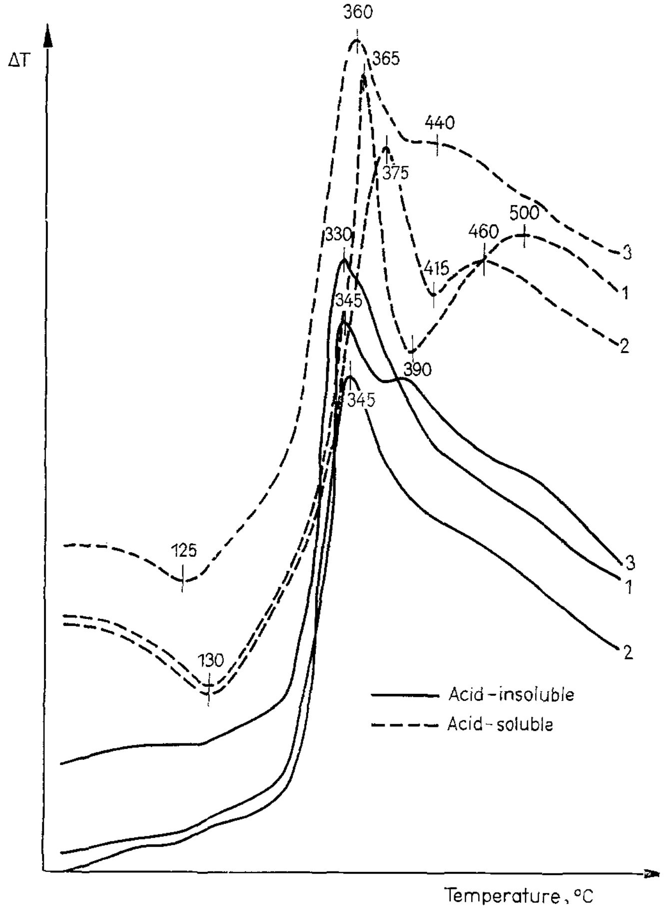

Fig. 1. DTA curves of sulphuric acid lignins of birch (1), aspen (2) and oak (3) when vapours and gases are removed

Table 2

Characteristics of thermal degradation

| Wood species | Lignin preparation | Stage I | | |
|---|---|---|---|---|
| | | Temperature range, °C | weight loss, % | rate of weight loss, %/min. |
| | | | when | vapours and |
| Birch | acid-insoluble | 200—255 | 2.5 | 0.8 |
| | acid-soluble | 200—325 | 8.1 | 1.1 |
| Aspen | acid-insoluble | 200—280 | 4.1 | 0.8 |
| | acid-soluble | 200—305 | 6.4 | 1.0 |
| Oak | acid-insoluble | 200—285 | 4.6 | 0.9 |
| | acid-soluble | 200—310 | 8.1 | 1.3 |
| | | | in | vapour—gas |
| Birch | acid-insoluble | 200—320 | 8.2 | 1.0 |
| | acid-soluble | 200—345 | 9.6 | 1.0 |
| Aspen | acid-insoluble | 200—260 | 2.0 | 0.4 |
| | acid-soluble | 200—340 | 8.4 | 1.0 |

A plot of $\ln \ln \frac{w_0 - w_t^f}{w_t - w_t^f}$ against $\Theta$ should give a straight line whose slope is then

$$E = \mathrm{tg}\,\alpha \cdot RT_s^2$$

Molecular weight distributions for lignin preparations of birch and aspen were determined by the gel filtration method through Sephadex $G-50$ in dimethylsulphoxide. The measurements were carried out by means of a photoelectrocolorimeter FEKI-57.

## Discussion

A great similarity in chemical characteristics (Table 1) and identity of IR spectra of acid-insoluble lignins prove the similarity of these preparations. However, as can be observed from DTA and DTG curves in Figs 1, 2, 3 and from the data given in Tables 2 and 3, the mechanism of thermal degradation of sulphuric acid lignins is different.

