

THERMOGRAVIMETRIC ANALYSIS OF LOBLOLLY PINE BARK COMPONENTS¹

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(Received 21 May 1975)

ABSTRACT

Thermogravimetric analysis of loblolly pine bark components (extractive-free bark, alkali-soluble material, alkali-extracted residue, Klason lignin, and holocellulose) was performed under different atmospheres. Degradation patterns of these bark components were different depending on composition and on the pyrolytic atmosphere. In the presence of oxygen, the rate of thermal decomposition was greater, and all bark materials were converted to volatile products. Thermal reactions under nitrogen and hydrogen and in vacuum were much slower and gave larger amounts of nonvolatile residue. Thermal curves obtained under nitrogen and hydrogen were very similar, while pyrolysis under vacuum conditions gave decreased amounts of char residue with the greatest effect in the holocellulose fraction.

Additional keywords: *Pinus taeda*, holocellulose, Klason lignin, atmospheric effects.

INTRODUCTION

It has been estimated that each year in the United States 14–20 million tons of bark residue are produced. Disposal of the vast amounts of bark has been one of the major problems facing the wood industry (Wood Products Sub-Council 1971). However, conditions have changed in the last year because of the increased cost of petroleum-based fuels. Presently more and more of the bark residues are being used as a low-grade fuel (Sarles 1969; Corder et al. 1970). Bark could also be a potentially valuable source of organic chemicals, provided that an efficient and economical method for their isolation could be developed. One potentially new method for converting bark into commercially useful organic chemicals is pyrolysis. Several articles have been published (Vroom 1952; Zavarin and Snajberk 1963; Erman and Lyness 1965; Martin 1968) concerning the pyrolysis of bark and its individual components; however, most of the studies were done under relatively harsh conditions, and little or nothing is known about the effects of temperature, pressure, and various atmospheres on the pyrolysis of bark.

In this study, loblolly pine bark (*Pinus taeda* L.) was separated into five different fractions: (1) extractive-free bark, (2) alkali-soluble material, (3) alkali-extracted residue, (4) Klason lignin, and (5) holocellulose. The thermal decomposition properties of these bark materials were characterized by using thermogravimetry (TG) and differential thermogravimetry (DTG). The decomposition studies were done under nitrogen, oxygen, and hydrogen and under a vacuum. Thermogravimetry measures the weight loss as a function of temperature, while differential thermogravimetry measures the rate of weight loss versus temperature. These techniques have been used widely to study the thermal decomposition of wood, cellulose, and a variety of other synthetic and naturally occurring polymer systems.

MATERIALS AND METHODS

Preparation of the bark materials

The loblolly pine bark used in this study and its overall composition have been described in an earlier publication (McGinnis and Parikh 1975). Approximately 80% of the dry weight of the bark was obtained after successive extractions with neutral solvents. The extractive-free bark consisted

¹This study was supported by funds from National Science Foundation Grant, P-213294.

