

KINETIC PROPERTIES OF THE COMPONENTS OF DOUGLAS-FIR AND THE HEAT OF COMBUSTION OF THEIR VOLATILE PYROLYSIS PRODUCTS

William J. Parker

Physicist
National Bureau of Standards, Gaithersburg, MD 20899

and

Susan L. LeVan

Chemical Engineer
USDA, Forest Products Laboratory,¹Madison, WI 53705-2398

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ABSTRACT

Specimens of the chemical components of Douglas-fir, which include cellulose, lignin, mannan, and xylan, were pyrolyzed in nitrogen in the temperature range between 290 and 370 C, which is characteristic of the pyrolysis temperature range of wood in a fire environment. From these data, the effective activation energy, preexponential factor, and the net heat of combustion of the volatiles were calculated as a function of the mass retention fraction of the specimen. These kinetic parameters were used to calculate the mass loss rate of Douglas-fir and a prepared mixture of the components in a pyrolyzer based on their measured temperature histories. The calculated mass loss rates were within a factor of two of the measured values.

Keywords: Cellulose, lignin, mannan, xylan, wood, heat of combustion, activation energy, pyrolysis.

INTRODUCTION

A preliminary model for the heat release rate of wood has been described (Parker 1985a). It builds on earlier mass loss rate models such as the one by Atreya (1983). It takes char shrinkage into account. In the model, the rate of mass generation is expressed as a function of the temperature and the residual mass fraction for each component using an Arrhenius-type expression. Therefore, the production of volatile material and its energy is dependent on the kinetic parameters and the heat of combustion of the volatiles of the individual wood components (cellulose, lignin, and hemicellulose). The kinetic parameters used in the Arrhenius expression describe the rate of mass generation. The heat of combustion of the volatiles used in the equation describes its associated energy. However, the testing of the model and its utilization are both limited by the availability of the necessary input data. The necessary data include the kinetic parameters that describe the rate of mass loss, and heats of combustion of the volatiles generated by each of the chemical components as a function of its residual mass fraction. (The residual mass fraction is the amount of material remaining, minus the ash divided by the original weight minus the ash.) This paper describes the initial work to determine

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these kinetic parameters and the heat of combustion of the volatiles generated by each of the chemical components of Douglas-fir.

Ordinarily, the kinetic parameters (i.e., the effective activation energy and preexponential factor) are determined by thermogravimetric analysis (TGA). However, TGA heating rates are typically less than 20 C per minute. Consequently, a considerable fraction of the material has pyrolyzed by the time it reaches the temperature range of rapid pyrolysis that is typical in the interior of a burning piece of wood. Thus, the calculated activation energy based on TGA is characteristic of a lower temperature reaction, perhaps more typical of smoldering. While 100 C per minute heating rates are available, they produce unacceptably large temperature gradients in the specimen. Measurements are needed in the pyrolysis temperature range similar to that of flaming wood combustion. Therefore, kinetic parameters must be determined under conditions more representative of those in the interior of a flaming slab of wood. Parker (1988) has developed an apparatus that closely represents the phenomena of flaming. This paper reports on results obtained in that apparatus.

The pyrolysis temperature range depends on the component. It is relatively high for lignin, low for hemicellulose, and in between for cellulose (Beall and Eickner 1970). Generally, most of the pyrolysis occurs at temperatures between 300 and 400 C, even though the pyrolysis process is initiated below 300 C. The char continues to degrade at temperatures above 400 C.

The heat of the combustion of the volatiles can be deduced by the difference between measurements in an oxygen bomb calorimeter on virgin material and on chars of the same material at a series of mass retention fractions. However, the oxygen bomb calorimeter measures the gross heat of combustion, while the net heat of combustion is required for fire modeling. To correct for the net heat of combustion, the quantity of liquid water formed must be known at each mass retention fraction. For a series of mass retention fractions, many specimens are required, each of which must have a mass of a gram or more of charred material for accurate determination. This requires several grams of the original material. The large quantities required to determine the net heat of combustion by the oxygen bomb calorimeter make it an unacceptable procedure because the separation of pure hemicellulose, lignin, and alpha-cellulose from wood is difficult and time-consuming.

Susott (1982) measured the heat of combustion of the volatiles from forest fuels, using a combination of TGA and evolved gas analysis (EGA). The EGA uses a catalytic converter to completely oxidize the volatile pyrolysis products to carbon dioxide and water. The amount of oxygen consumed in this oxidation process is measured and used to calculate the potential heat release rate. This rate is divided by the mass loss rate (determined by TGA) to yield the heat of combustion of the volatiles. This technique has the advantage of requiring very small specimen size, roughly 5 mg. However, the rate of temperature rise of the specimen is limited to around 20 C per minute, limiting the applicability to the lower temperature reactions.

MATERIALS

Douglas-fir heartwood was used for this preliminary investigation. The source was a 12-foot-long clear 1-inch board obtained from a lumberyard. The average

TABLE 1. Physical characteristics of the Douglas-fir used in these experiments.

| | |
|------------------------------|-----|
| Density (kg/m ³) | 516 |
| Rings/inch | 7 |
| Summer wood (%) | 44 |
| Moisture content (%) | 6.3 |

physical characteristics are listed in Table 1. Sections of the board were oven-dried and then ground to 40 mesh. Portions of the ground wood were used to isolate the various fractions to be tested. These fractions included oven-dry wood; oven-dry wood extracted with benzene/ethanol mixture and followed by cold water; milled-wood enzyme lignin; and holocellulose. The other materials tested were obtained commercially and included alpha-cellulose (Rayonier²), mannan (Sigma Chemicals), and xylan (Tridom). We assumed that the commercial material would yield similar thermal decomposition products as those of the Douglas-fir wood components.