Pyrolysis of lignins in air and at normal pressure proceeds in three stages according to the rate of weight loss: 1. Stage of short side chains with small bond energy of sulphuric-acid lignins

| Stage II | | | Stage III | | | Total weight loss, % |
|---|---|---|---|---|---|---|
| Temperature range, °C | weight loss, % | rate of weight loss, %/min. | Temperature range °C | weight loss, % | rate of weight loss, %/min. | |
| gases are removed | | | | | | |
| 255—325 | 11.7 | 4.0 | 325—600 | 50.7 | 2.1 | 67.9 |
| 325—375 | 28.0 | 11.6 | 375—600 | 33.2 | 1.6 | 73.7 |
| 280—345 | 11.6 | 4.4 | 345—600 | 52.5 | 2.3 | 71.1 |
| 305—410 | 19.2 | 3.0 | 410—600 | 25.5 | 1.5 | 56.7 |
| 285—345 | 13.3 | 5.1 | 345—600 | 56.0 | 2.5 | 77.9 |
| 310—405 | 19.8 | 3.3 | 405—600 | 29.2 | 1.8 | 61.6 |
| atmosphere | | | | | | |
| 320—430 | 19.6 | 2.3 | 430—600 | 19.0 | 1.4 | 49.0 |
| 345—425 | 18.3 | 4.5 | 425—600 | 21.8 | 1.3 | 52.3 |
| 260—440 | 28.0 | 2.2 | 440—600 | 21.3 | 1.6 | 53.3 |
| 340—435 | 18.1 | 3.0 | 435—600 | 15.6 | 0.8 | 47.2 |

breaking off a macromolecule; this results in primary condensation processes. 2. Zone of active pyrolysis with bond breaking between structural units. A great quantity of volatile products is isolated and structural fragments of a free radical type are formed in solid phase [4]. A considerable amount of heat is generated in the recombination of these fragments. For this reason the exothermic effect can overlap endothermy of bond breaking on the thermogram. 3. A series of destructive-condensation processes proceeding with the formation of volatile products and accumulation of condensed aromatic structures in solid phase [5].

Acid-insoluble lignins begin to decompose in the temperature range 250° – 280°, reaching the maximum rate of decomposition at 290° – 340° in pyrolysis, conducted in air with the removal of volatile products. Acid-insoluble lignin of birch has the lowest thermostability of the lignins studied. Its main destruction proceeds at the rate of 4%/min. at rather low temperature ranges (255° – 325°, Fig. 2).

The maximum rate of thermal degradation of acid-soluble lignins is found at higher temperatures (355°–365°). Acid-soluble lignin of birch decomposes at 325°–375° at the rate of 11,6%/min., which is the highest value for sulphuric acid lignins.

The pyrolysis of lignins in an atmosphere of vapour–gas mixture (Fig. 3) is slowed down by the evolution of volatile products and is characterized by a

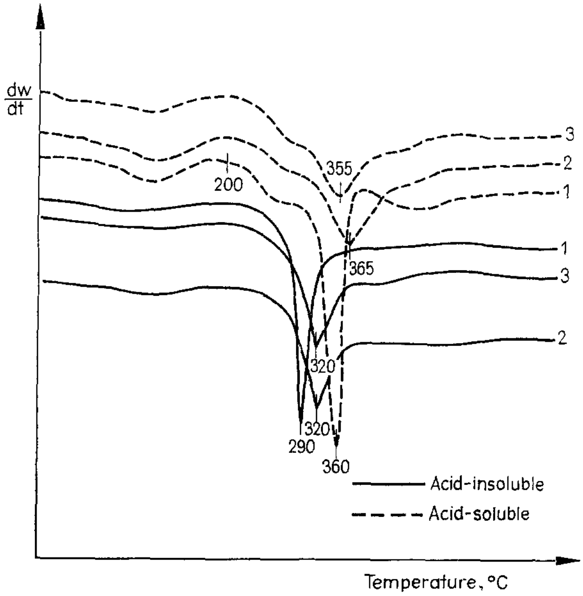

Fig. 2. DTG curves of sulphuric acid lignins when vapours and gases are removed

Table 3

Activation energy of thermal degradation of sulphuric acid lignins at the temperature range from 200° to the DTG maximum

| Wood species | Lignin preparation | Temperature range, °C | Weight loss, % | E, kcal mole |
|---|---|---|---|---|
| | when vapours and gases are removed | | | |
| Birch | acid-insoluble | 200–290 | 10.2 | 25.8 |
| | acid-soluble | 200–360 | 33.9 | 38.3 |
| Aspen | acid-insoluble | 200–320 | 11.1 | 24.5 |
| | acid-soluble | 200–365 | 15.2 | 17.8 |
| Oak | acid-insoluble | 200–320 | 12.1 | 26.1 |
| | acid-soluble | 200–355 | 16.4 | 18.6 |
| | in vapour-gas atmosphere | | | |
| Birch | acid-insoluble | 200–385 | 18.5 | 19.6 |
| | acid-soluble | 200–390 | 18.3 | 24.0 |
| Aspen | acid-insoluble | 200–370 | 17.1 | 19.1 |
| | acid-soluble | 200–400 | 18.5 | 17.1 |