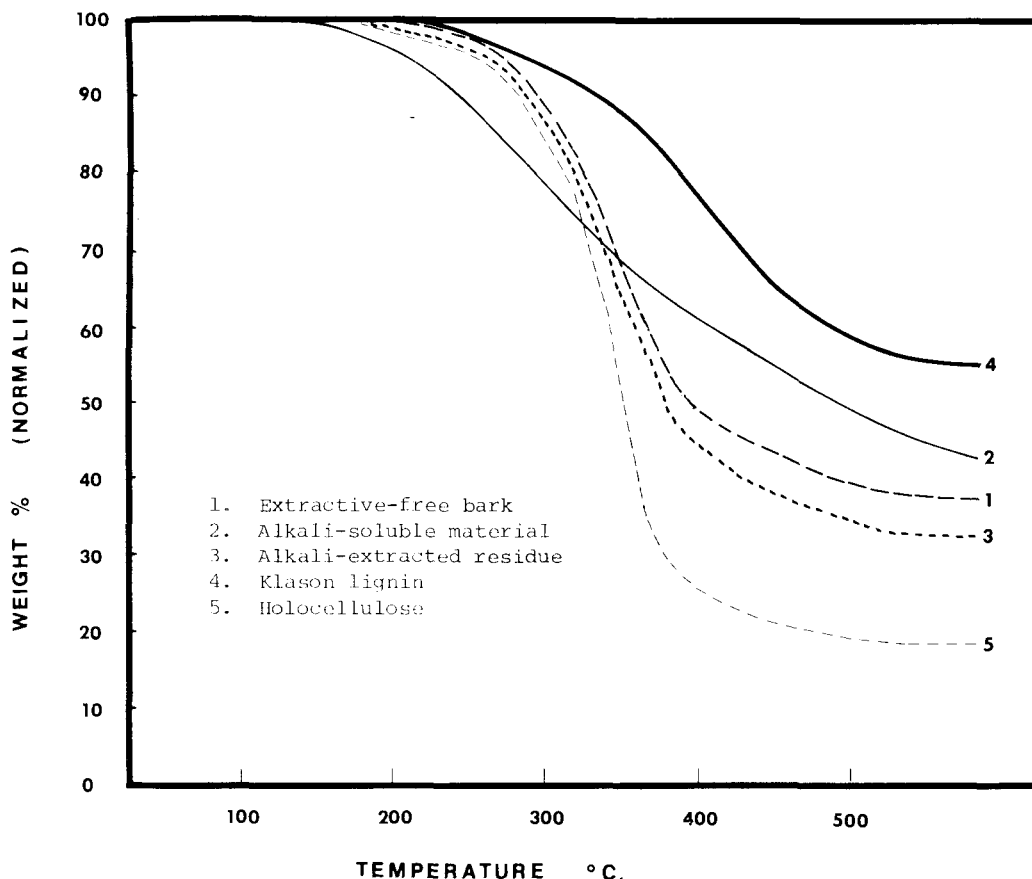


FIG. 1. TGA curves of different components from loblolly pine bark in nitrogen at 10 C/min.

mainly of polyphenolic materials, lignin, and polysaccharides.

Alkali-soluble material was obtained by stirring 20 grams of extractive-free bark with one liter of 1% sodium hydroxide solution at room temperature under nitrogen for 72 h. The samples were then immediately filtered and deionized under nitrogen with Rexyn 101 (H^+) and evaporated to dryness under reduced pressure at 45–50 C. The yield of this material, which was mainly polyphenolics, was 18% based on the weight of extractive-free bark. A more detailed discussion of the methods of isolation and characterization of the alkali-soluble material can be found in an earlier publication (Fang and McGinnis 1975).

The insoluble residue from the above ex-

traction was washed with a large excess of water and acetic acid and dried to a constant weight. This alkali-extracted residue consisted mainly of lignin and polysaccharides.

The fraction of Klason lignin was obtained from alkali-extracted bark following the method of Ritter et al. (1932). The insoluble lignin (41% based on extractive-free bark) was removed by filtration, washed free of acid, and dried in a vacuum oven at 45–50 C.

Holocellulose fraction was obtained by removing lignin from the sodium hydroxide-extracted residue by using a sodium chlorite-acetic acid method (Browning 1952). The yield of holocellulose was 42% based on the oven-dry weight of extractive-free bark.