A milled-wood enzymatic degradation procedure (Obst 1982) was used for the lignin preparation. The holocellulose was prepared by delignifying some of the extracted wood with sodium perchlorate and acetic acid, using the procedure of Thompson and Kaustinen (1972). This resulted in a residual lignin content of about 9%. A portion of this material was saved for testing (holocellulose 1), and the remainder was further delignified with sodium perchlorate and acetic acid followed by dimethylsulfoxide (holocellulose 2). The chemical analysis results for holocellulose are reported here for completeness. However, because of the difficulty of preparing the holocellulose, pyrolysis runs were not done on holocellulose until the experimental results on other components were analyzed and experimental techniques were perfected.

The commercial mannan was prepared from yeast (*Saccharomyces cerevisiae*) and has an alpha 1 → 4 hemiacetal linkage instead of the beta 1 → 4 linkage found in wood mannan. The commercial xylan was prepared from larchwood and was

TABLE 2. Fundamental chemical compositions of Douglas-fir and commercial components.¹

| | Chemical compositions and commercial components | | | | | | | | | |
|----------------------------|---|--------|-----------|-----------|-------|---------------|----------------|--------|-------------------|-------------|
| | Glucan | Mannan | Ara-binan | Galac-tan | Xylan | Klason lignin | Soluble lignin | Acetyl | Uronic anhy-dride | Extractives |
| | % | | | | | | | | | |
| Unextracted wood | 36.5 | 12.3 | 0.4 | 3.6 | 3.5 | 29.4 | 0.4 | 0.8 | 1.3 | 8.4 |
| Extracted wood | 39.9 | 13.4 | 0.5 | 3.9 | 3.8 | 32.1 | 0.4 | 0.8 | 1.4 | — |
| MWEL lignin | 4.2 | 4.3 | — | 4.3 | 2 | 78 | — | — | — | — |
| Holocellulose 1 | 58.4 | 18.2 | 0.8 | 3.7 | 4.9 | 2.6 | 6.2 | 1 | 1.8 | — |
| Holocellulose 2 | 62.9 | 17.6 | 0.3 | 1.8 | 4.5 | 0.01 | — | 0.62 | 1.3 | — |
| Commercial alpha-cellulose | 100.4 | 1.1 | — | — | — | 0.6 | 0.4 | — | 0.2 | — |
| Commercial mannan (Sigma) | — | 81 | — | — | — | — | — | — | — | — |
| Commercial xylan (Tridom) | 1.8 | 11.3 | 7.6 | 1.4 | 69.5 | 0.9 | — | — | 1.4 | — |

¹ All values based on extractive-free oven-dry wood.

TABLE 3. Reconstructed chemical analysis of Douglas-fir.

| | Reconstructed values | | | | | | |
|----------------------------------|----------------------|-----------|-------------------------|-----------------|------------|----------------------------|------|
| | Douglas-fir | | | Alpha-cellulose | MWE lignin | Holocellulose ² | |
| | Unex-tracted | Extracted | Literature ¹ | | | 1 | 2 |
| % | | | | | | | |
| Klason and soluble lignin | 29.9 | 32.5 | 29.1 | 1.0 | 78 | 8.8 | 0.01 |
| Alpha-cellulose | 32.6 | 35.5 | 38.8 | 100.4 | 2.7 | 52.1 | 57.1 |
| Galactoglucomannan | 19.9 | 21.7 | 17.4 | — | 10 | 27.9 | 25.2 |
| 4-O-methylglucurono-arabinoxylan | 6.1 | 6.6 | 8.4 | 1.3 | 2.5 | 8.5 | 6.6 |
| Extractives | 8.3 | — | 5.3 | — | — | — | — |
| Other polysaccharides | — | — | 2.7 | — | — | — | — |
| Totals | 96.8 | 96.3 | 101.7 | 102.7 | 93.2 | 97.3 | 88.9 |

¹ From Sjostrom (1981).

² Holocellulose 1 had one delignification reaction; holocellulose 2 had a second delignification reaction.

composed of β -D-xylopyranose units linked by beta 1 \rightarrow 4 bonds. The impact of this difference is not known.

The amounts of extractives, Klason lignin, soluble lignin, glucan, xylan, galactan, arabinan, mannan, acetyl, and uronic anhydride were determined for each material evaluated (Table 2). From these quantities, the amount of each of the components of lignin, cellulose, galactoglucomannan (softwood mannan), and 4-O-methylglucuronoarabinoxylan (softwood xylan) was reconstructed. These reconstructed values are listed in Table 3. Certain assumptions have to be applied to reconstruct these values:

1. To determine the amount of galactoglucomannan, we assumed a 1:3 ratio of anhydroglucose to anhydromannose. This ratio can vary depending on the particular species, but 1:3 seems to be the most common (Timell 1965). Thus, the amount of galactoglucomannan is the amount of galactan plus the amount of mannan, plus the amount of glucan associated with the mannan (mannan times 0.33).

2. The amount of cellulose is equal to the total amount of glucan minus the amount of glucan associated with the galactoglucomannan previously mentioned (mannan times 0.33).

3. The amount of softwood xylan is much more difficult to determine, since the bond between the xylose unit and the 4-O-methylglucuronic acid unit is very difficult to hydrolyze. It is estimated that roughly 60% of these bonds survive primary and secondary hydrolysis; therefore some of the xylan goes undetected. To correct for these losses, it is assumed that for each mole of uronic anhydride detected, 0.6 mole of xylose goes undetected (Timell 1964). The total amount of 4-O-methylglucuronoarabinoxylan is then the amount of xylan detected as xylose, plus the amount of xylan undetected based on the uronic anhydride level, plus the amount of arabinan and the amount of 4-O-methylglucurono anhydride. The 4-O-methylglucurono anhydride is calculated from the amount of uronic anhydride.