widening of the temperature range of degradation and by a shift of the basic exothermy towards higher temperatures. Evidently, under these conditions of pyrolysis, recombination processes of high molecular fragments proceed with a greater yield than if the vapour–gas mixture is removed. This is confirmed by the total loss of the yield of volatile products and by decrease in the percentage degradation at stage 3 of pyrolysis. If the degradation at stage 3 for acid-insoluble lignins reaches 75% out of the total decomposition at the removal of volatile products, this figure is half as much in an atmosphere of vapour–gases.

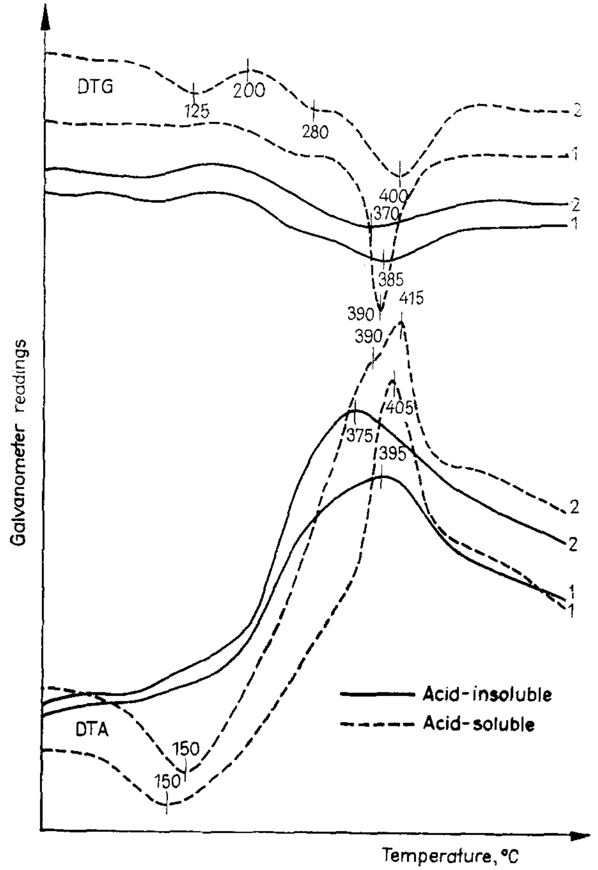

Fig. 3. DTA and DTG curves of sulphuric acid lignins of birch (1) and aspen (2) in vapour–gas atmosphere

The stage with increasing rate of decomposition is characteristic of the thermal degradation of lignins. This stage lies in the temperature interval from 200° to the maximum on the DTG curve. The percentage of lignin degradation increases with widening of this temperature interval, but the average degradation rate is constant. The pyrolysis of acid-soluble lignin of birch in air is an exception. Its degradation rate is twice as high as that of other lignins at this stage (Table 3).

At the stage of increasing rate of degradation the values of total activation energy for pyrolysis of sulphuric acid lignins fall within the limits of 17,1 – 38,3 which agrees with the data of other authors [6 – 8]. It should be noted that many different reactions take place simultaneously during the process of thermal degradation of lignins. The specific chemical changes that occur are obscure. Therefore, the values of activation energy obtained are to be regarded rather as comparative values which do not reflect the real thermal stability of the system.