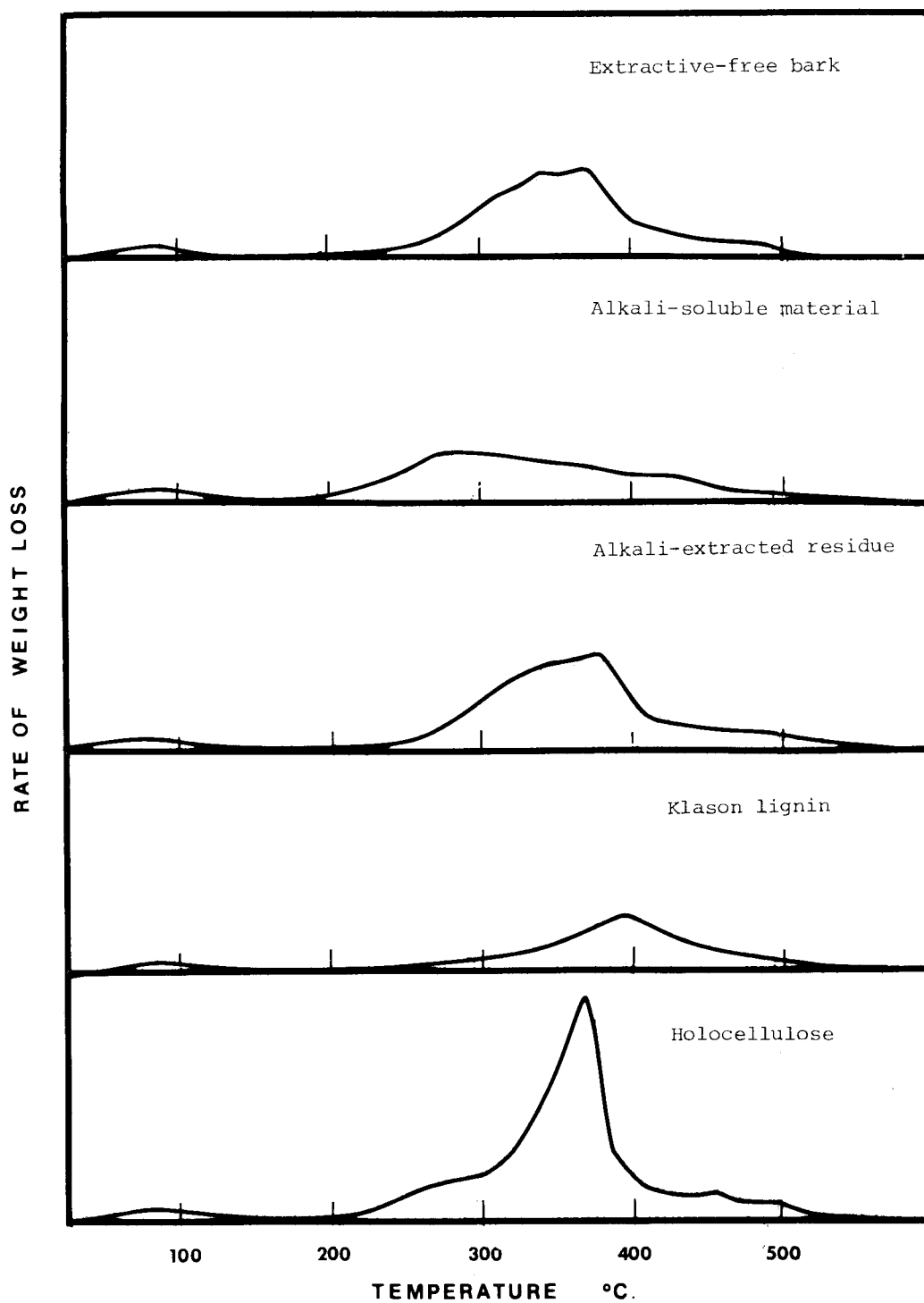


FIG. 2. DTG curves of different components from loblolly pine bark in nitrogen at 10 C/min.