4. The amount of lignin is equal to the amount of Klason lignin plus the acid soluble lignin.

EXPERIMENTAL METHODS

Pyrocat

The Pyrocat (combination *pyrolyzer* and *catalytic converter*) was developed to measure the kinetic parameters and the heat of combustion of the volatiles (Parker 1988). In its present configuration, the Pyrocat method is applicable to materials containing only carbon, hydrogen, and oxygen. By heating the specimen rapidly to the temperature region where the measurements are being made, steep temperature gradients in the specimen are confined to the early period where less than 10% of the mass is lost. The specimen is pyrolyzed in a stream of nitrogen, and the volatiles are swept into a catalytic converter where they are converted to carbon dioxide and water as in Susott's (1982) method. In the Pyrocat, however, the converted gases are passed through carbon dioxide and water vapor analyzers as well as the oxygen analyzer. From the volume fractions of oxygen (X_{O_2}), carbon dioxide (X_{CO_2}), and water vapor (X_{H_2O}) measured in the analyzers and the mass flow rate of nitrogen (m_{N_2}) flowing into the system, the mass flows of carbon (m_C), hydrogen (m_H) and oxygen (m_O) from the specimen can be calculated from the following formulas (Parker 1985b):

$$m_C = 3m_{N_2}X_{CO_2}/(1 - X_{O_2} - X_{CO_2})/7 \quad (1)$$

$$m_H = m_{N_2} X_{H_2O}/(1 - X_{H_2O})/(1 - X_{O_2} - X_{CO_2})/14 \quad (2)$$

$$m_O = 4m_{N_2} [(X_{H_2O}/(1 - X_{H_2O})/(1 - X_{O_2} - X_{CO_2}) + 2(X_{O_2} + X_{CO_2})/ (1 - X_{O_2} - X_{CO_2}) - 2X_{O_2}^{\circ}/(1 - X_{O_2}^{\circ})]/7 \quad (3)$$

where

$X_{O_2}^{\circ}$ is the measured oxygen volume fraction prior to the run.

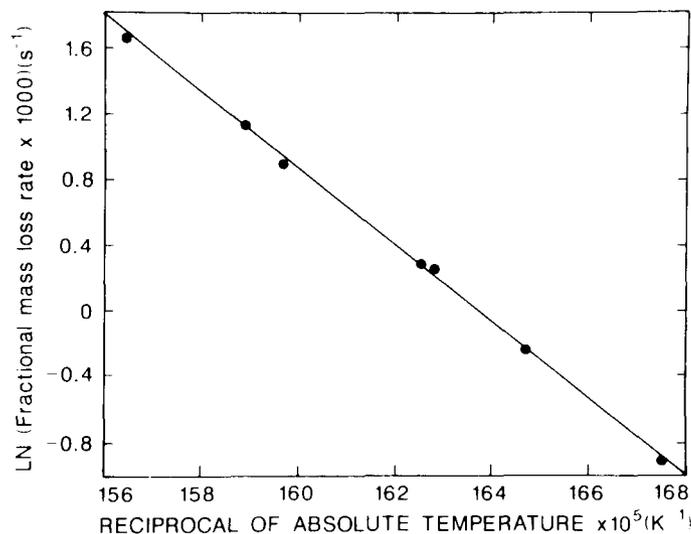
The calculation does not depend on nor provide any information on how these elements are combined in the hundreds of different chemical species making up the volatile pyrolysis products. However, the total mass flow from the specimen is equal to the sum of the masses of these three elements, assuming that the specimen contains only C, H, and O. Furthermore, the external oxygen supply rate required for complete combustion of these volatiles is given by

$$m_{O_2} = (8m_C/3 + 8m_H - m_O) \quad (4)$$

Huggett (1980) found that, to within an engineering approximation of 5%, the heat released per unit mass of oxygen consumed is 13.1 MJ/kg for a large variety of polymeric solids. The potential rate of heat release can be calculated by multiplying the oxygen mass requirement evaluated in Eq. (4) by this constant. The heat of combustion of the volatiles is simply the ratio of the calculated rate of heat release to the calculated rate of mass loss. Thus, both the heat of combustion of the volatiles and the mass loss rate for the calculation of the kinetic parameters can be determined on a single specimen. However, data from several specimens at different temperatures need to be accumulated to determine the kinetic parameters. The Pyrocat is described in detail by Parker (1988).

Oxygen bomb calorimeter

The heat of combustion of the volatiles from unextracted Douglas-fir, extracted Douglas-fir, milled wood enzyme lignin, and alpha-cellulose was also obtained using the oxygen bomb calorimeter. The specimens to be charred were pyrolyzed



ML88 5529

FIG. 1. Arrhenius plot for alpha-cellulose at a mass retention fraction of 0.6. (ML88 5529)

in a muffle oven with a flowing nitrogen atmosphere to remove the volatiles and prevent oxidation. The lignin specimens were pyrolyzed at 375 C. The other materials were pyrolyzed at 300 C. The gross heat of combustion of the volatiles was determined from the formula

$$H_{\text{vol}} = (H_s - ZH_c)/(1 - Z) \quad (5)$$

where

H_s is the gross heat of combustion of the uncharred material and

H_c is the gross heat of combustion of its char at the mass retention fraction, Z .

These values should be higher than the net heats of combustion measured in the Pyrocat due to the latent heat of vaporization of the water produced. The difference, which depends on the chemical composition of the volatiles, was not calculated.