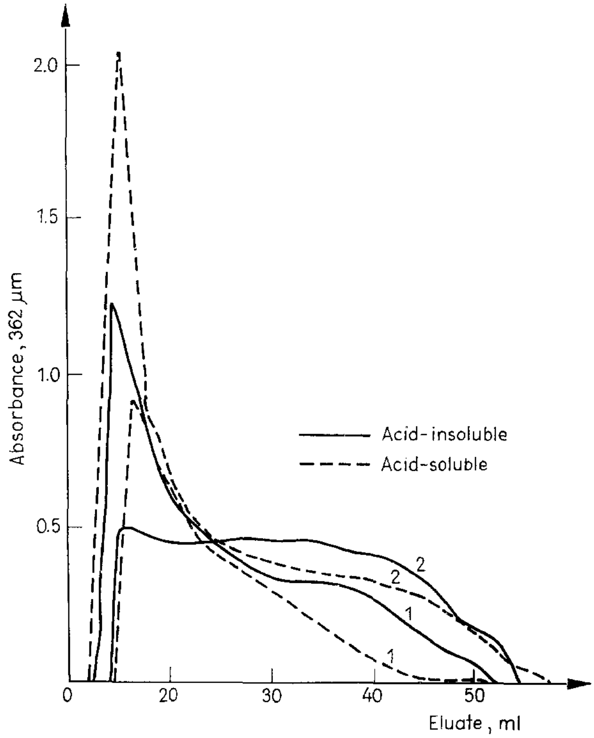

Fig. 4. Curves for molecular weight distribution of sulphuric acid lignins of birch (1) and aspen (2)

The process of degradation proceeds rather energetically in air. A chain character of degradation may be assumed in some cases (pyrolysis of acid-soluble lignin of birch). Yet the loss of the activity of free radicals is possible in air owing to their oxidation. As a result recombination reactions of radicals are slowed down. That is why with the removal of vapour and gases the total activation energy is just above that in an atmosphere of vapour – gas mixture.

In lignins subjected to strong thermal or thermochemical pre-treatment the changes of the original structure are reflected by the shift of the basic exothermic peak towards lower temperatures [9, 10]. It permits the assumption that acid-soluble lignins have a different structure from that of acid-insoluble ones although they are built of the same structural units. As is seen from the data obtained, their structure is more thermostable. Acid-soluble lignin of birch is an exception. 73,7% of it is decomposed and the nature of its thermal degradation (a marked thermal effect) indicates a definite regularity of the chemical structure. Evidently, the peculiarities of the natural lignin structure of birch, which cause the high yield of acid-soluble lignin (Table 1), specify its structure.

The increased homogeneity of sulphuric acid lignins of birch and especially of acid-soluble lignin, is reflected by the curves of molecular weight distribution of lignins (Fig. 4), illustrating that the homogeneity of acid-soluble lignin amounts to 55%.

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Résumé. — On a fait l'étude par ATD du processus de la dégradation thermique des lignines de bois durs (chêne, bouleau,) obtenues sous forme de fractions solubles et insolubles dans l'acide sulfurique à 66% utilisé pour traiter le bois. On a déterminé les valeurs des énergies d'activation au moment oú la vitesse de perte de poids augmentait. On a montré que les différences observées dans leurs propriétés thermiques étaient une conséquence des changements de structure provoqués pendant le traitement du bois. On a établi que les lignines solubles dans l'acide ont une structure plus dense que celles qui sont insolubles. Les lignines de bouleau isolées par l'acide sulfurique, surtout celles qui sont solubles, montrent une structure plus homogène que les lignines obtenues de manière comparable avec d'autres espèces.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Ligninen aus Hartholz (Eiche, Beberesche, Birke), erhalten in Form von säurelöslichen und unlöslichen Fraktionen der Holzbehandlung mit 66%iger Schwefelsäure, wurde thermoanalytisch untersucht. Die Werte der Aktivierungsenergie der Ligninpyrolyse wurden bei zunehmenden Gewichtsverlustgeschwindigkeiten bestimmt. Es wurde gefunden, daß die Unterschiede ihrer thermischen Eigenschaften auf die während der Abtrennung aus dem Holz erlittenen strukturellen Änderungen zurückzuführen sind.

Säurelösliche Lignine besitzen einen höheren Grad von Densität als säureunlösliche. Schwefelsäurelignine von Birke, besonders die säurelöslichen, zeigen bedeutend homogänere Struktur als die Schwefelsäurelignine anderer Sorten.

Резюме. — Термическим методом исследован процесс термораспада лигнинов, выделенных обработкой лиственных пород древесины (береза, осина, дуб) 66%-ной серной кислотой в форме кислоторастворимой и кислотонерастворимой фракций. Значения энергии активации пиролиза лигнина определены на стадии возрастающей скорости потери веса. Установлено, что разница в термических свойствах этих фракций лигнинов обусловлена изменениями их структур в процессе выделения из древесины. Предполагается, что кислоторастворимые лигнины имеют более уплотненную структуру, чем кислотонерастворимые. Сернокислые лигнины березы, особенно кислоторастворимый лигнин, обладают значительно более высокой степенью гомогенности, чем сернокислотные лигнины других пород.