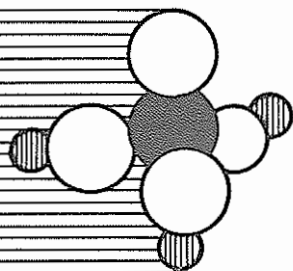
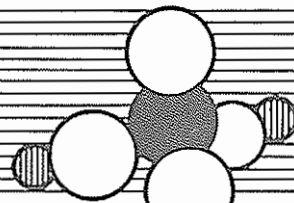
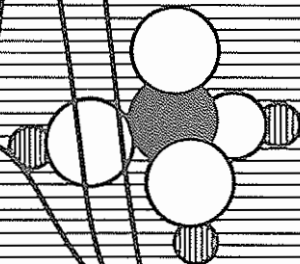
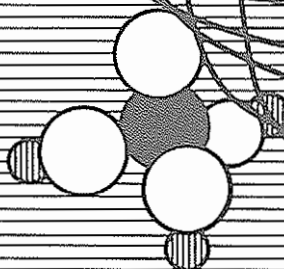
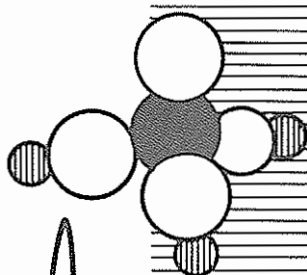
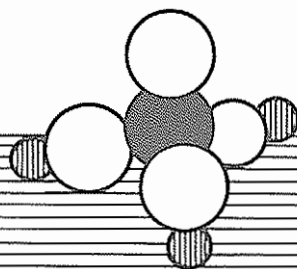


Effects of Ammonium Phosphate And Sulfate On The Pyrolysis And Combustion Of Cellulose

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CHARLES W. GEORGE AND RONALD A. SUSOTT



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THE PYROLYSIS AND COMBUSTION OF CELLULOSE**

Charles W. George and Ronald A. Susott

INTERMOUNTAIN FOREST AND RANGE EXPERIMENT STATION
Forest Service
U. S. Department of Agriculture
Ogden, Utah 84401
Joseph F. Pechanec, Director

Table 7.--TGA-DTG thermal behavior of cellulose and $(NH_4)_2SO_4$ treated cellulose in air

Treatment	Residue at 450° C.	Cellulose residue at 450° C.	Low temperature peak			High temperature peak		
			Rate of weight loss	Normalized rate of weight loss	Peak temperature	Rate of weight loss	Normalized rate of weight loss	Peak temperature
	Percent	Percent	Mg./min.	Mg./min.	°C.	Mg./min.	Mg./min.	°C.
Untreated cellulose	7.7	7.7	--	--	--	8.41	8.41	349
Treated cellulose ¹								
0.0500	10.4	10.4	--	--	--	6.29	6.29	344
.100	13.2	13.2	--	--	--	5.00	5.01	332
.200	13.8	13.8	--	--	--	4.56	4.57	332
.300	14.3	14.3	0.46	0.46	255	4.11	4.12	330
.400	15.0	15.1	.60	.60	251	4.01	4.03	326
.500	16.0	16.1	.71	.72	252	3.71	3.73	325
.700	18.3	18.4	1.02	1.03	257	2.93	2.95	330
1.00	18.8	19.0	1.12	1.13	255	2.90	2.93	327
1.50	19.6	19.9	1.43	1.45	253	2.72	2.76	324
2.00	22.6	23.1	2.13	2.17	256	1.75	1.78	318
3.00	24.1	24.7	2.69	2.77	251	1.37	1.41	311
4.00	24.8	25.7	3.22	3.35	251	1.90	1.98	306
5.00	25.2	26.4	3.38	3.56	255	1.66	1.75	310
8.00	26.9	29.0	3.45	3.75	256	1.75	1.90	309
10.0	27.0	29.8	4.13	4.57	255	.96	1.06	308
12.0	26.4	29.7	3.69	4.19	257	2.11	2.39	307
15.0	26.3	30.6	3.50	4.12	257	1.48	1.74	312
20.0	25.7	31.6	2.88	3.60	255	--	--	--
25.0	25.8	33.7	3.00	4.00	257	--	--	--

¹Percent by weight chemical.

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Table 3.--Effect of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on pyrolysis and combustion threshold temperature ($^{\circ}\text{C}.$)¹

Treatment	$(\text{NH}_4)_2\text{HPO}_4$ treated cellulose		$(\text{NH}_4)_2\text{SO}_4$ treated cellulose	
	Pyrolysis (N_2)	Combustion (air)	Pyrolysis (N_2)	Combustion (air)
Untreated cellulose	290	298	290	298
Treated cellulose ²				
0.0500	286	294	257	280
.100	274	285	239	250
.200	264	272	234	242
.300	255	266	230	239
.400	253	262	231	231
.500	250	254	229	229
.700	243	252	228	231
1.00	234	249	224	230
1.50	230	241	229	225
2.00	216	237	213	228
3.00	212	221	210	221
4.00	209	213	202	217
5.00	207	210	201	213
6.00	199	209	200	212
8.00	196	208	199	211
10.0	189	206	196	208
12.0	190	202	195	210
15.0	187	200	194	208
20.0	190	199	195	205
25.0	186	193	190	203

¹ The threshold temperature is arbitrarily denoted as the temperature required to produce a weight loss rate of 0.09 milligrams per minute (< 1 percent of the maximum weight loss rate).

² Percent by weight chemical.

Table 4.--TGA-DTG thermal behavior of cellulose and $(\text{NH}_4)_2\text{HPO}_4$ treated cellulose in nitrogen

Treatment	Residue	Normalized	Peak rate	Normalized peak	Peak
	at $450^{\circ}\text{C}.$	cellulose	of weight	rate of weight	temperature
	Percent	Percent	Mg./min.	Mg./min.	$^{\circ}\text{C}.$
Untreated cellulose	7.6	7.6	5.13	5.13	367
Treated cellulose ¹					
0.0500	12.2	12.2	5.50	5.50	348
.100	15.0	14.9	5.00	5.00	340
.200	19.6	19.5	4.48	4.49	334
.300	22.2	22.1	4.38	4.39	329
.400	24.4	24.3	4.26	4.28	328
.500	25.8	25.6	4.20	4.22	326
.700	28.6	28.4	4.05	4.08	321
1.00	30.2	29.9	3.96	4.00	316
1.50	34.4	34.0	3.52	3.57	311
2.00	35.8	35.2	3.43	3.50	306
3.00	39.4	38.4	2.90	3.02	298
6.00	42.8	41.4	2.52	2.68	281
10.0	45.2	43.2	2.19	2.43	264
12.0	46.0	43.6	2.33	2.65	261
15.0	47.4	44.6	3.05	3.59	259
20.0	48.4	44.8	3.23	4.04	253
25.0	49.2	44.5	3.66	4.88	250

¹Percent by weight chemical.

INTRODUCTION

For the past 10 years, ammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ and ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ have been used as primary ingredients in forest fire retardant formulations. These chemicals, when applied to forest fuels, are known to alter or inhibit thermal degradation and combustion reactions. Because of the reduced flammability of chemically treated fuels, the use of such fire retarding chemicals has become an important tool in wildfire suppression. Knowledge of the reactions or mechanisms taking place and their relation to flammability will assist in a systematic selection of fire retardant chemicals and may lead to more effective methods of application.

Recent studies performed at the Northern Forest Fire Laboratory have indicated significant differences in the effects ammonium phosphate and ammonium sulfate have on flammability as measured indirectly by such parameters as rate of spread, fire intensity, radiant energy, flame height, and residue.¹ We do not know whether these differences in effects are due to the chemicals' physical differences, a difference in their thermal decomposition and availability, or to a difference in the actual mechanism by which they alter fuel degradation.

Truax, Harrison, and Baechler (1956) noted that both compounds were effective in retarding flaming combustion, but ammonium phosphate was superior in retarding glowing combustion. Browne and Tang (1963), on the basis of thermogravimetric analyses in a nitrogen atmosphere, found that the compounds have similar effects on the volatilization of wood and the threshold temperature for pyrolysis, although a difference in their volatilization rate was exhibited. Tang (1967) in a similar study found that ammonium phosphate had the same effects as ammonium sulphate on the pyrolysis of wood and cellulose but had little effect on the volatilization rate of lignin; the cellulose portion of wood was found to have the highest volatilization rate. The volatilization rate for wood seemed to be a combination of the effects on alpha-cellulose and lignin. Tang and Eickner (1968), using differential thermal analysis, compared the effects of 2-percent by weight ammonium sulfate and a 2-percent by weight ammonium phosphate treatment on pyrolysis and combustion of wood, cellulose, and lignin. Little difference was noted in thermograms and relative maximum heat intensities and it was concluded that these parallel results probably were produced by a similar mechanism.

Past research (Shafizadeh 1968; Kilzer and Broido 1965) has indicated that combustion adds secondary and competitive reactions to initial degradation reactions. It is likely that the occurrence of flaming combustion causes cellulose as well as the retardant chemicals to undergo different reactions and at different rates. Although relationships undoubtedly exist between the pyrolysis and combustion of cellulose and the role retardant chemicals play in altering related reactions, it may not be possible to predict combustion characteristics on the basis of pyrolysis characteristics. Thermal analysis in oxygen, or in an air atmosphere, may or may not accurately represent flaming and glowing combustion.

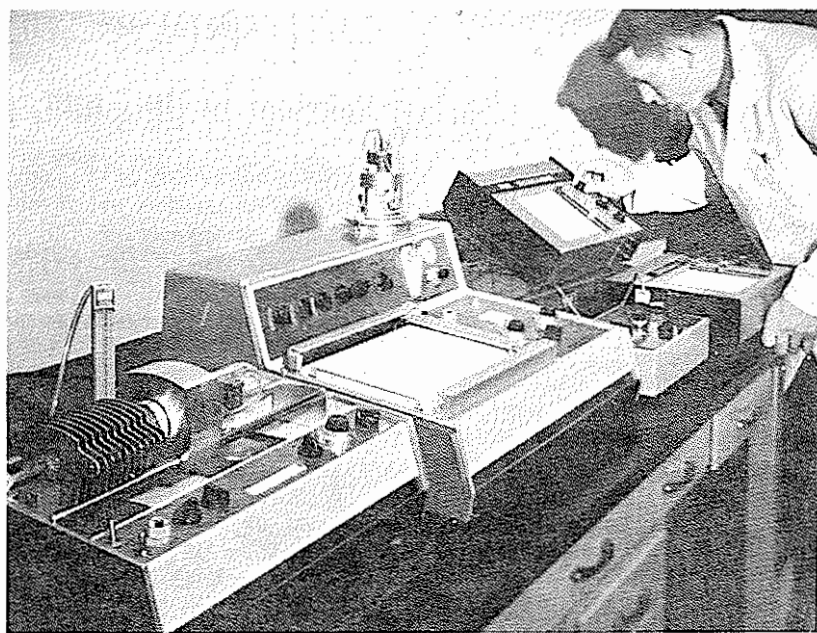
The purpose of the study was to provide extensive thermal analysis data that could be used to categorize the effects of these retardant chemicals on the pyrolysis and combustion of cellulose.²

¹Charles W. George and Aylmer D. Blakely. Study of the effects of diammonium phosphate and ammonium sulfate on flammability. 1968. (Unpublished report on file at the Northern Forest Fire Laboratory, USDA Forest Serv., Missoula, Montana.)

²For the purpose of this paper, pyrolysis is defined as the degradation of a material in an inert atmosphere or vacuum. Combustion refers to the process taking place when the initial material, as well as its degradation products, are in contact with oxygen or air.

APPENDIX

Figure 1.--Thermal analysis apparatus for obtaining DTA, TGA, and DTG thermograms.