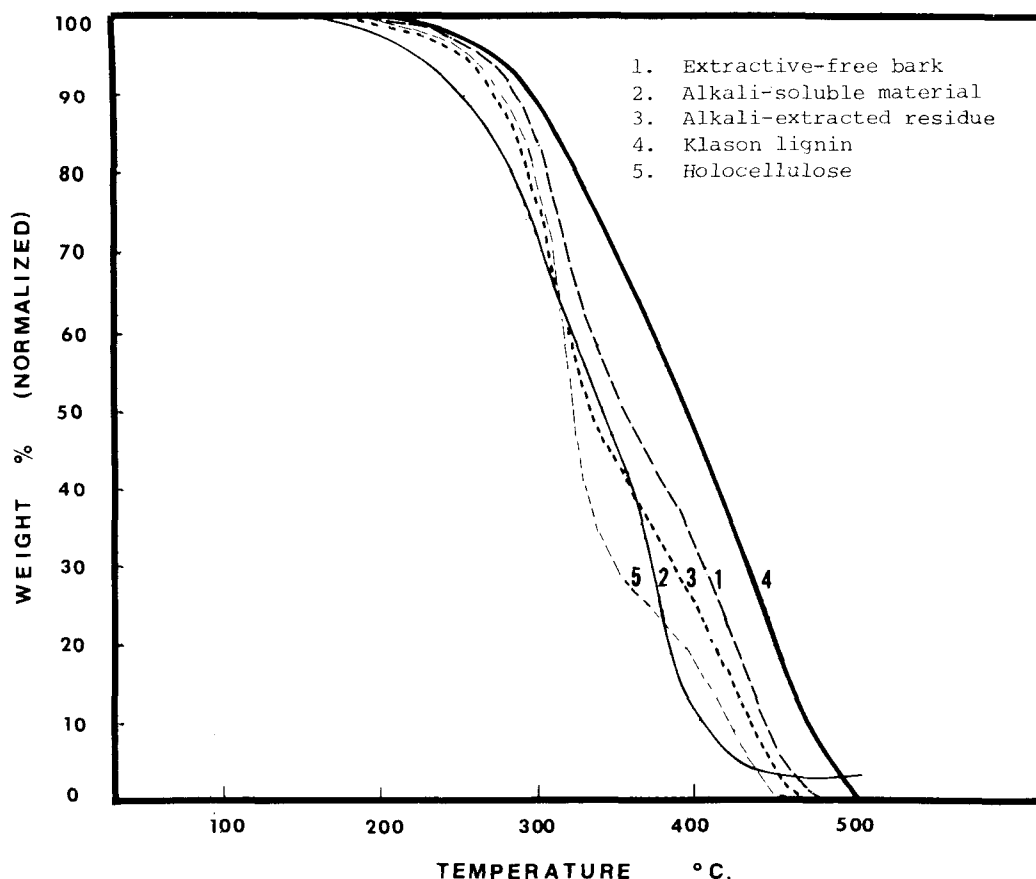


Fig. 3. TGA curves of bark and its components in oxygen at 10 C/min.

Thermal analysis

The TG and DTG data were obtained with a Perkin-Elmer model TGS-1 thermal analyzer programmed at the rate of 10 C/min from 27 to 500 C. A gas flow of 60 ml/min was used for experiments under nitrogen, oxygen, and hydrogen. Three to five runs were made for each condition. Variations in temperature were less than ± 5 C and weight variations were less than $\pm 2\%$. Pyrolysis in vacuum was performed at a pressure of 4 mm Hg. Samples used in pyrolysis were ground to a fine powder (less than 44 μm dia.) and 1 mg samples were used for TG and 5 mg for DTG. In the oxygen study, 1-mg samples were used for both TG and DTG analyses. The temperature

and weight were recalibrated for each atmosphere and for the vacuum studies.

RESULTS AND DISCUSSIONS

Nitrogen

The TG and DTG curves for bark and its components are shown in Figs. 1 and 2. The results of these runs, as well as the results obtained from pyrolysis in the presence of oxygen and hydrogen and in a vacuum, are summarized in Table 1.

The TG curve (Fig. 1) of each bark component and the summarized data in Table 1 indicate wide differences in the maximum rate of decomposition, amount of nonvolatile residue and overall temperature-weight loss curves of the individual bark com-