RESULTS

Pyrocat

Alpha-cellulose. — Seven runs on alpha-cellulose yielded data with pyrolysis temperatures ranging from 320 to 370 C. Both the temperature and the fractional mass loss rate z were plotted as functions of the mass retention fraction Z . The mass loss rate and the temperatures were taken from these plots at mass retention fractions of 0.3, 0.4, 0.5 0.9 and used to produce the set of Arrhenius plots, one plot for each mass retention fraction (Fig. 1 shows the Arrhenius plot for mass retention of 0.6). The fractional mass loss rate z is taken to be

$$z = A \exp(-E/RT) \quad (6)$$

where

A is a preexponential factor, which depends on the mass retention fraction and has units of reciprocal seconds

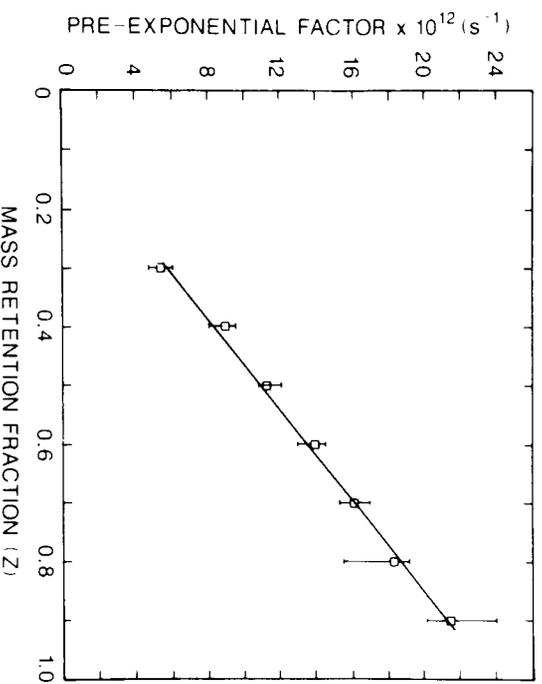


Fig. 2. Preexponential factor for alpha-cellulose as a function of the mass retention fraction. (ML88 5530)

ML88 5530

E is the effective activation energy (cal/mole)
 R is the gas constant (1.987 cal/mole-K) and
 T is the absolute temperature (K).

From the Arrhenius plots, the effective activation energy was determined as a function of the mass retention fraction. Thus, the effect of the series of sequential reactions occurring during the decomposition of these complex materials can be taken into account. It must be emphasized that the effective activation energy

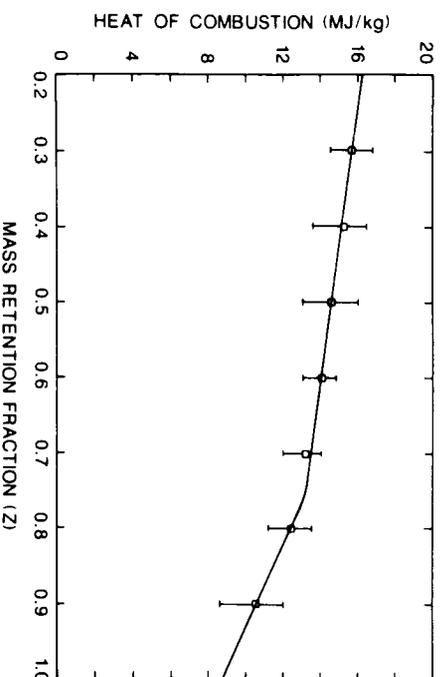


Fig. 3. Average heat of combustion of the volatiles from alpha-cellulose. (ML88 5531)

ML88 5531

TABLE 4. Heat of combustion of volatiles from alpha-cellulose.

| Test number | Heat of combustion for various mass retention fractions | | | | | | |
|---|---|------|------|------|------|------|------|
| | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 | 0.4 | 0.3 |
| | MJ/kg | | | | | | |
| 21 | 11 | 13 | 13 | 14 | 14 | 17 | 14 |
| 22 | 12 | 13 | 14 | 15 | 16 | 15 | 15 |
| 23 | 10 | 12 | 14 | 15 | 14 | 15 | 16 |
| 24 | 10 | 13 | 13 | 14 | 15 | 16 | 15 |
| 26 | 12 | 13 | 13 | 15 | 16 | 16 | 16 |
| 27 | 9 | 11 | 12 | 13 | 13 | 14 | 17 |
| Average | 10.6 | 12.5 | 13.2 | 14.3 | 14.7 | 15.5 | 15.5 |
| Overall average = 13.8 MJ/kg | | | | | | | |
| Average for Parr bomb = 13.1 MJ/kg ¹ | | | | | | | |

¹ Gross heat of combustion of volatiles measured in oxygen bomb calorimeter.

used here has no physical significance other than being a convenient parameter for describing the temperature dependence of the mass loss rate.

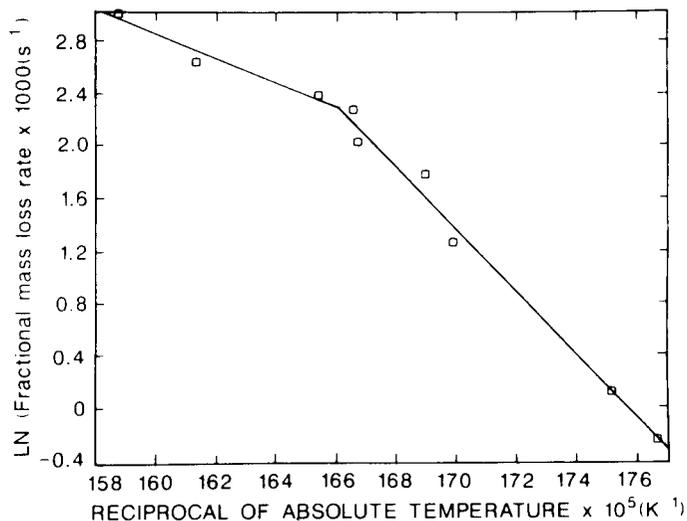
The average value of the effective activation energy as determined from the slopes of the Arrhenius plots for the seven mass retention fractions Z was 45 kcal/mole. All of the fractional mass loss rates measured for the seven specimens were multiplied by $\exp(E/RT)$ using this average value of E along with the measured temperatures. These products were then averaged for each mass retention fraction to obtain the preexponential factor as a function of the mass retention fraction for alpha-cellulose as see in Fig. 2. This can be expressed by the formula:

$$A = 2.55 \times 10^{13}(Z - 0.06) \quad (7)$$

By combining Eqs. (6) and (7), one gets an expression for the fractional mass loss rate for cellulose that is suitable for use in the heat release rate model for wood (Parker 1985a).