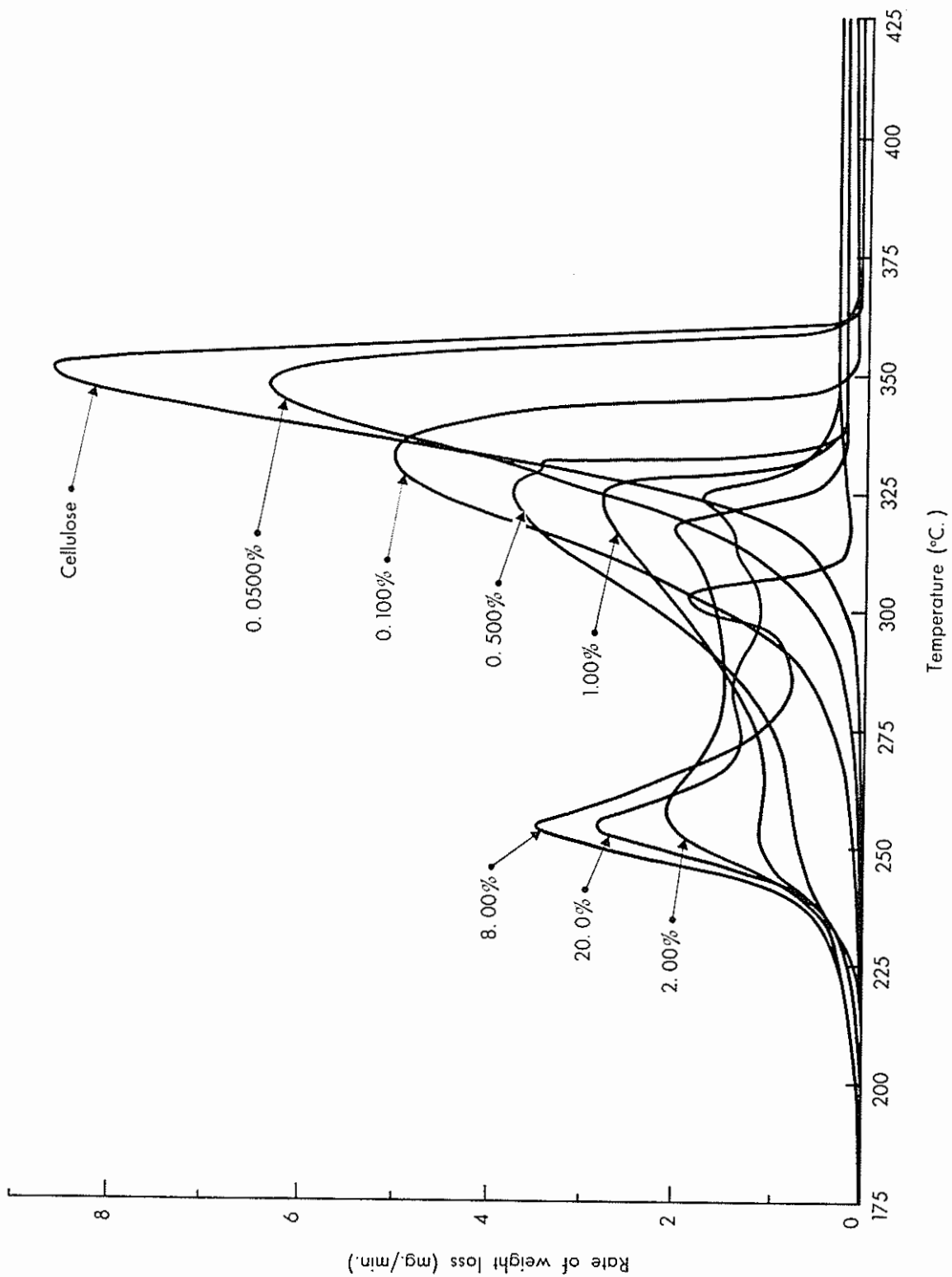


Pyrolysis was studied in a nitrogen atmosphere at a flow rate of 100 cubic centimeters per minute. A similar flow rate of air was used in investigations of combustion. For samples pyrolyzed in nitrogen, the percent of weight remaining as a function of sample temperature was monitored. For combustion analysis, an alternate method of recording data was needed due to the highly exothermic character of the reaction. The oven temperature and sample temperature were monitored for several blank runs using a Moseley Autograf 7100B two-pen strip-chart recorder. After correlating the two readings, the percent of weight remaining as a function of sample environment temperature could be calculated. In this way, decomposition in nitrogen and air could be compared in terms of similar environmental temperatures instead of sample temperatures. Endotherms and exotherms in N_2 had a negligible effect making sample and sample environment temperature essentially equivalent.)

Derivative thermogravimetric analyses (DTG) were obtained simultaneously with TGA by differentiating the mass signal from the DuPont 950 using a Cahn 2030 Time Derivative Computer.⁴ Calibration was accomplished using a constant weight loss rate, provided by a Knudsen diffusion cell containing a 50 μ l sample of 95 percent ethanol. The Knudsen cell was placed in the furnace at 40° C. and TGA-DTG curves recorded. The Moseley two-pen recorder was used to record both the DTG curves and sample or sample environment temperature so a comparison of rate of weight loss and temperature could be made.

The apparatus used for obtaining DTA, TGA, and DTG data is shown in figure 1.

⁴This derivative computer provided a noise-free response that was not significantly different in time to the weight loss response.



DTG thermograms of cellulose and $(\text{NH}_4)_2\text{SO}_4$ treated cellulose heated at 25°C . per minute in a flow of 100 cc. per minute air.

A major difference in thermograms for the pyrolysis of the two cellulose treatments is indicated. As $(\text{NH}_4)_2\text{HPO}_4$ is added to cellulose and pyrolyzed in nitrogen (page 12), the strong endotherm at 364°C . in untreated cellulose gradually shifts to lower temperatures. However, as the $(\text{NH}_4)_2\text{SO}_4$ concentration is increased to 0.50 percent, a new endotherm appears near 250°C .; this endotherm dominates the DTA curves at higher concentrations. The endotherm near 210°C . for $(\text{NH}_4)_2\text{HPO}_4$ treatments of cellulose greater than 4.00 percent is attributed to the inorganic fraction. Monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, which could be formed as the sample was dried, has an endotherm near 210°C . (A, page 11). An endotherm due to the presence of $(\text{NH}_4)_2\text{SO}_4$ is not readily discernible.

The DTA thermograms for combustion in air (page 13) of both $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ treated cellulose are dominated by a strong exotherm from about 300° to 450°C . The endotherm near 250°C . for $(\text{NH}_4)_2\text{SO}_4$ treated samples is apparent at a concentration of 0.70 percent, and above, but is small compared to the latter exotherm. A prominent difference between the effects of the two chemicals on the combustion of cellulose is that $(\text{NH}_4)_2\text{SO}_4$ causes a larger exotherm (note the difference in the ΔT scale used, pages 12 and 13).

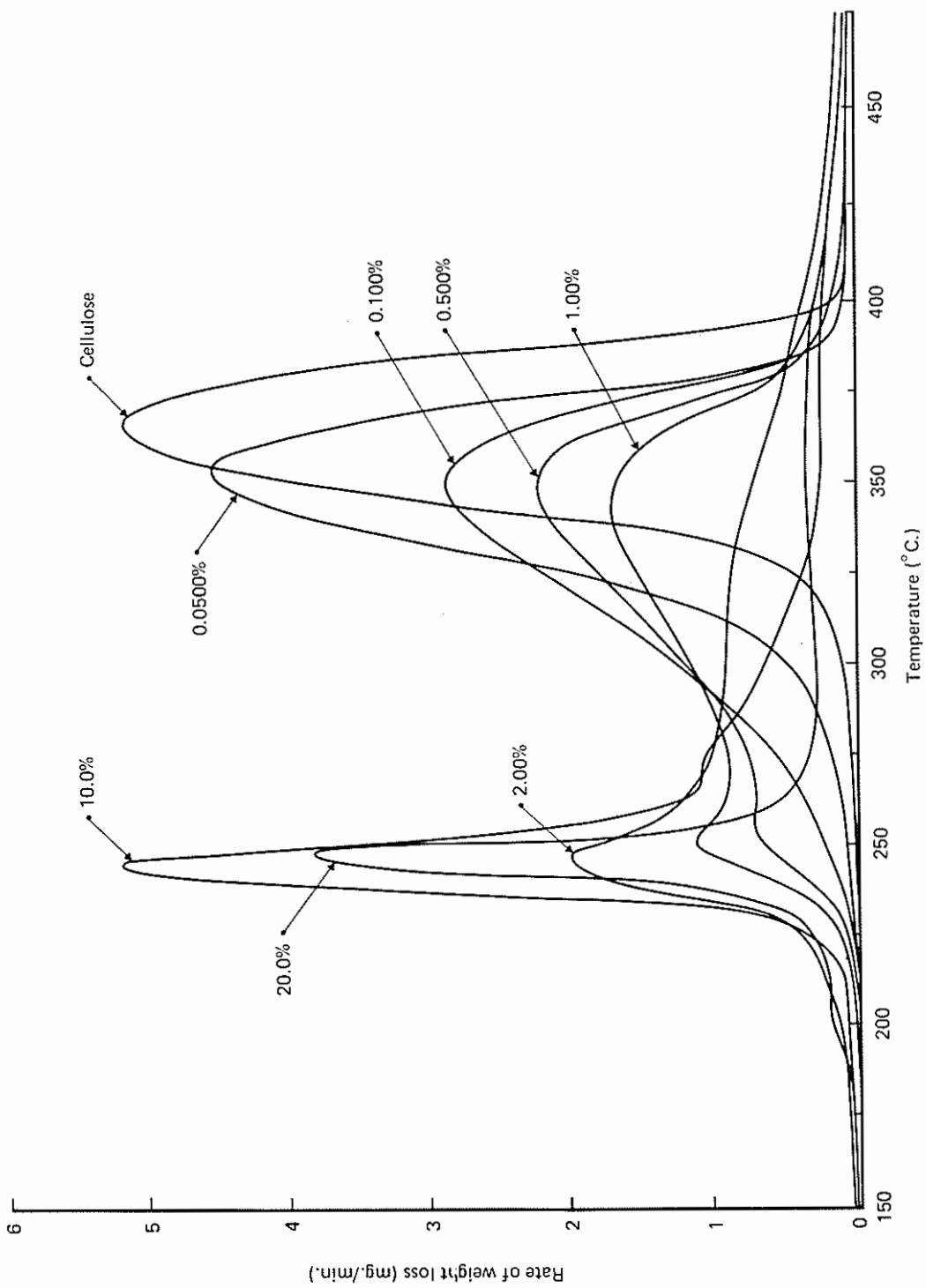
Thermogravimetric and Derivative Thermogravimetric Analyses

The cellulose samples, treated with $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ in concentrations from 0 to 25 percent by weight were investigated for thermal behavior in air and nitrogen by TGA and DTG. After initial water loss and setting of sample weight to 100 percent, the TGA curves are horizontal until pyrolysis (pages 14,15) and combustion (pages 16,17) begin. As the chemical percent is increased, there is a lowering of the pyrolysis and combustion threshold temperature. The threshold temperature was determined using the DTG curves and arbitrarily denoted as the temperature required to produce a weight loss rate of 0.09 milligram per minute (< 1 percent of the maximum weight loss rate). Table 3 shows the effect of amount of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on the threshold temperature for pyrolysis and combustion. The slight difference (8°C .) in the threshold temperatures for untreated cellulose in nitrogen and air is probably due to the difference in procedures for obtaining the environmental temperature in nitrogen and air. The lowering of threshold temperatures for treated fuels in air and nitrogen is also accompanied by a lowering of the temperature at which the maximum weight loss or reaction rate is observed. The temperature of the maximum weight loss was equally useful in comparing the effect of the different chemical concentrations.