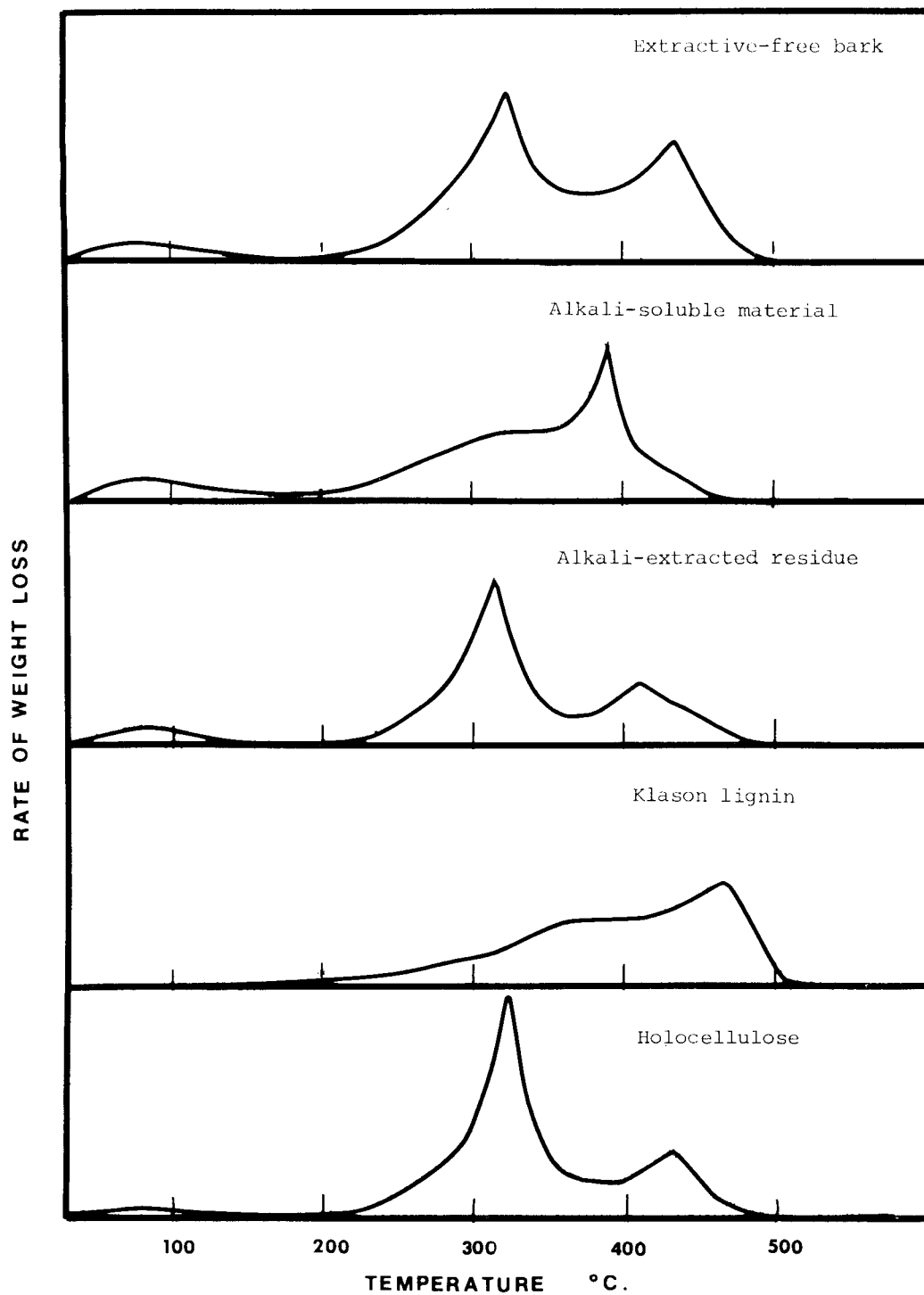


FIG. 4. DTG curves of 1 mg of bark components in oxygen at 10 C/min.

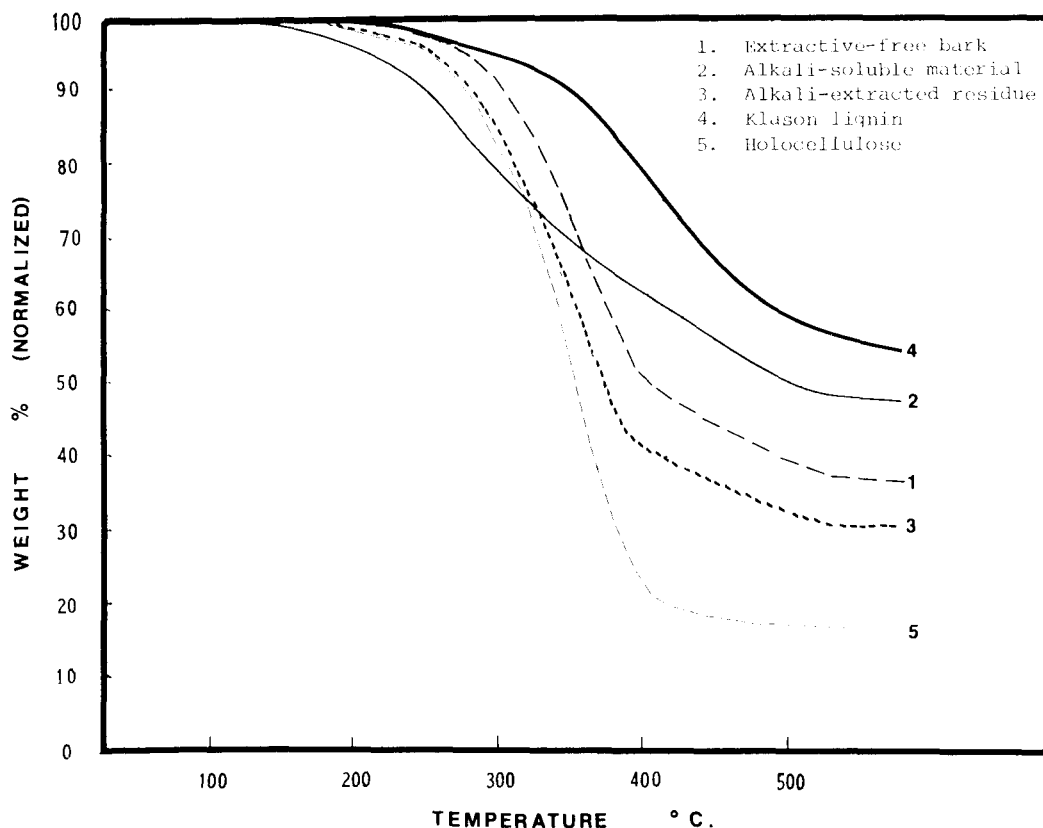


FIG. 5. TGA curves of different components from loblolly pine bark in hydrogen at 10 C/min.