In Table 4, the measured value of the instantaneous heat of combustion of the volatiles is tabulated for each of the seven mass retention fractions on the seven tests. By averaging all the alpha-cellulose runs, the overall heat of combustion was determined as a function of the mass retention fraction (Fig. 3). The vertical bars indicate the range of the data and the points represent the averages. The average over the complete pyrolysis period is 14 MJ/kg.

Mannan. – The data on mannan were obtained from nine runs with pyrolysis temperatures ranging from 290 to 370 C. Using the same procedure as with alpha-cellulose, the Arrhenius plots were constructed for mass retention fractions from 0.4 to 0.9. The plots exhibited a nonlinear relationship, which can be represented by two straight lines joining at a reciprocal temperature of 0.00167 K^{-1} , which corresponds to 326 C (Fig. 4). The average effective activation energies are 47 kcal/mole below 326 C and 17 kcal/mole above it. The preexponential factors were obtained in the same manner as for alpha-cellulose and were plotted against the mass retention fraction in Figs. 5 and 6 for temperatures below 326 C and above it, respectively. The points represent the average values and the vertical lines represent the ranges of the data. These curves can be represented by

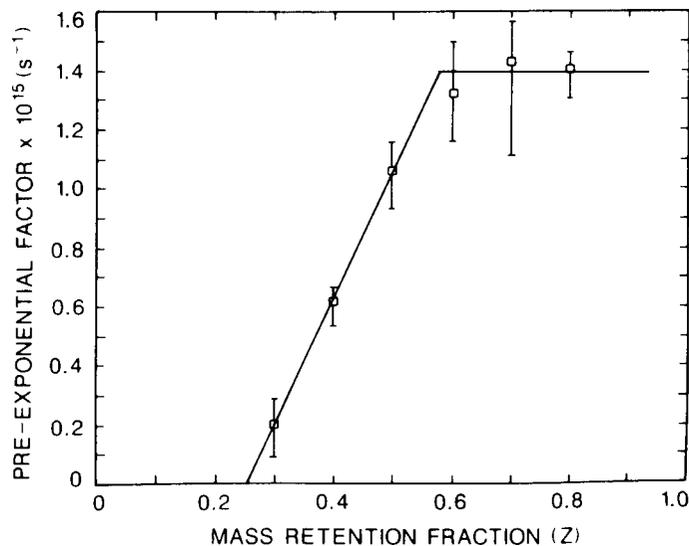


ML88 5532

FIG. 4. Arrhenius plot for mannan at a mass retention fraction of 0.5. (ML88 5532)

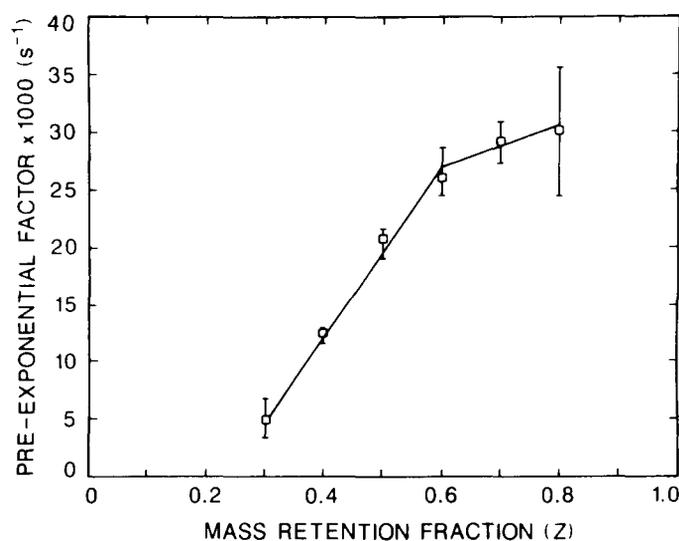
$$\begin{aligned}
 A &= 4.2 \times 10^{15}(Z - 0.25) \text{ when } (Z < 0.56 \text{ and } T < 326 \text{ C}) \\
 A &= 1.3 \times 10^{15} \text{ when } (Z > 0.56 \text{ and } T < 326 \text{ C}) \\
 A &= 7.2 \times 10^4(Z - 0.24) \text{ when } (Z < 0.60 \text{ and } T > 326 \text{ C}) \\
 A &= 1.9 \times 10^4(Z + 0.80) \text{ when } (Z > 0.60 \text{ and } T > 326 \text{ C})
 \end{aligned}
 \tag{8}$$

Table 5 gives the values of the heat combustion of the volatiles measured with the Pyrocat for mannan at mass retention fractions from 0.9 down to 0.4. Again



ML88 5533

FIG. 5. Preexponential factor for mannan at temperatures below 326 C as a function of mass retention fraction. (ML88 5533)



ML88 5534

FIG. 6. Preexponential factor for mannan at temperatures above 326 C as a function of mass retention fraction. (ML88 5534)