Although the trends in TGA curves appear very similar for both chemicals, the DTG curves (pages 18, 19, 20, 21) which were run simultaneously with TGA, were much more sensitive to small differences in weight loss rates. These DTG curves, as well as the TGA curves, were very reproducible. In both air and nitrogen, the DTG curves show $(\text{NH}_4)_2\text{SO}_4$ treatment causes a rate of weight loss peak at about 250°C . In nitrogen, treatments as low as 0.500 percent cause this peak; in air, 1.00-percent treatments have the same effect. The curves for $(\text{NH}_4)_2\text{HPO}_4$ show a much more gradual shift of the peak to lower temperatures, with a peak at 250°C . developing only with high (greater than 10.0 percent) concentrations of chemical. Tables 4, 5, 6, and 7 give data for the rate of weight loss for peaks in the DTG curves and the temperature at which those peaks occur. Although numerical data are useful for comparison purposes, viewing the entire DTG thermograms (pages 18-21) provides a better picture of reaction differences.

The rate was normalized to correct for decreasing initial cellulose weights with increasing chemical treatment. The normalized rate was determined by:

$$\text{Normalized peak rate (mg. per minute)} = \frac{\text{Actual peak rate (mg. per minute)}}{\text{Fraction of cellulose in sample}}$$



DTG thermograms of cellulose and (NH₄)₂SO₄ treated cellulose heated at 25° C. per minute in a flow of 100 cc. per minute nitrogen.

An increase in the percent by weight chemical usually was accompanied by a decrease in the peak rate of weight loss. However, cellulose treated with 0.050 percent $(\text{NH}_4)_2\text{HPO}_4$ caused an increase over untreated in the maximum peak rate of weight loss during pyrolysis (page 18). The only other peak rates which exceeded untreated occurred at the low temperature peak (250° C.) with higher levels of $(\text{NH}_4)_2\text{SO}_4$ treated cellulose during pyrolysis. The maximum rate of weight loss for the low temperature peak increased with percent by weight chemical until a 10-percent treatment was reached. The rate decreased at treatment levels above 10 percent (page 19). The DTG curves for each particular chemical are quite similar for nitrogen and air except that rates of weight loss are somewhat higher in air.

Tables 4 through 7 also give data taken from TGA curves showing the effect of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on residue at 450° C. in both nitrogen and air. Cellulose residue can be estimated if the amount of inorganic chemical remaining at 450° C. is known. The TGA curves, shown on page 11, for the two chemicals indicate a 100-percent weight loss for $(\text{NH}_4)_2\text{SO}_4$ and 37-percent weight loss for $(\text{NH}_4)_2\text{HPO}_4$. Assuming the inorganic chemicals decompose the same whether cellulose is present or not, the normalized cellulose residue can be determined:

Normalized cellulose residue at 450° C. (percent) =

$$\frac{\text{Percent residue} - (\text{percent chemical residue} \times \text{fraction chemical treatment})}{\text{Fraction cellulose in sample}}$$

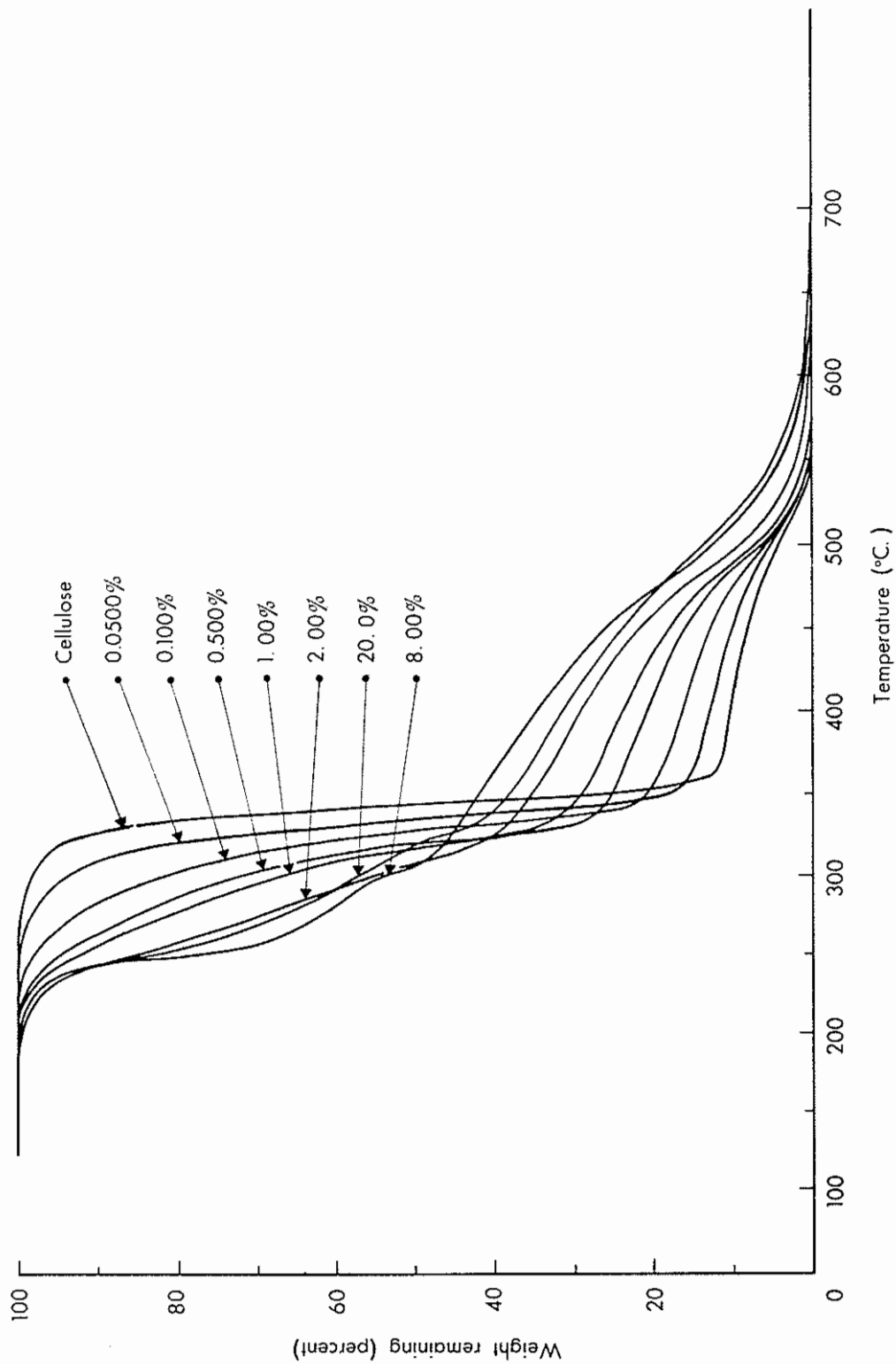
The effect of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on cellulose residue after pyrolysis and combustion is shown in figures 2 and 3. As the chemical is increased (percent by weight), both chemicals increase residue at 450° C. In air and at the lower concentrations in nitrogen, $(\text{NH}_4)_2\text{HPO}_4$ causes a greater increase in residue than $(\text{NH}_4)_2\text{SO}_4$. The rate of volatilization of residue at 450° C. is less for $(\text{NH}_4)_2\text{HPO}_4$ treatments and the temperature required for its complete volatilization is higher (compare pages 16 and 17).

COMPARISON OF METHODS AND RESULTS

Comparison of DTA, TGA, and DTG curves for cellulose pyrolysis and combustion and cellulose treated with various concentrations of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ shows reasonable agreement for each method. Small endothermic and exothermic reactions made determination of maximum rate temperatures impossible in TGA. The use of DTG provided information not otherwise obtainable and its sensitivity greatly added to ease of interpretation.

When cellulose is treated with $(\text{NH}_4)_2\text{HPO}_4$ and this retardant is increased between 0 and 25 percent, the following temperatures are lowered: the threshold temperatures for pyrolysis and combustion (table 3); the temperature of maximum rate of weight loss (tables 4 and 6); the temperature of the major pyrolysis endotherm (table 1); the temperature of the combustion exotherm (table 1). This increase in retardant exponentially increases the amount of cellulose residue (tables 4 and 6). Similar trends are observable in $(\text{NH}_4)_2\text{SO}_4$ treatments; furthermore, the effects of this retardant are usually more pronounced for lower treatment levels than for $(\text{NH}_4)_2\text{HPO}_4$ treatments. For example, a treatment of 0.0500 percent $(\text{NH}_4)_2\text{SO}_4$ lowers the threshold temperature for pyrolysis 33° C. while the same treatment of $(\text{NH}_4)_2\text{HPO}_4$ lowers it only 4° C. Though similar comparisons can be made for other treatments of less than 1.00 percent, treatments from 1.50 to 25 percent result in nearly the same threshold temperature for both $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ (table 3).

The differences in chemicals and similarities in analysis methods are graphically depicted in figure 4.



TGA thermograms of cellulose and (NH₄)₂SO₄ treated cellulose heated at 25° C. per minute in a flow of 100 cc. per minute air.

Discussion

Differential thermal (DTA), thermogravimetric (TGA), and derivative thermogravimetric (DTG) methods of analyses show significant differences in the effects ammonium sulfate and ammonium phosphate have on the degradation of cellulose in either nitrogen or air atmosphere. Some of the general effects and the differences can be summarized:

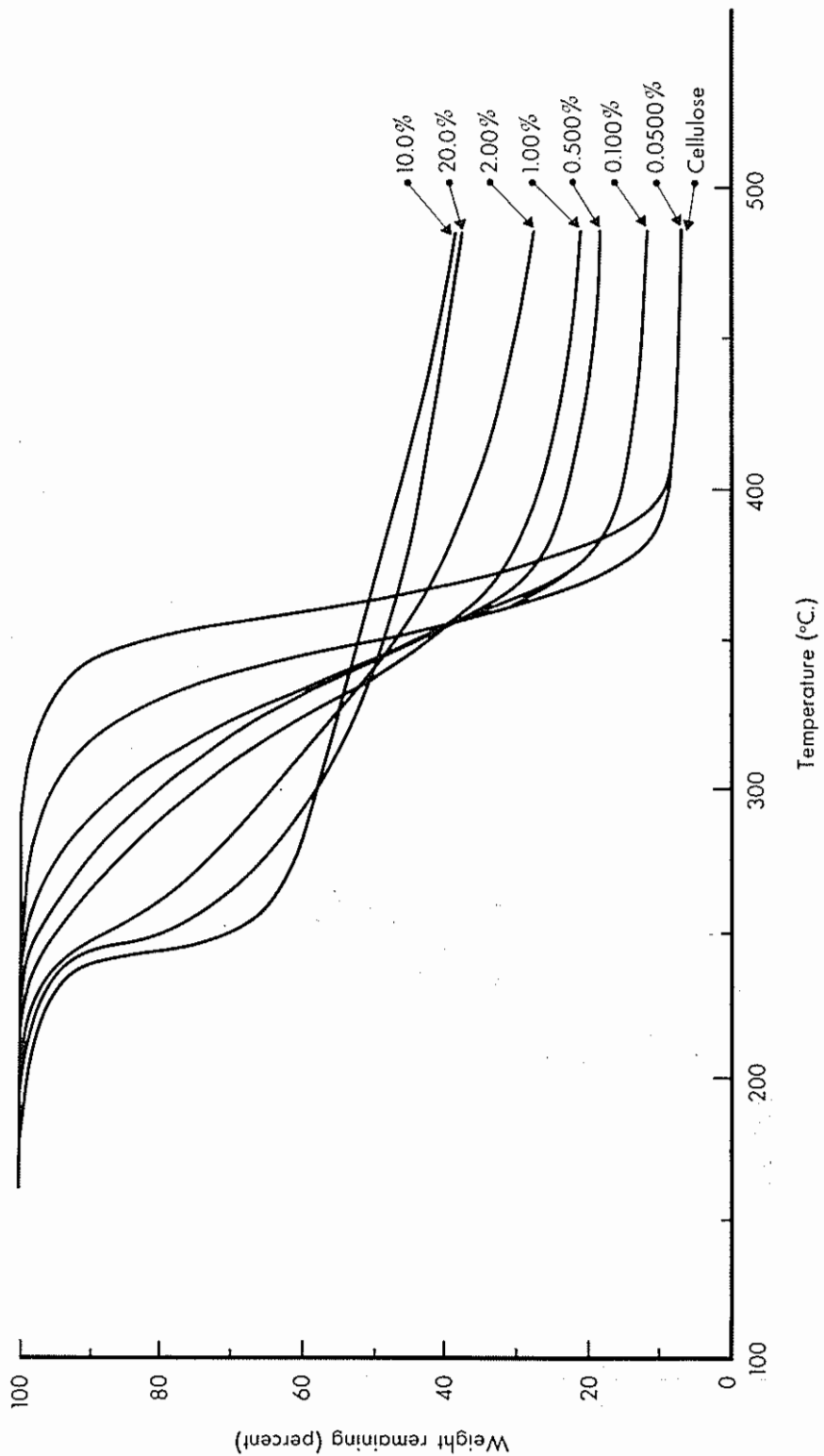
1. Both ammonium sulfate and ammonium phosphate lower the threshold temperature and activation energy required to initiate cellulose decomposition in nitrogen and air.
2. Increasing the amount of either retardant chemical decreases the maximum weight loss rate occurring during decomposition until the temperature of the peak nears 250° C. An increase in the amount of either retardant beyond the concentration required to obtain a maximum rate at 250° C. causes an increase in the peak rate without shifting its temperature. Any additional increase further reduces the maximum weight loss rate.
3. Increasing retardant chemical causes an increase in the residue or char production.
4. Ammonium phosphate is more effective in increasing char production in an air atmosphere than is ammonium sulfate.
5. While a 2-percent treatment of ammonium sulfate causes a shift to near 250° C. in the maximum decomposition rate, five times this quantity of ammonium phosphate (on a molar fraction basis) is required to produce the same effect, indicating a sizable difference in the action of the two chemicals on cellulose.