ponents. Klason lignin and the alkali-soluble material that contained polymerized phenolic units decomposed at the slowest rate, gave the highest amount of nonvolatile residue, and generated very broad DTG curves. In contrast, the holocellulose decomposed at a much faster rate, gave much less nonvolatile material, and gave a relatively sharp DTG curve.

There was also considerable difference between the thermograms of the alkali-soluble material and those of the Klason lignin. The alkali-soluble material decomposed at a much lower temperature and at a slower maximum rate of weight loss than the Klason lignin. The difference in the thermograms could reflect the differences in the structure of these molecules. The alkali-extractible material consists mainly of polymerized flavonoid units (Erman and

Lyness 1965), while the lignin is made up of polymerized phenyl propane units. Another possibility is that the differences are due to the methods of isolation. It is known in the case of wood lignin that considerable polymerization occurs when lignin is isolated using the Klason procedure. Beall (1969) and Shafizadeh and McGinnis (1971) have shown that Klason lignin is thermally much more stable than lignin isolated under milder conditions, such as milled wood lignin.

The thermal profiles of the extractive-free material and the alkali-extracted residue were similar (Table 1). The values of their thermal behaviors are in between the values of holocellulose, the alkali-soluble material, and Klason lignin. The overall thermal decomposition patterns are strongly influenced by the polysaccharides present.

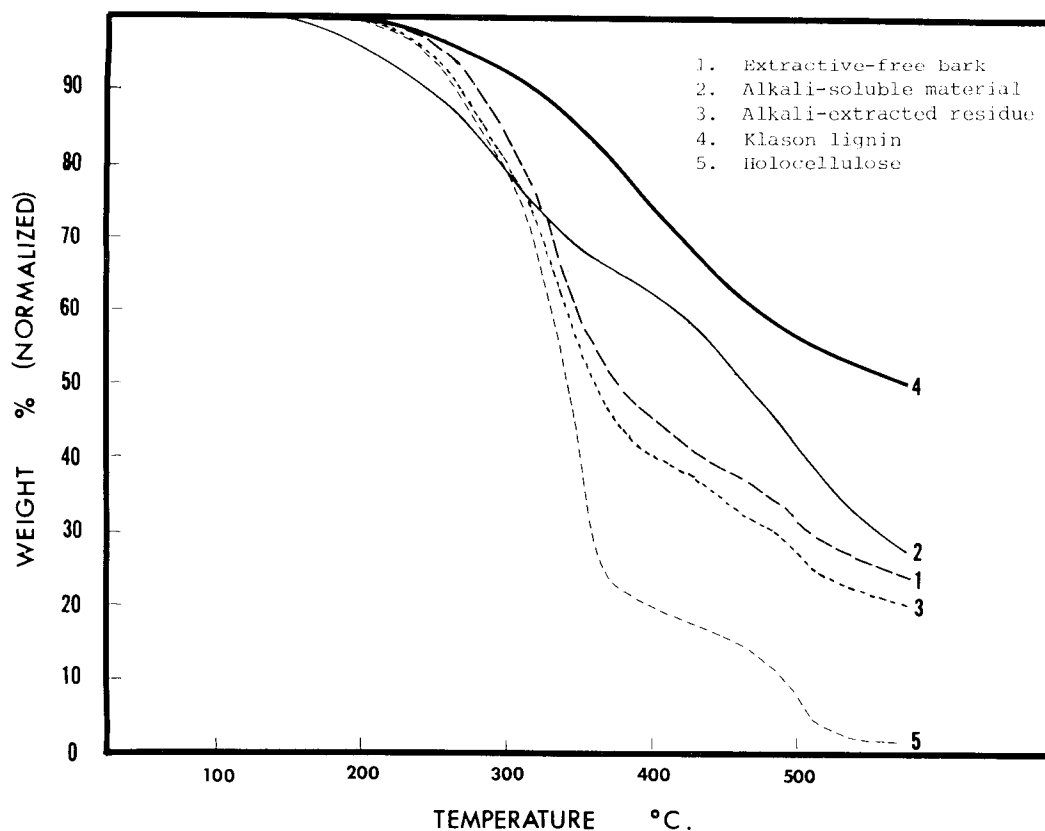


Fig. 6. TGA curves of different components from bark in vacuum (4 mm Hg) at 10 C/min.