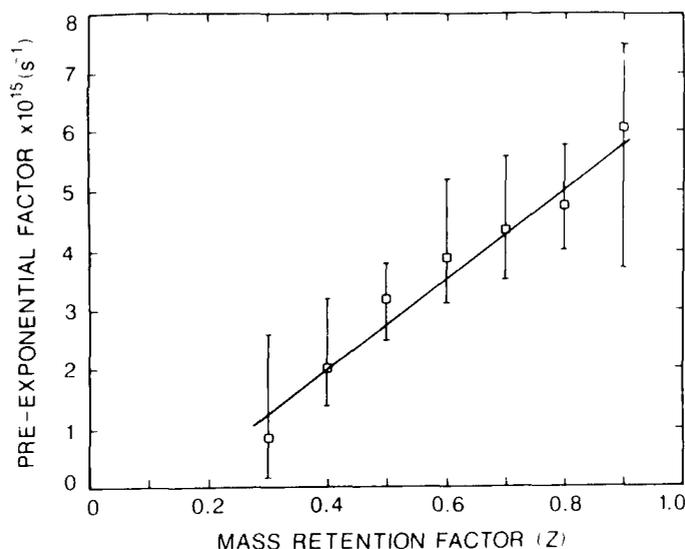
there is a great deal of noise in the data, but the average values for the nine runs are essentially independent of the mass retention fraction. The overall average heat of combustion of the volatiles for mannan was determined to be 12 MJ/kg.

Xylan. —The data on xylan were derived from six runs with pyrolysis temperatures ranging from 290 to 325 C. Again, Arrhenius plots for xylan were obtained in the same manner as for alpha-cellulose. The average effective activation energy determined from these plots was 48 kcal/mole. The preexponential factor is plotted as a function of the mass retention fraction in Fig. 7. The points represent the averages, the vertical lines indicate the ranges, and the straight line is a least squares fit to the points. This relationship can be expressed by

$$A = 8.0 \times 10^{15}(Z - 0.15) \quad (9)$$

TABLE 5. Heat of combustion of volatiles from mannan.

| Test number | Heat of combustion for various mass retention fractions | | | | | |
|------------------------------|---|------|------|------|------|------|
| | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 | 0.4 |
| | MJ/kg | | | | | |
| 2 | 4 | 14 | 16 | 18 | 17 | 14 |
| 3 | 15 | 14 | 14 | 14 | 13 | 15 |
| 4 | 14 | 12 | 12 | 12 | 10 | 10 |
| 7 | 15 | 12 | 12 | 12 | 14 | 14 |
| 8 | 17 | 12 | 10 | 12 | 9 | 11 |
| 13 | 15 | 9 | 11 | 11 | 11 | 12 |
| 14 | 14 | 12 | 12 | 12 | 11 | 11 |
| 15 | 10 | 9 | 11 | 11 | 10 | 9 |
| 16 | 7 | 17 | 14 | 15 | 14 | 16 |
| Average | 12.3 | 12.3 | 12.4 | 13.0 | 12.1 | 12.4 |
| Overall average = 12.4 MJ/kg | | | | | | |



ML88 5535

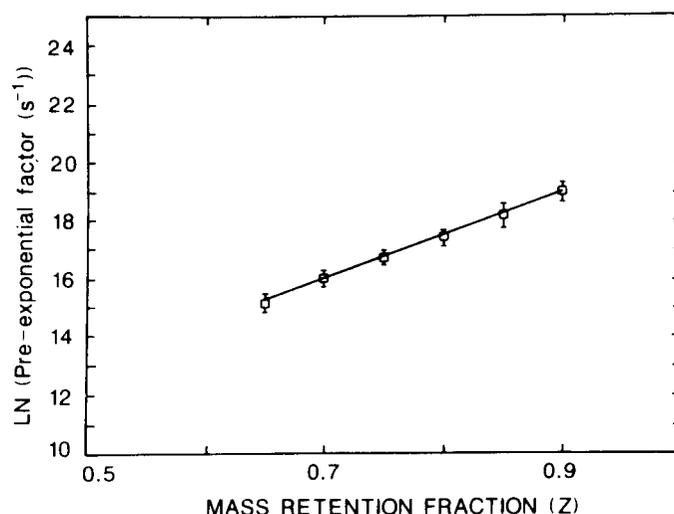
FIG. 7. Preexponential factor for xylan as a function of mass retention fraction. (ML88 5535)

Table 6 shows the heat of combustion data from xylan. Again, there is considerable scatter. There is no trend of the data with the mass retention fraction beyond this scatter. The average value of the heat of combustion of the volatiles for xylan was determined to be 11 MJ/kg.

Lignin. – The data on lignin were limited to five tests in which the final mass retention fractions ranged from 0.57 to 0.65 and the pyrolysis temperatures ranged from 295 to 365 C. The mass loss rates for the mass retention fraction at 0.65 were too low to be measured accurately for two of the runs. The Klason lignin content produced by the enzyme method was about 78%, with another 2% of acid soluble lignin. The remaining 20% represent carbohydrates and inorganic components. Thus, the measured mass loss rates at mass retention fractions higher than 0.80 were probably due primarily to the impurities and are not included

TABLE 6. Heat of combustion of volatiles from xylan.

| Test number | Heat of combustion for various mass retention fractions | | | | | |
|------------------------------|---|------|------|------|------|-----|
| | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 | 0.4 |
| | MJ/kg | | | | | |
| 8 | 10 | 12 | 13 | 12 | 12 | 15 |
| 9 | 10 | 11 | 12 | 11 | 9 | 9 |
| 10 | 17 | 14 | 12 | 10 | 8 | 5 |
| 13 | 6 | 11 | 10 | 10 | 10 | 11 |
| 15 | 9 | 10 | 12 | 11 | 10 | 10 |
| 16 | 6 | 11 | 13 | 13 | 12 | 10 |
| 18 | 7 | 11 | 16 | 12 | 10 | 8 |
| Average | 9.3 | 11.4 | 12.6 | 11.3 | 10.1 | 9.7 |
| Overall average = 10.7 MJ/kg | | | | | | |