It is theorized that the differences ammonium sulfate and phosphate have on cellulose pyrolysis and combustion are either due to the availability of the inorganic fraction involved in the reaction or to a different mechanism by which these chemicals alter pyrolysis and combustion.

1. Such theorizing is based on the fact that ammonium sulfate decomposes at a lower temperature than ammonium phosphate and may not be available in similar concentrations or at the necessary time. For instance, ammonium sulfate is completely decomposed by 420° C., a temperature which may preclude glowing combustion reactions. This is borne out by the fact that ammonium sulfate treated cellulose produces less residue at 450° C. than does ammonium phosphate.

2. Major shifts in cellulose decomposition occurred prior to losses of significant amounts of the sulfate or phosphate portion of the compound. Because the molecular weight is the same for both compounds (132.05 and 132.14 for $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$, respectively), the treatments can be considered as being on a molar basis. Thus, provided the difference in NH_3 production rates is not responsible for the difference (equal total amounts of NH_3 are produced by both compounds) it is likely there is a difference in the mechanism by which these compounds alter both pyrolysis and combustion. It is unlikely that NH_3 is important in the process since $(\text{NH}_4)_2\text{HPO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ have the same effect on pyrolysis and combustion when the comparison is made on an equivalent PO_4 basis. This is also supported by the fact empirical fire tests have shown H_3PO_4 as well as $(\text{NH}_4)_2\text{HPO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ to be equally effective when compared on an equivalent PO_4 basis.

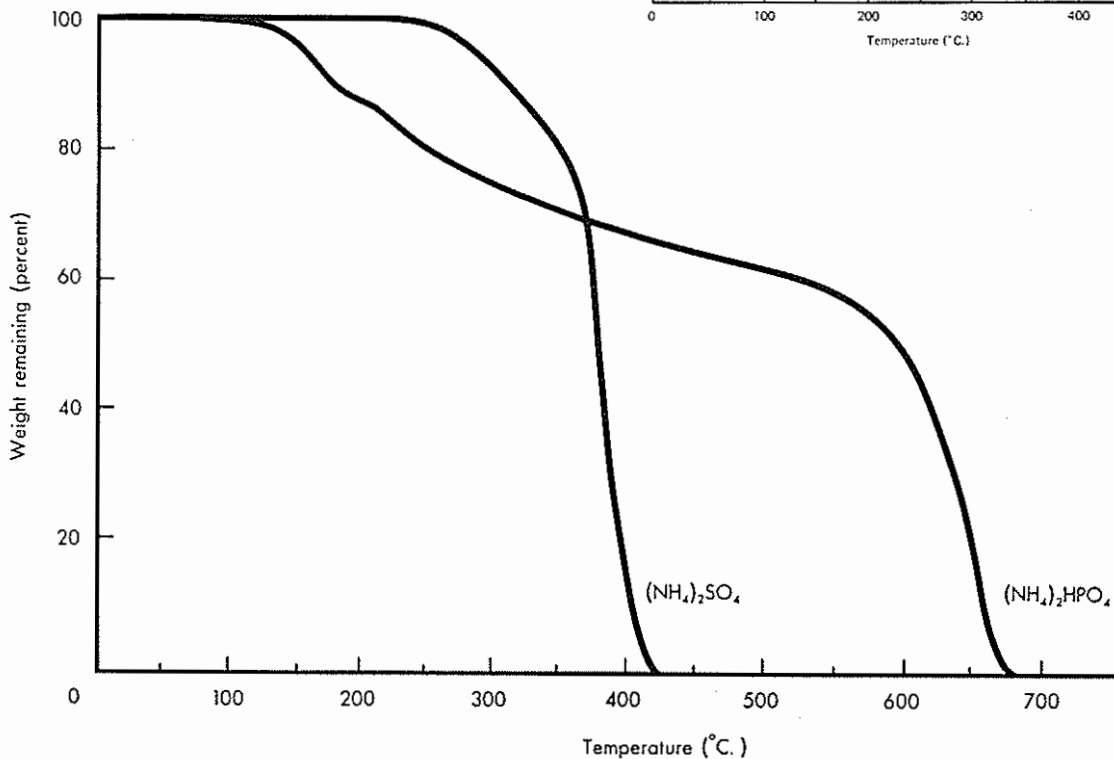
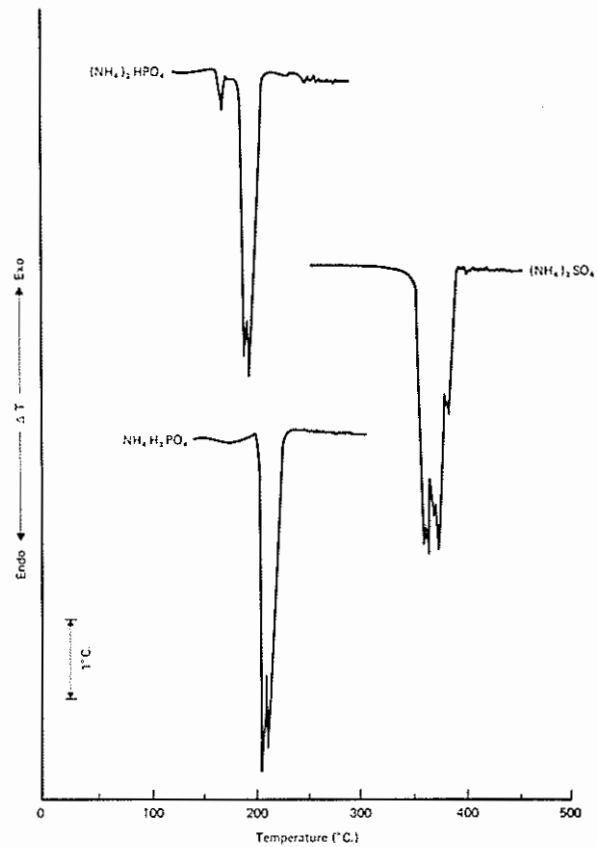
It is possible that the differences in the effects of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ can be attributed to both theorized causes previously mentioned. A different mechanism by which pyrolysis and combustion are altered may exist at lower temperatures for the compounds while the difference in high temperature availability of a portion of the compound may affect glowing combustion, and thus residue, differently.



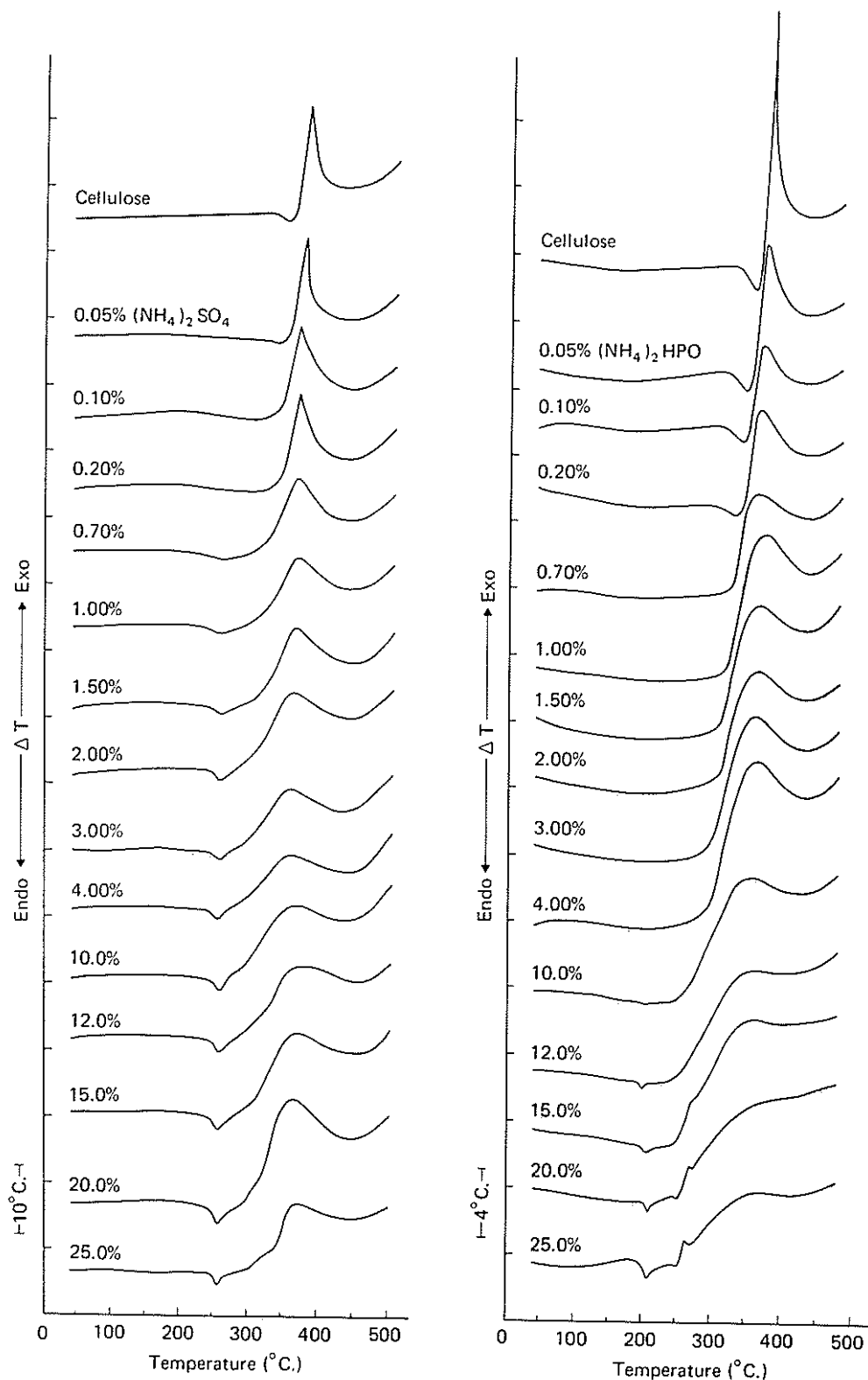
TGA thermograms of cellulose and $(\text{NH}_4)_2\text{SO}_4$ treated cellulose heated at 25°C . per minute in a flow of 100 cc. per minute nitrogen.