Both of these materials have DTG maximums (372 C and 377 C) that correspond very closely to the maximum at 367 C found in holocellulose.

Oxygen

The thermograms of the individual bark components under oxygen are shown in Figs. 3 and 4 and summarized in Table I. These analyses were done using small amounts of samples so that combustion of the volatile decomposition products did not occur. Comparison between the thermal reactions done under nitrogen with those occurring under oxygen indicated that oxygen had a pronounced effect on the reaction. Both reactions started at about the same temperature (150–200 C); however, the reaction under oxygen proceeded at a much faster rate and gave very small

amounts of nonvolatile residue. In addition, the DTG curves (Fig. 4) contained well-defined rate maximums that were not found with nitrogen. The holocellulose had a maximum at 327 C, the alkali-extractible material had a maximum at 389 C, and Klason lignin had a maximum at 467 C. The temperatures at the maximum decomposition rates for the extractive-free bark and the alkali-extracted residue were about the same as the holocellulose (317–327 C). This maximum probably corresponds to the thermal decomposition of the polysaccharides within the bark.

Hydrogen

The effect of hydrogen on pyrolysis was also studied. The results shown in Fig. 5 and Table I indicate that there is only a slight difference between the pyrolysis un-

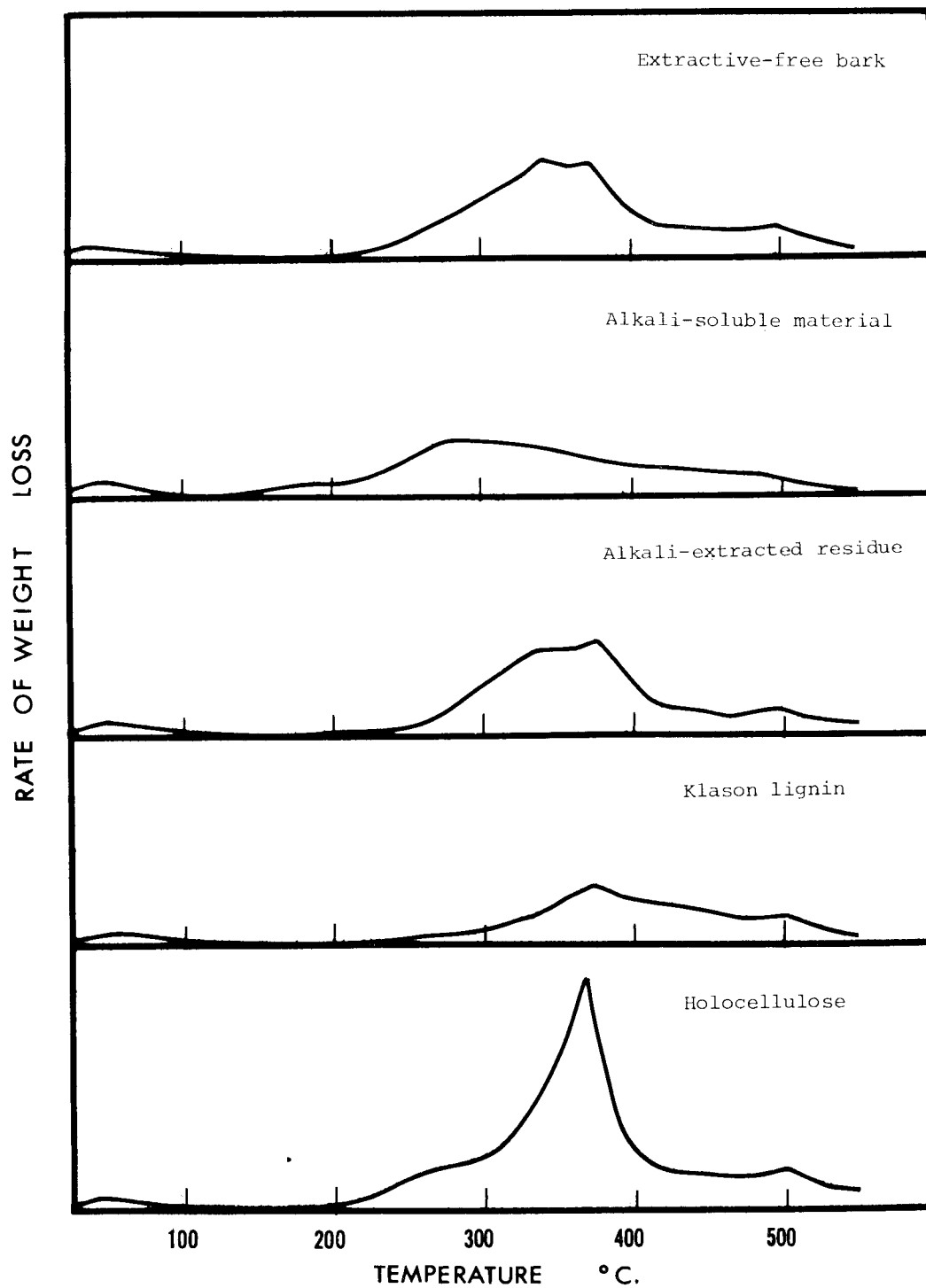


FIG. 7. DTG curves of different components from bark in vacuum condition at 10 C/min.

TABLE 1. *Thermal behavior of bark and its components during pyrolysis at 10 C/min*

Component Type	Pyrolysis ^{a/} Condition	Maximum Rate at Wt. Loss (% per min.)	Temp. at Max. Rate of Wt. Loss (°C)	Decomposition Temperature		Residue at 500°C (%)
				10% (°C)	50%	
1. Extractive-free bark	N ₂	4.8	372	297	402	38
	H ₂	4.7	372	302	402	39
	Vac.	5.1	342,377	282	377	31
	O ₂	11.4	327	287	357	<0.1
2. Alkali-soluble material	N ₂	2.2	271-327	250	497	48
	H ₂	2.2	272-298	247	497	49
	Vac.	2.1	272-327	247	467	40
	O ₂	10.4	389	253	342	3
3. Alkali-extracted residue	N ₂	4.8	377	287	382	34
	H ₂	5.0	372	277	372	32
	Vac.	4.9	377	267	362	26
	O ₂	10.5	317	274	337	<0.1
4. Klason lignin	N ₂	2.6	397	337	---	58
	H ₂	2.6	397	348	---	58