ML88 5536

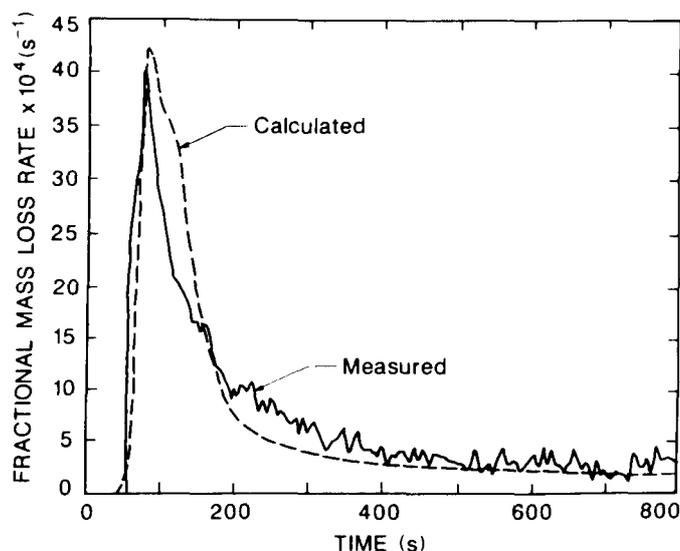
FIG. 8. Preexponential factor for lignin as a function of mass retention fraction. (ML88 5536)

here in the kinetic calculations. The Arrhenius plots for mass retention fractions between 0.65 and 0.80 were derived from curves of temperature and mass loss rate as a function of mass retention fraction for each of the five runs. We used least squares analysis to fit the data. The effective activation energies determined from the slopes were 27, 30, 32, and 26 kcal/mole for mass retention fractions of 0.8, 0.75, 0.7, and 0.65, respectively. The average effective activation energy was 29 kcal/mole. The average value for the preexponential factor at each mass retention fraction was determined for lignin in the same manner as for alpha-cellulose. It was not possible to express the preexponential factor as a linear function of the mass retention fraction in the case of lignin. This may be due to the use of an effective activation energy averaged over the range of mass retention fractions. However, a good fit was obtained using an exponential function as seen in Fig. 8, ignoring the point at $Z = 0.9$ where impurities are likely to have a

TABLE 7. Heat of combustion of volatiles from lignin.

| Test number | Heat of combustion for various mass retention fractions | | | | |
|---|---|------|------|------|------|
| | 0.90 | 0.85 | 0.80 | 0.75 | 0.70 |
| | MJ/kg | | | | |
| 5 | 15 | 13 | 12 | 13 | 12 |
| 6 | 14 | 10 | 10 | 12 | 18 |
| 7 | 15 | 14 | 16 | 20 | 12 |
| 8 | 15 | 15 | 18 | 21 | 16 |
| 9 | 11 | 14 | 17 | 17 | 15 |
| Average | 14.0 | 13.2 | 14.6 | 16.6 | 15.0 |
| Overall average = 14.7 MJ/kg | | | | | |
| Average for Parr bomb = 14.8 MJ/kg ¹ | | | | | |

¹ Gross heat of combustion of volatiles measured in oxygen bomb calorimeter.



ML88 5537

FIG. 9. Calculated and measured mass loss rate for mixture test 5 as a function of time. (ML88 5537)

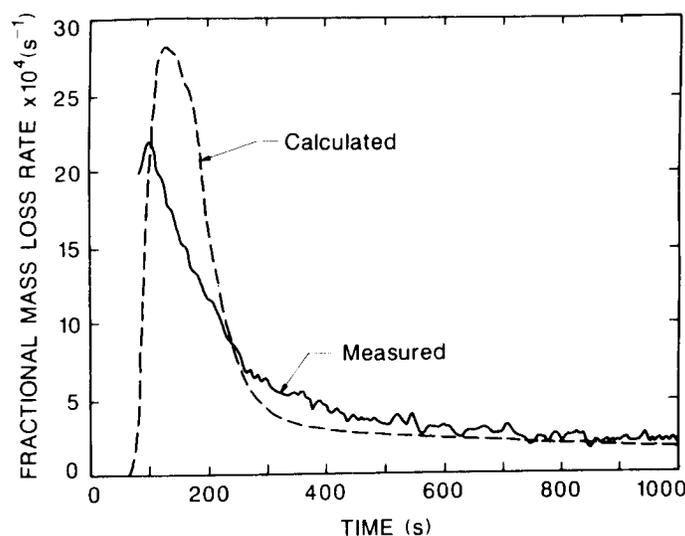
dominant effect. From this plot the preexponential factor for lignin was found to be

$$A = 245 \exp(15Z) \quad (10)$$

Table 7 shows the measured heat of combustion from the five lignin specimens over five different mass retention fractions, yielding an average heat of combustion of the volatiles as 15 MJ/kg. The data are too scattered to show a trend with the mass retention fraction.

Mixtures. –The fractional mass loss rate and temperature were measured for a mixture of cellulose (32.3%), lignin (36.4%), mannan (25.0%), and xylan (7.3%) during a Pyrocat run. These percentages refer to the mass of each sample material included in the mixture. When the impurities were taken into account, the four components were present in almost the same proportions as determined in the analysis of the extracted Douglas-fir heartwood. The measured temperature increased from 318 C to 339 C as the mass retention fraction dropped from 0.9 to 0.35. The measured temperature history, along with the preexponential factors from Eqs. (7) through (10), was then substituted into Eq. (6) to calculate the mass loss rates for the individual components. These were multiplied by their respective original mass fractions in the mixture and added together to yield the total mass loss rate. Figure 9 shows the comparison of the measured and calculated fractional mass loss rates as a function of time.