THERMOGRAMS

A--DTA thermograms of $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{SO}_4$ when heated at 25°C . per minute in a flow of 1 liter per minute air.



B--TGA thermograms for $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ heated at 25°C . per minute in a flow of 1 liter per minute air.



DTA thermograms of cellulose and treated cellulose heated at 25° C. per minute when fluidized with 100 cc. per minute air.

GEORGE, CHARLES W. and SUSOTT, RONALD A.

1971. Effects of ammonium phosphate and sulfate on the pyrolysis and combustion of cellulose. USDA Forest Serv. Res. Pap. INT-90, 27 p., illus.

DTA, TGA, and DTG analyses were used to study the effects of ammonium phosphate and ammonium sulfate on the pyrolysis and combustion of cellulose. These flame retardants were found to have certain similar effects but reaction temperatures and rates indicated differences in chemical availability, reaction mechanism, or both.

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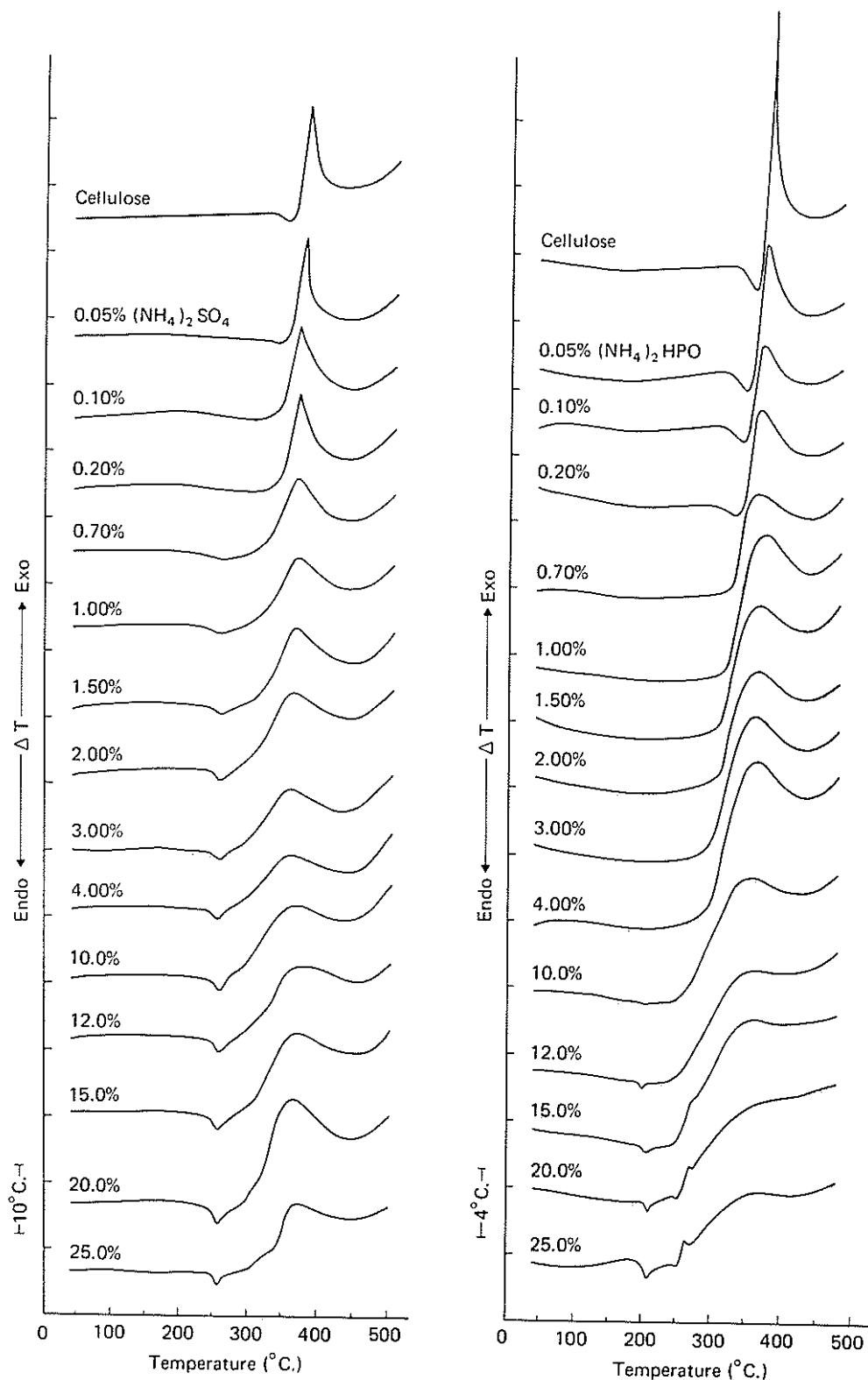
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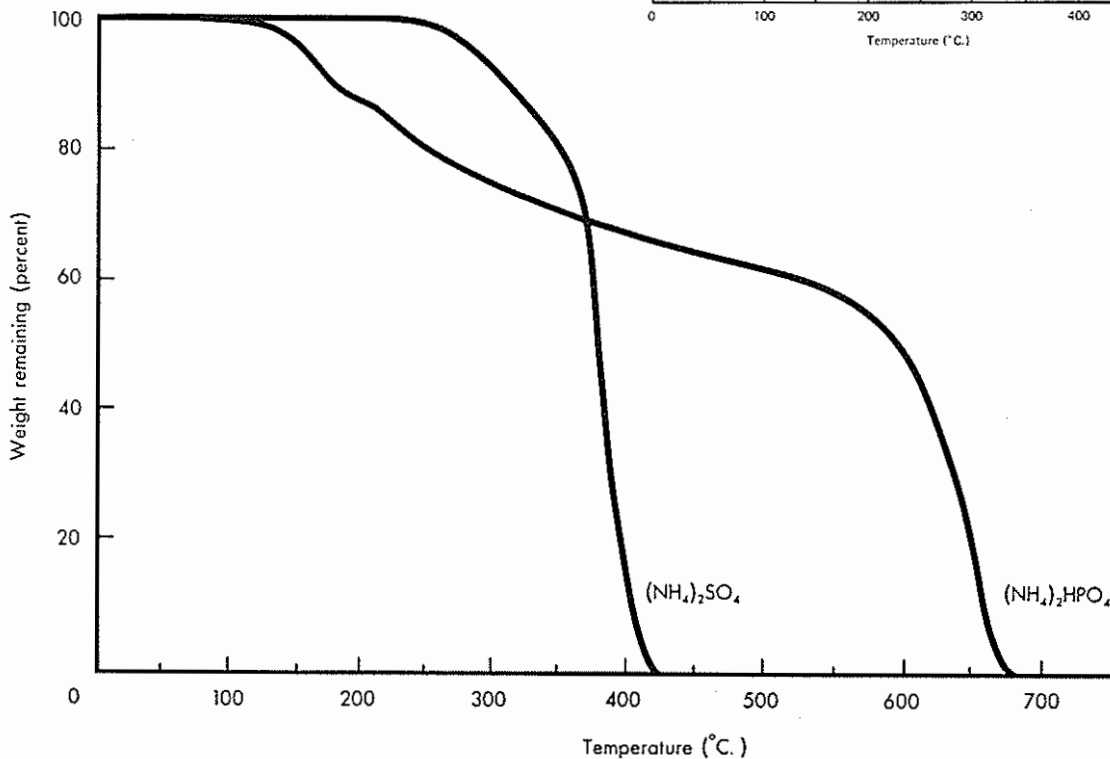
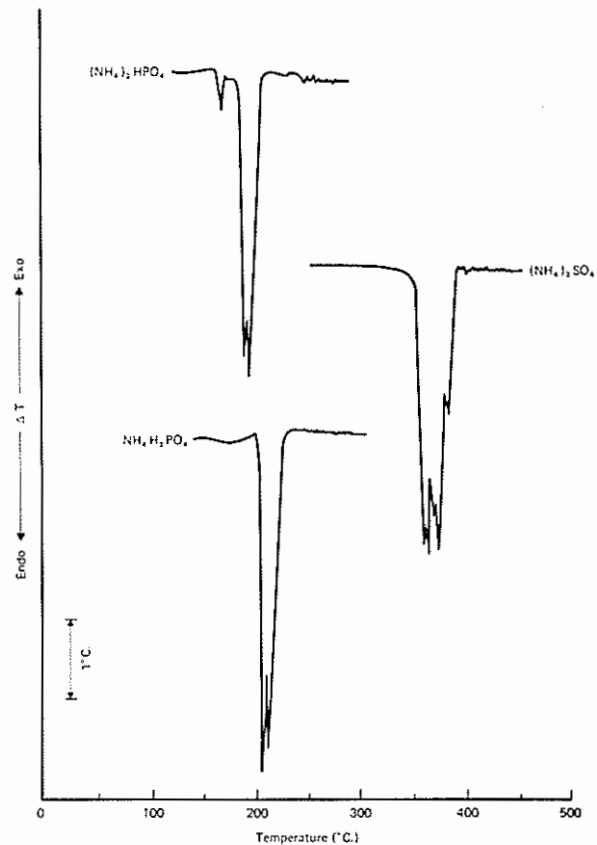
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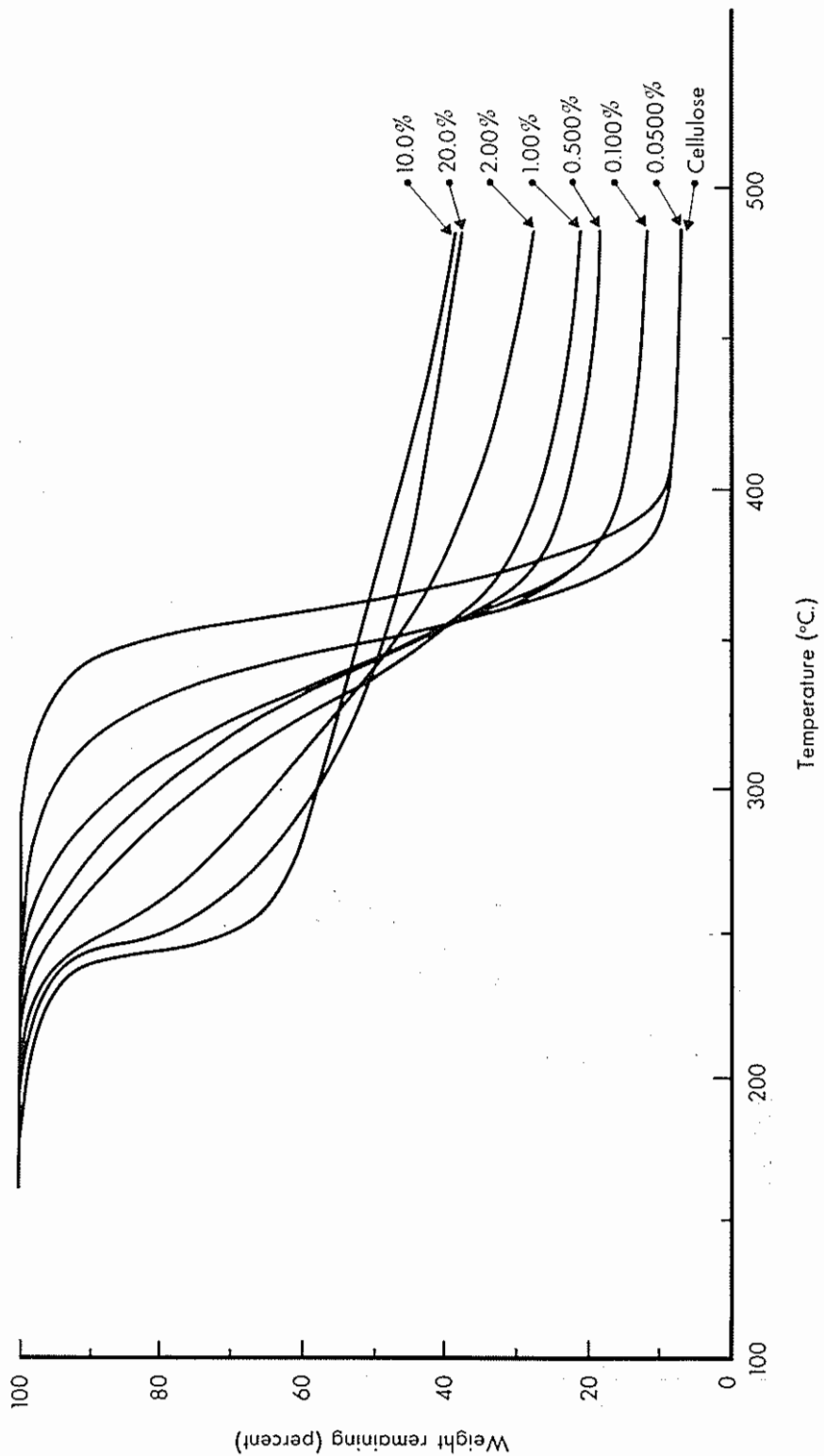
DTA thermograms of cellulose and treated cellulose heated at 25° C. per minute when fluidized with 100 cc. per minute air.