	Vac.	2.6	372	322	---	55
	O ₂	7.4	467	297	397	<0.1
5. Holocellulose	N ₂	11.3	367	282	354	19
	H ₂	11.4	367	277	350	17
	Vac.	11.4	367	267	340	7
	O ₂	16.1	327	269	322	0.9

^{a/}Values were obtained from the average of three to five runs.

der hydrogen and that under nitrogen. These differences are probably not significant. Apparently the hydrogenation reaction of the bark materials during pyrolysis does not occur without a catalyst or high pressure (Swan 1963; Erman and Lyness 1965).

Vacuum

Studies of the bark components were also done under vacuum. The results of pyrolysis under vacuum are given in Figs. 6 and 7 and Table 1. It was found that the nonvolatile residue was decreased. This change is probably due to the more effective removal of decomposition products. This effect was particularly significant for the holocellulose, where the nonvolatile residue decreased from 19% under nitrogen to 7% under vacuum. It was also found that the maximum rate of weight loss of the Klason lignin decreased from 397 C under nitrogen to 372 C under vacuum.

CONCLUSIONS

This paper summarizes a fundamental study of the thermal decomposition of lob-

lolly pine bark and its components in four different atmospheres: oxygen, hydrogen and nitrogen, and in a vacuum. Under conditions unfavorable to combustion, oxygen strongly accelerated the thermal decomposition and led to an increase in both the rate and the yield of volatile products. Pyrolysis under hydrogen, nitrogen, and in a vacuum gave similar thermal decomposition profiles. The major difference was that pyrolysis under vacuum gave lower amounts of nonvolatile residue, presumably due to the more effective removal of the breakdown products.

It was also found in this study that the thermal decomposition of bark fractions was quite dependent on their chemical composition. Holocellulose and aromatic phenolic-type components had widely different pyrolytic patterns. The thermal behaviors of the other components, which contained both types of materials, were in between them and were proportional to their compositions. These results hopefully will provide the basic information necessary for continued research on the thermal decomposition of bark.

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