Wood. – The fractional mass loss rate and temperature were also measured for a specimen of unextracted Douglas-fir during a Pyrocat run. The fractional mass loss rate was then calculated from the measured temperature history using the same procedure as that for the mixture. The mass fractions of the individual components used in the calculations were the values for extracted wood given in



ML88 5538

FIG. 10. Calculated and measured mass loss rate of unextracted wood as a function of time. (ML88 5538)

Table 3. No attempt was made to account for the extratives. A comparison of the measured and calculated mass loss rates is shown in Fig. 10.

Oxygen bomb calorimeter

The gross heats of combustion of unextracted wood, extracted wood, alpha-cellulose, and lignin measured in the Parr oxygen bomb calorimeter at various mass retention fractions are listed in Table 8. The gross heat of combustion of the volatiles released from alpha-cellulose during a fractional mass loss of 0.76 was 13.1 MJ/kg. The volatiles released from lignin over a fractional mass loss of 0.36 had a gross heat of combustion of 14.8 MJ/kg. These values were calculated using Eq. (5), and are included in Tables 4 and 7.

DISCUSSION

The pyrolytic behavior of the four chemical components of wood has been characterized and expressed by formulas suitable for use in the heat release rate model for the temperature range over which most of their mass loss occurs. Some changes in these formulas would be expected when precision and accuracy of measurements are improved. The present measurements do not include the high-temperature charring reactions. Because of the complexity of the reactions involved, it would be difficult to assign any physical significance to an activation energy. Hence, the term "effective activation energy" is used here simply as a parameter to calculate the mass loss rate.

The mass loss rates for alpha-cellulose could be described quite well by an Arrhenius equation. There is a wide range of activation energies reported in the literature for alpha-cellulose in nitrogen, with a number of investigators reporting values around 54 kcal/mole (Roberts 1970) primarily using TGA. Although it varied some with the mass retention fraction, an average value of 45 kcal/mole

TABLE 8. Heats of combustion determined in the Parr oxygen bomb.

| Material | Residual weight (%) | H _c (MJ/kg) |
|---------------------------|---------------------|------------------------|
| Douglas-fir (unextracted) | 100 | 19.7 |
| | 87 | 20.4 |
| | 71 | 22.6 |
| | 63 | 23.4 |
| | 59 | 23.8 |
| | 49 | 25.1 |
| | 44 | 26.3 |
| | 41 | 26.4 |
| | 39 | 26.4 |
| | 31 | 26.7 |
| Douglas-fir (extracted) | 100 | 19.1 |
| | 68 | 22.3 |
| | 55 | 25.2 |
| | 51 | 25.2 |
| | 47 | 26.2 |
| | 44 | 26.6 |
| Alpha-cellulose | 100 | 16.7 |
| | 81 | 18.6 |
| | 66 | 20.2 |
| | 45 | 22.3 |
| | 28 | 27.1 |
| | 28 | 27.3 |
| | 24 | 28.0 |
| Milled wood enzyme lignin | 100 | 23.2 |
| | 64 | 27.9 |
| | 54 | 28.9 |
| | 53 | 28.9 |

was obtained on this project. This is in reasonable agreement with the 42 kcal/mole reported by Lipska and Wodley (1969) between 276 and 360 C using isothermal pyrolysis.

According to Huggett (1980), the net heat of combustion of alpha-cellulose is 16.1 MJ/kg, accompanied by 13.6 MJ/kg of O₂ consumed. The net heat of combustion of the volatiles is significantly less than the 16.1 MJ/kg because of the retention of carbon during the char forming process. The 13.6 MJ/kg of O₂ consumed applies to the alpha-cellulose but not necessarily to its volatiles. The usual value of 13.1 MJ/kg of O₂ was used in the calculations. The calculated net heat of combustion of 14 MJ/kg was 5% higher than the measured gross heat of combustion of the volatiles in the oxygen bomb calorimeter. However, when the bomb value is corrected for the condensed water, the difference would be expected to be closer to 15%.

The precision of the measurements for the other components was not as good as that for alpha-cellulose. Tang (1967) found two stages of first order decomposition for sulfuric acid-processed spruce lignin. In the range of 280 to 344 C, lignin had an activation energy of 21 kcal/mole, and between 344 to 435 C, an activation energy of 9 kcal/mole. Ramiah (1970) found activation energies of 13 kcal/mole for periodate lignin and 19 kcal/mole for Klason lignin. Both of these authors were using TGA, and their values were slightly lower than the 29 kcal/mole obtained for enzyme lignin measured with the Pyrocat.

The peak mass loss rate for the mixture was adequately predicted by combining the calculated mass loss rates of the individual components. However, significant differences occurred over the course of the run. These cannot be explained by the impurities present in the mixture, because the impurities were also present in the specimens of the individual components when the kinetic parameters were measured. In addition to the errors inherent in the determination of the kinetic parameters, interfering and secondary reactions between the components are probable explanations for the differences.

The agreement can only be said to be within a factor of two between the calculated and measured mass loss rates for the unextracted wood. Some of the factors accounting for the difference include: 1) the impact of the extratives, 2) the unknowns in the lignin specimens, 3) the chemical differences between commercial xylan and mannan and the hemicelluloses xylan and mannan contained in the wood, 4) interfering and secondary reactions between the components, and 5) experimental errors.

The experimental errors included temperature variations across the specimen, errors in the measurement of the flow of nitrogen and oxygen into the system, errors in the measurement of the volume fractions in the analyzers, drift in the analyzers, noise in the amplifiers between the analyzers and the computer, and a transient in the oxygen concentration caused by the introduction of the specimen.

In spite of the large scatter of data from the Pyrocat, it appears to be a promising technique for the determination of the kinetic parameters and the heat of combustion of the volatiles needed for the heat release rate model for wood. Improvements in the apparatus should result in more precise values for these properties.

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