THERMOGRAMS

A--DTA thermograms of $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{SO}_4$ when heated at 25°C . per minute in a flow of 1 liter per minute air.



B--TGA thermograms for $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ heated at 25°C . per minute in a flow of 1 liter per minute air.



TGA thermograms of cellulose and $(\text{NH}_4)_2\text{SO}_4$ treated cellulose heated at 25°C . per minute in a flow of 100 cc. per minute nitrogen.

Discussion

Differential thermal (DTA), thermogravimetric (TGA), and derivative thermogravimetric (DTG) methods of analyses show significant differences in the effects ammonium sulfate and ammonium phosphate have on the degradation of cellulose in either nitrogen or air atmosphere. Some of the general effects and the differences can be summarized:

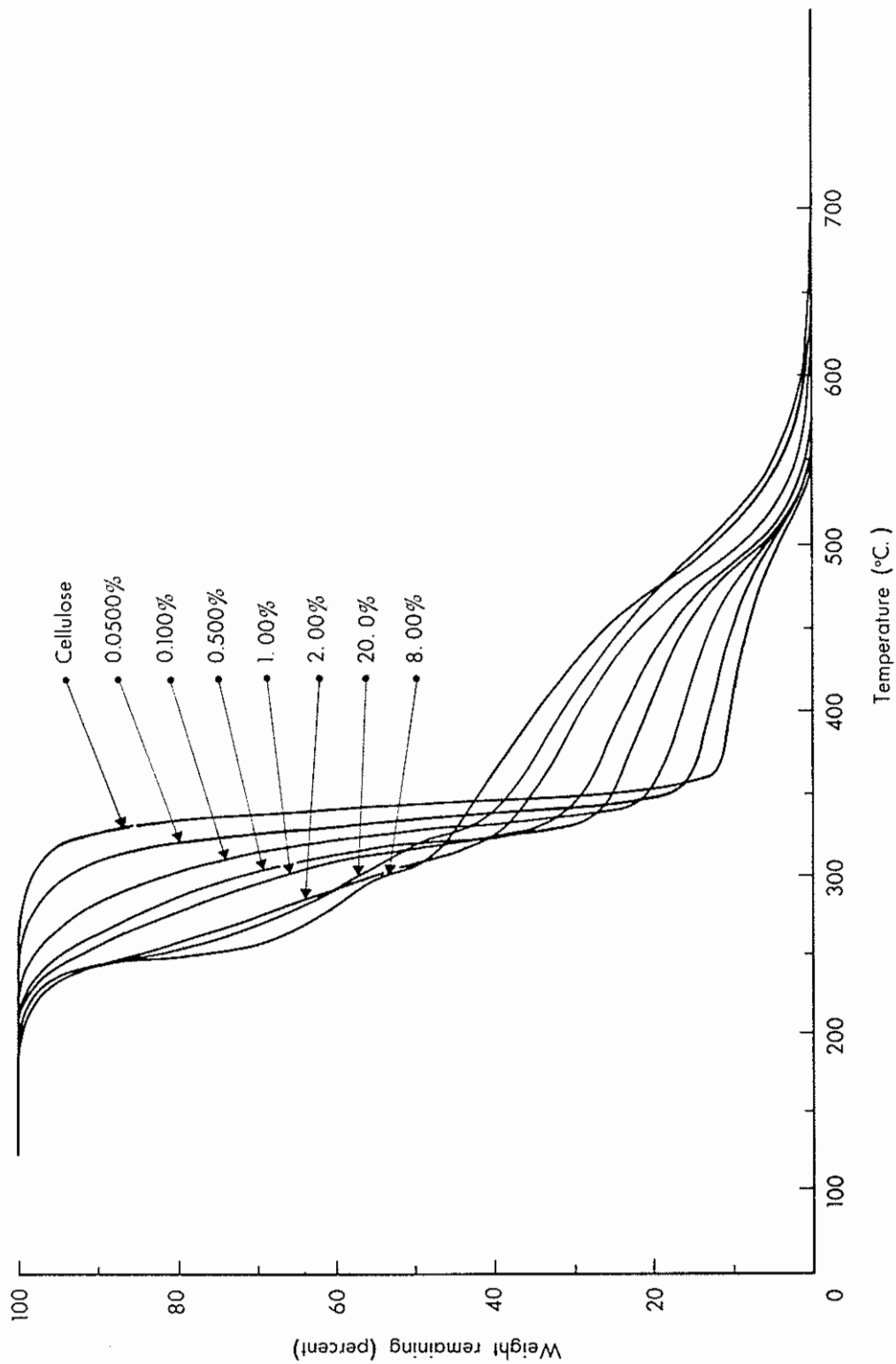
1. Both ammonium sulfate and ammonium phosphate lower the threshold temperature and activation energy required to initiate cellulose decomposition in nitrogen and air.
2. Increasing the amount of either retardant chemical decreases the maximum weight loss rate occurring during decomposition until the temperature of the peak nears 250° C. An increase in the amount of either retardant beyond the concentration required to obtain a maximum rate at 250° C. causes an increase in the peak rate without shifting its temperature. Any additional increase further reduces the maximum weight loss rate.
3. Increasing retardant chemical causes an increase in the residue or char production.
4. Ammonium phosphate is more effective in increasing char production in an air atmosphere than is ammonium sulfate.
5. While a 2-percent treatment of ammonium sulfate causes a shift to near 250° C. in the maximum decomposition rate, five times this quantity of ammonium phosphate (on a molar fraction basis) is required to produce the same effect, indicating a sizable difference in the action of the two chemicals on cellulose.

It is theorized that the differences ammonium sulfate and phosphate have on cellulose pyrolysis and combustion are either due to the availability of the inorganic fraction involved in the reaction or to a different mechanism by which these chemicals alter pyrolysis and combustion.

1. Such theorizing is based on the fact that ammonium sulfate decomposes at a lower temperature than ammonium phosphate and may not be available in similar concentrations or at the necessary time. For instance, ammonium sulfate is completely decomposed by 420° C., a temperature which may preclude glowing combustion reactions. This is borne out by the fact that ammonium sulfate treated cellulose produces less residue at 450° C. than does ammonium phosphate.

2. Major shifts in cellulose decomposition occurred prior to losses of significant amounts of the sulfate or phosphate portion of the compound. Because the molecular weight is the same for both compounds (132.05 and 132.14 for $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$, respectively), the treatments can be considered as being on a molar basis. Thus, provided the difference in NH_3 production rates is not responsible for the difference (equal total amounts of NH_3 are produced by both compounds) it is likely there is a difference in the mechanism by which these compounds alter both pyrolysis and combustion. It is unlikely that NH_3 is important in the process since $(\text{NH}_4)_2\text{HPO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ have the same effect on pyrolysis and combustion when the comparison is made on an equivalent PO_4 basis. This is also supported by the fact empirical fire tests have shown H_3PO_4 as well as $(\text{NH}_4)_2\text{HPO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ to be equally effective when compared on an equivalent PO_4 basis.

It is possible that the differences in the effects of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ can be attributed to both theorized causes previously mentioned. A different mechanism by which pyrolysis and combustion are altered may exist at lower temperatures for the compounds while the difference in high temperature availability of a portion of the compound may affect glowing combustion, and thus residue, differently.



TGA thermograms of cellulose and $(\text{NH}_4)_2\text{SO}_4$ treated cellulose heated at 25°C . per minute in a flow of 100 cc. per minute air.

An increase in the percent by weight chemical usually was accompanied by a decrease in the peak rate of weight loss. However, cellulose treated with 0.050 percent $(\text{NH}_4)_2\text{HPO}_4$ caused an increase over untreated in the maximum peak rate of weight loss during pyrolysis (page 18). The only other peak rates which exceeded untreated occurred at the low temperature peak (250° C.) with higher levels of $(\text{NH}_4)_2\text{SO}_4$ treated cellulose during pyrolysis. The maximum rate of weight loss for the low temperature peak increased with percent by weight chemical until a 10-percent treatment was reached. The rate decreased at treatment levels above 10 percent (page 19). The DTG curves for each particular chemical are quite similar for nitrogen and air except that rates of weight loss are somewhat higher in air.

Tables 4 through 7 also give data taken from TGA curves showing the effect of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on residue at 450° C. in both nitrogen and air. Cellulose residue can be estimated if the amount of inorganic chemical remaining at 450° C. is known. The TGA curves, shown on page 11, for the two chemicals indicate a 100-percent weight loss for $(\text{NH}_4)_2\text{SO}_4$ and 37-percent weight loss for $(\text{NH}_4)_2\text{HPO}_4$. Assuming the inorganic chemicals decompose the same whether cellulose is present or not, the normalized cellulose residue can be determined:

Normalized cellulose residue at 450° C. (percent) =

$$\frac{\text{Percent residue} - (\text{percent chemical residue} \times \text{fraction chemical treatment})}{\text{Fraction cellulose in sample}}$$

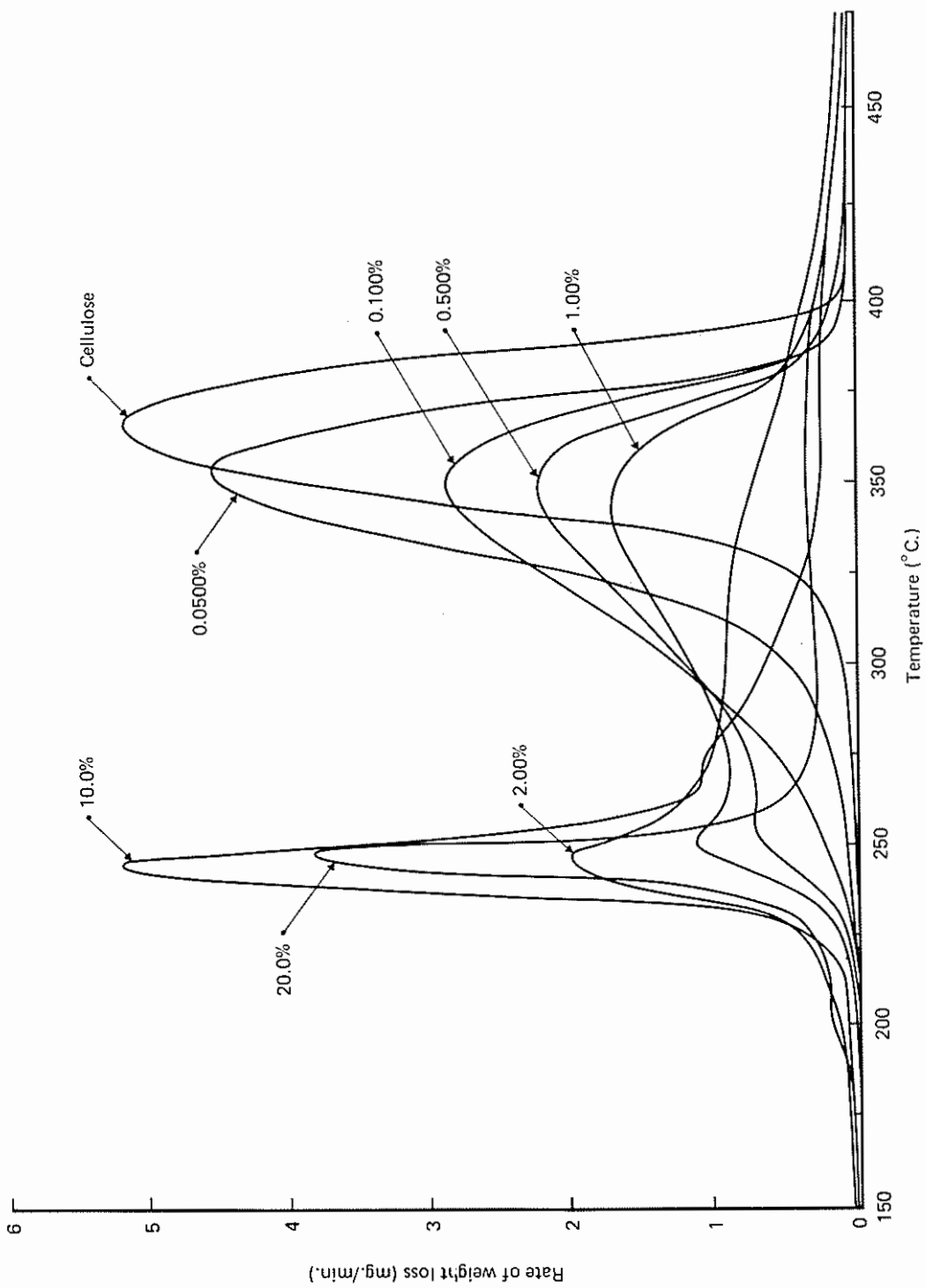
The effect of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on cellulose residue after pyrolysis and combustion is shown in figures 2 and 3. As the chemical is increased (percent by weight), both chemicals increase residue at 450° C. In air and at the lower concentrations in nitrogen, $(\text{NH}_4)_2\text{HPO}_4$ causes a greater increase in residue than $(\text{NH}_4)_2\text{SO}_4$. The rate of volatilization of residue at 450° C. is less for $(\text{NH}_4)_2\text{HPO}_4$ treatments and the temperature required for its complete volatilization is higher (compare pages 16 and 17).

COMPARISON OF METHODS AND RESULTS

Comparison of DTA, TGA, and DTG curves for cellulose pyrolysis and combustion and cellulose treated with various concentrations of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ shows reasonable agreement for each method. Small endothermic and exothermic reactions made determination of maximum rate temperatures impossible in TGA. The use of DTG provided information not otherwise obtainable and its sensitivity greatly added to ease of interpretation.

When cellulose is treated with $(\text{NH}_4)_2\text{HPO}_4$ and this retardant is increased between 0 and 25 percent, the following temperatures are lowered: the threshold temperatures for pyrolysis and combustion (table 3); the temperature of maximum rate of weight loss (tables 4 and 6); the temperature of the major pyrolysis endotherm (table 1); the temperature of the combustion exotherm (table 1). This increase in retardant exponentially increases the amount of cellulose residue (tables 4 and 6). Similar trends are observable in $(\text{NH}_4)_2\text{SO}_4$ treatments; furthermore, the effects of this retardant are usually more pronounced for lower treatment levels than for $(\text{NH}_4)_2\text{HPO}_4$ treatments. For example, a treatment of 0.0500 percent $(\text{NH}_4)_2\text{SO}_4$ lowers the threshold temperature for pyrolysis 33° C. while the same treatment of $(\text{NH}_4)_2\text{HPO}_4$ lowers it only 4° C. Though similar comparisons can be made for other treatments of less than 1.00 percent, treatments from 1.50 to 25 percent result in nearly the same threshold temperature for both $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ (table 3).

The differences in chemicals and similarities in analysis methods are graphically depicted in figure 4.



DTG thermograms of cellulose and $(\text{NH}_4)_2\text{SO}_4$ treated cellulose heated at 25°C . per minute in a flow of 100 cc. per minute nitrogen.

A major difference in thermograms for the pyrolysis of the two cellulose treatments is indicated. As $(\text{NH}_4)_2\text{HPO}_4$ is added to cellulose and pyrolyzed in nitrogen (page 12), the strong endotherm at 364°C . in untreated cellulose gradually shifts to lower temperatures. However, as the $(\text{NH}_4)_2\text{SO}_4$ concentration is increased to 0.50 percent, a new endotherm appears near 250°C .; this endotherm dominates the DTA curves at higher concentrations. The endotherm near 210°C . for $(\text{NH}_4)_2\text{HPO}_4$ treatments of cellulose greater than 4.00 percent is attributed to the inorganic fraction. Monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, which could be formed as the sample was dried, has an endotherm near 210°C . (A, page 11). An endotherm due to the presence of $(\text{NH}_4)_2\text{SO}_4$ is not readily discernible.

The DTA thermograms for combustion in air (page 13) of both $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ treated cellulose are dominated by a strong exotherm from about 300° to 450°C . The endotherm near 250°C . for $(\text{NH}_4)_2\text{SO}_4$ treated samples is apparent at a concentration of 0.70 percent, and above, but is small compared to the latter exotherm. A prominent difference between the effects of the two chemicals on the combustion of cellulose is that $(\text{NH}_4)_2\text{SO}_4$ causes a larger exotherm (note the difference in the ΔT scale used, pages 12 and 13).

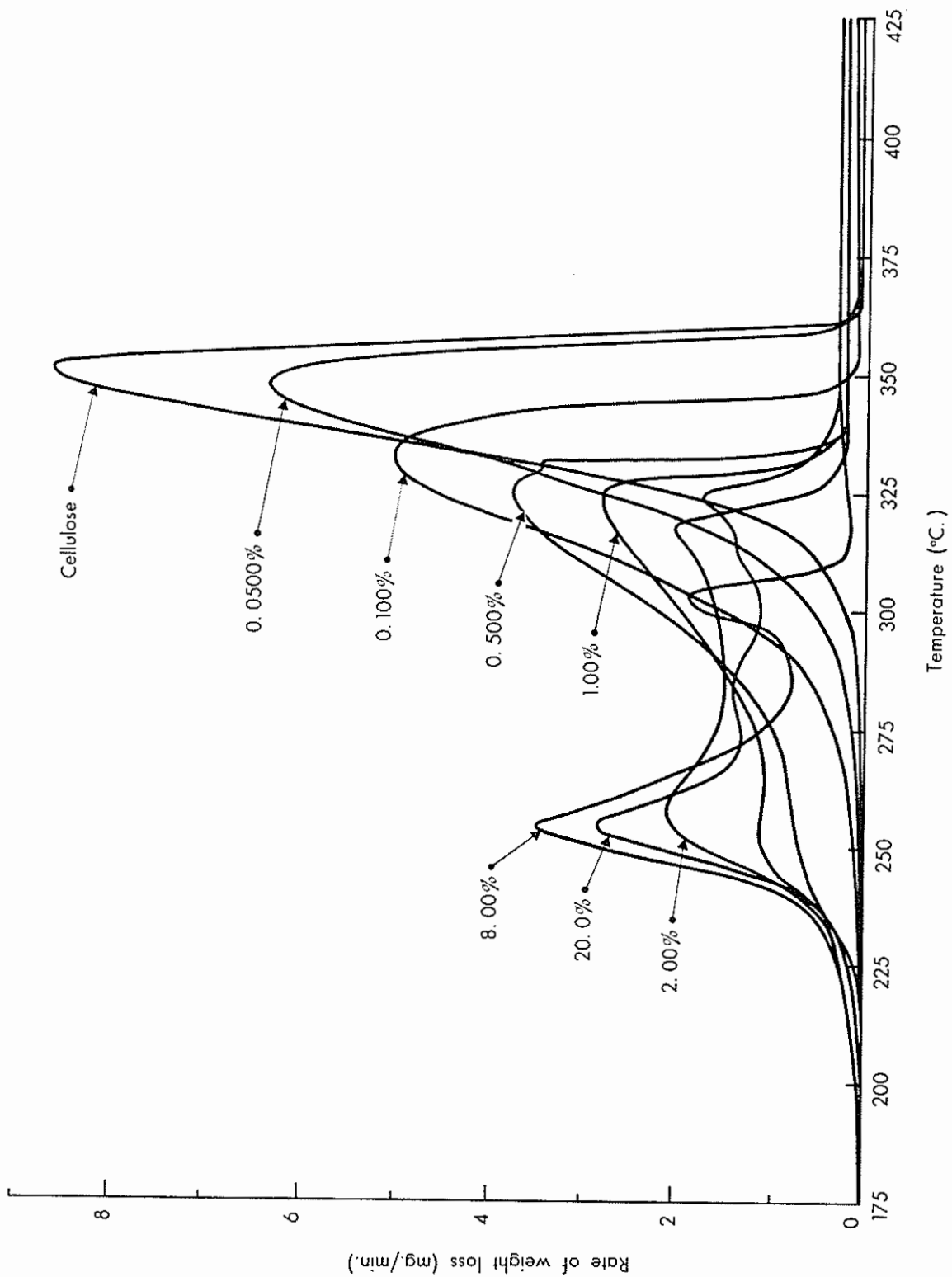
Thermogravimetric and Derivative Thermogravimetric Analyses

The cellulose samples, treated with $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ in concentrations from 0 to 25 percent by weight were investigated for thermal behavior in air and nitrogen by TGA and DTG. After initial water loss and setting of sample weight to 100 percent, the TGA curves are horizontal until pyrolysis (pages 14,15) and combustion (pages 16,17) begin. As the chemical percent is increased, there is a lowering of the pyrolysis and combustion threshold temperature. The threshold temperature was determined using the DTG curves and arbitrarily denoted as the temperature required to produce a weight loss rate of 0.09 milligram per minute (< 1 percent of the maximum weight loss rate). Table 3 shows the effect of amount of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on the threshold temperature for pyrolysis and combustion. The slight difference (8°C .) in the threshold temperatures for untreated cellulose in nitrogen and air is probably due to the difference in procedures for obtaining the environmental temperature in nitrogen and air. The lowering of threshold temperatures for treated fuels in air and nitrogen is also accompanied by a lowering of the temperature at which the maximum weight loss or reaction rate is observed. The temperature of the maximum weight loss was equally useful in comparing the effect of the different chemical concentrations.

Although the trends in TGA curves appear very similar for both chemicals, the DTG curves (pages 18, 19, 20, 21) which were run simultaneously with TGA, were much more sensitive to small differences in weight loss rates. These DTG curves, as well as the TGA curves, were very reproducible. In both air and nitrogen, the DTG curves show $(\text{NH}_4)_2\text{SO}_4$ treatment causes a rate of weight loss peak at about 250°C . In nitrogen, treatments as low as 0.500 percent cause this peak; in air, 1.00-percent treatments have the same effect. The curves for $(\text{NH}_4)_2\text{HPO}_4$ show a much more gradual shift of the peak to lower temperatures, with a peak at 250°C . developing only with high (greater than 10.0 percent) concentrations of chemical. Tables 4, 5, 6, and 7 give data for the rate of weight loss for peaks in the DTG curves and the temperature at which those peaks occur. Although numerical data are useful for comparison purposes, viewing the entire DTG thermograms (pages 18-21) provides a better picture of reaction differences.

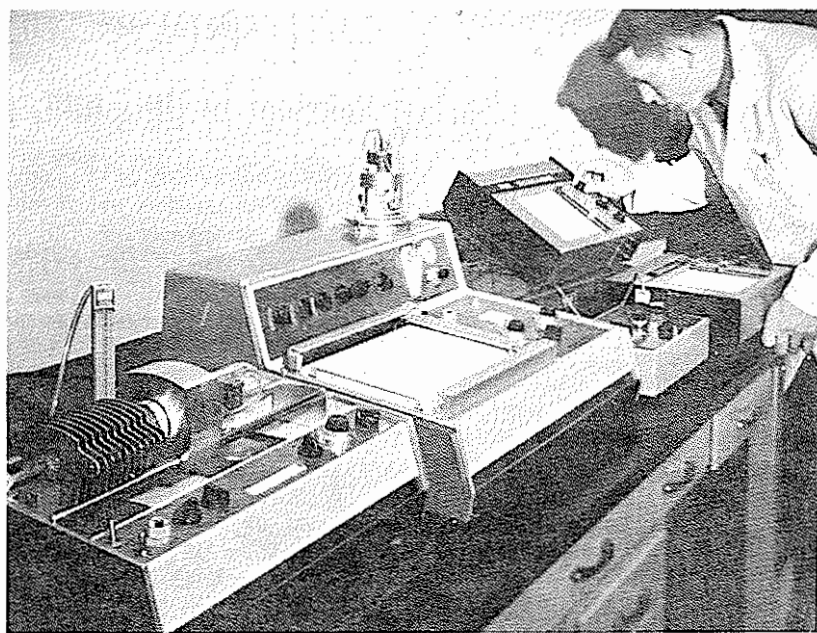
The rate was normalized to correct for decreasing initial cellulose weights with increasing chemical treatment. The normalized rate was determined by:

$$\text{Normalized peak rate (mg. per minute)} = \frac{\text{Actual peak rate (mg. per minute)}}{\text{Fraction of cellulose in sample}}$$



DTG thermograms of cellulose and $(\text{NH}_4)_2\text{SO}_4$ treated cellulose heated at 25°C . per minute in a flow of 100 cc. per minute air.

Figure 1.--Thermal analysis apparatus for obtaining DTA, TGA, and DTG thermograms.



Pyrolysis was studied in a nitrogen atmosphere at a flow rate of 100 cubic centimeters per minute. A similar flow rate of air was used in investigations of combustion. For samples pyrolyzed in nitrogen, the percent of weight remaining as a function of sample temperature was monitored. For combustion analysis, an alternate method of recording data was needed due to the highly exothermic character of the reaction. The oven temperature and sample temperature were monitored for several blank runs using a Moseley Autograf 7100B two-pen strip-chart recorder. After correlating the two readings, the percent of weight remaining as a function of sample environment temperature could be calculated. In this way, decomposition in nitrogen and air could be compared in terms of similar environmental temperatures instead of sample temperatures. Endotherms and exotherms in N_2 had a negligible effect making sample and sample environment temperature essentially equivalent.)

Derivative thermogravimetric analyses (DTG) were obtained simultaneously with TGA by differentiating the mass signal from the DuPont 950 using a Cahn 2030 Time Derivative Computer.⁴ Calibration was accomplished using a constant weight loss rate, provided by a Knudsen diffusion cell containing a 50 μ l sample of 95 percent ethanol. The Knudsen cell was placed in the furnace at 40° C. and TGA-DTG curves recorded. The Moseley two-pen recorder was used to record both the DTG curves and sample or sample environment temperature so a comparison of rate of weight loss and temperature could be made.

The apparatus used for obtaining DTA, TGA, and DTG data is shown in figure 1.

⁴This derivative computer provided a noise-free response that was not significantly different in time to the weight loss response.

APPENDIX

INTRODUCTION

For the past 10 years, ammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ and ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ have been used as primary ingredients in forest fire retardant formulations. These chemicals, when applied to forest fuels, are known to alter or inhibit thermal degradation and combustion reactions. Because of the reduced flammability of chemically treated fuels, the use of such fire retarding chemicals has become an important tool in wildfire suppression. Knowledge of the reactions or mechanisms taking place and their relation to flammability will assist in a systematic selection of fire retardant chemicals and may lead to more effective methods of application.

Recent studies performed at the Northern Forest Fire Laboratory have indicated significant differences in the effects ammonium phosphate and ammonium sulfate have on flammability as measured indirectly by such parameters as rate of spread, fire intensity, radiant energy, flame height, and residue.¹ We do not know whether these differences in effects are due to the chemicals' physical differences, a difference in their thermal decomposition and availability, or to a difference in the actual mechanism by which they alter fuel degradation.

Truax, Harrison, and Baechler (1956) noted that both compounds were effective in retarding flaming combustion, but ammonium phosphate was superior in retarding glowing combustion. Browne and Tang (1963), on the basis of thermogravimetric analyses in a nitrogen atmosphere, found that the compounds have similar effects on the volatilization of wood and the threshold temperature for pyrolysis, although a difference in their volatilization rate was exhibited. Tang (1967) in a similar study found that ammonium phosphate had the same effects as ammonium sulphate on the pyrolysis of wood and cellulose but had little effect on the volatilization rate of lignin; the cellulose portion of wood was found to have the highest volatilization rate. The volatilization rate for wood seemed to be a combination of the effects on alpha-cellulose and lignin. Tang and Eickner (1968), using differential thermal analysis, compared the effects of 2-percent by weight ammonium sulfate and a 2-percent by weight ammonium phosphate treatment on pyrolysis and combustion of wood, cellulose, and lignin. Little difference was noted in thermograms and relative maximum heat intensities and it was concluded that these parallel results probably were produced by a similar mechanism.

Past research (Shafizadeh 1968; Kilzer and Broido 1965) has indicated that combustion adds secondary and competitive reactions to initial degradation reactions. It is likely that the occurrence of flaming combustion causes cellulose as well as the retardant chemicals to undergo different reactions and at different rates. Although relationships undoubtedly exist between the pyrolysis and combustion of cellulose and the role retardant chemicals play in altering related reactions, it may not be possible to predict combustion characteristics on the basis of pyrolysis characteristics. Thermal analysis in oxygen, or in an air atmosphere, may or may not accurately represent flaming and glowing combustion.

The purpose of the study was to provide extensive thermal analysis data that could be used to categorize the effects of these retardant chemicals on the pyrolysis and combustion of cellulose.²

¹Charles W. George and Aylmer D. Blakely. Study of the effects of diammonium phosphate and ammonium sulfate on flammability. 1968. (Unpublished report on file at the Northern Forest Fire Laboratory, USDA Forest Serv., Missoula, Montana.)

²For the purpose of this paper, pyrolysis is defined as the degradation of a material in an inert atmosphere or vacuum. Combustion refers to the process taking place when the initial material, as well as its degradation products, are in contact with oxygen or air.

Table 3.--Effect of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on pyrolysis and combustion threshold temperature ($^{\circ}\text{C}.$)¹

Treatment	$(\text{NH}_4)_2\text{HPO}_4$ treated cellulose		$(\text{NH}_4)_2\text{SO}_4$ treated cellulose	
	Pyrolysis (N_2)	Combustion (air)	Pyrolysis (N_2)	Combustion (air)
Untreated cellulose	290	298	290	298
Treated cellulose ²				
0.0500	286	294	257	280
.100	274	285	239	250
.200	264	272	234	242
.300	255	266	230	239
.400	253	262	231	231
.500	250	254	229	229
.700	243	252	228	231
1.00	234	249	224	230
1.50	230	241	229	225
2.00	216	237	213	228
3.00	212	221	210	221
4.00	209	213	202	217
5.00	207	210	201	213
6.00	199	209	200	212
8.00	196	208	199	211
10.0	189	206	196	208
12.0	190	202	195	210
15.0	187	200	194	208
20.0	190	199	195	205
25.0	186	193	190	203

¹ The threshold temperature is arbitrarily denoted as the temperature required to produce a weight loss rate of 0.09 milligrams per minute (< 1 percent of the maximum weight loss rate).

² Percent by weight chemical.

Table 4.--TGA-DTG thermal behavior of cellulose and $(\text{NH}_4)_2\text{HPO}_4$ treated cellulose in nitrogen

Treatment	Residue	Normalized	Peak rate	Normalized peak	Peak
	at 450 $^{\circ}$ C.	cellulose residue at 450 $^{\circ}$ C.	of weight loss	rate of weight loss	temperature
	Percent	Percent	Mg./min.	Mg./min.	$^{\circ}\text{C}.$
Untreated cellulose	7.6	7.6	5.13	5.13	367
Treated cellulose ¹					
0.0500	12.2	12.2	5.50	5.50	348
.100	15.0	14.9	5.00	5.00	340
.200	19.6	19.5	4.48	4.49	334
.300	22.2	22.1	4.38	4.39	329
.400	24.4	24.3	4.26	4.28	328
.500	25.8	25.6	4.20	4.22	326
.700	28.6	28.4	4.05	4.08	321
1.00	30.2	29.9	3.96	4.00	316
1.50	34.4	34.0	3.52	3.57	311
2.00	35.8	35.2	3.43	3.50	306
3.00	39.4	38.4	2.90	3.02	298
6.00	42.8	41.4	2.52	2.68	281
10.0	45.2	43.2	2.19	2.43	264
12.0	46.0	43.6	2.33	2.65	261
15.0	47.4	44.6	3.05	3.59	259
20.0	48.4	44.8	3.23	4.04	253
25.0	49.2	44.5	3.66	4.88	250

¹Percent by weight chemical.

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(con. next page)

Table 7.--TGA-DTG thermal behavior of cellulose and $(NH_4)_2SO_4$ treated cellulose in air

Treatment	Residue at 450° C.	Cellulose residue at 450° C.	Low temperature peak			High temperature peak		
			Rate of weight loss	Normalized rate of weight loss	Peak temperature	Rate of weight loss	Normalized rate of weight loss	Peak temperature
	Percent	Percent	Mg./min.	Mg./min.	°C.	Mg./min.	Mg./min.	°C.
Untreated cellulose	7.7	7.7	--	--	--	8.41	8.41	349
Treated cellulose ¹								
0.0500	10.4	10.4	--	--	--	6.29	6.29	344
.100	13.2	13.2	--	--	--	5.00	5.01	332
.200	13.8	13.8	--	--	--	4.56	4.57	332
.300	14.3	14.3	0.46	0.46	255	4.11	4.12	330
.400	15.0	15.1	.60	.60	251	4.01	4.03	326
.500	16.0	16.1	.71	.72	252	3.71	3.73	325
.700	18.3	18.4	1.02	1.03	257	2.93	2.95	330
1.00	18.8	19.0	1.12	1.13	255	2.90	2.93	327
1.50	19.6	19.9	1.43	1.45	253	2.72	2.76	324
2.00	22.6	23.1	2.13	2.17	256	1.75	1.78	318
3.00	24.1	24.7	2.69	2.77	251	1.37	1.41	311
4.00	24.8	25.7	3.22	3.35	251	1.90	1.98	306
5.00	25.2	26.4	3.38	3.56	255	1.66	1.75	310
8.00	26.9	29.0	3.45	3.75	256	1.75	1.90	309
10.0	27.0	29.8	4.13	4.57	255	.96	1.06	308
12.0	26.4	29.7	3.69	4.19	257	2.11	2.39	307
15.0	26.3	30.6	3.50	4.12	257	1.48	1.74	312
20.0	25.7	31.6	2.88	3.60	255	--	--	--
25.0	25.8	33.7	3.00	4.00	257	--	--	--

¹Percent by weight chemical.

Headquarters for the Intermountain Forest and Range Experiment Station are in Ogden, Utah. Field Research Work Units are maintained in:

Boise, Idaho

Bozeman, Montana (in cooperation with Montana State University)

Logan, Utah (in cooperation with Utah State University)

Missoula, Montana (in cooperation with University of Montana)

Moscow, Idaho (in cooperation with the University of Idaho)

Provo, Utah (in cooperation with Brigham Young University)