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August 1971

THE EFFECT OF FLAME RETARDANTS  
ON THERMAL DEGRADATION  
OF  $\alpha$ -CELLULOSE IN NITROGEN

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	ROLE	WT	ROLE	WT	ROLE	WT
Cellulose pyrolysis Inorganic additives Filter paper Isothermal-kinetic measurements gc/ms analyses Acidic-salt treatment Untreated and retardant-treated levoglucosan Untreated and retardant-treated cellulose Parker-Lipska model Acidic additives Pyrolytic unzipping						

The additives increase the amount of char and water and eliminate the lower organics. These findings, together with those on pyrolysis of levoglucosan, support the contention that the excess yield of char in retardant-treated cellulose results from degradation of these products of cellulose decomposition rather than of the cellulose molecule itself.

The current study reveals inadequacies in the Parker-Lipska model. Acidic additives cause the rates of pyrolysis to differ greatly from predicted values. This difference suggests that long cellulosic chains are hydrolyzed in the presence of acidic additives to shorter ones, thereby enhancing pyrolytic unzipping. Evidence for such a mechanism is inconclusive, but its plausibility is demonstrated. Modifications of the mathematical expression used to calculate the increase in rate of degradation of cellulose treated with additive entails estimating hydronium-ion concentrations in the cellulose during its pyrolysis, which, unfortunately, cannot be done in a rigorous theoretical way.

Extensive char data acquired during the present study are only weakly correlated with the negative-valence parachor of the Parker-Lipska model. No alternative predictor of char yields is offered because none has evolved to date. Correlation of char yield with additive concentration reveals that optimal values of retardant add-on are about  $2 \times 10^{-4}$  mols of additive/g of cellulose, corresponding to about 30 glucosan units per molecule of additive. The ratio  $\Delta C/\Delta R$ , representing the increase in char produced by a given additive relative to the corresponding increase in rate of decomposition, is proposed as an interim figure of merit for predicting retardant performance. Salts of strong bases and such weak-acid anions as  $\text{HCO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{B}_2\text{O}_4^-$  exhibit large values of this ratio. Identification of still better candidates must await an improved theory for char enhancement.

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*By:* ANNE E. LIPSKA and STANLEY B. MARTIN

*Prepared for:*

DEPARTMENT OF THE ARMY  
OFFICE OF THE SECRETARY OF THE ARMY  
OFFICE OF CIVIL DEFENSE  
WASHINGTON, D.C. 20310

Attention: STEPHEN W. BIRMINGHAM

CONTRACT DAHC20-70-C-0219  
OCD Work Unit 2531C

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This report has been reviewed in the Office of Civil Defense and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Office of Civil Defense.

*Approved by:*

NEVIN K. HIESTER, *Director*  
*Materials Laboratory*

CHARLES J. COOK, *Executive Director*  
*Physical Sciences Division*

## SUMMARY

### The Problem

Cellulose is a major constituent of the bulk of combustible materials available as fuel in destructive fires. For more effective prediction, control, and prevention of urban fires, it is necessary to learn more about the rate and mode of decomposition of cellulosic materials. Additionally, to develop more effective flame retardants, it is important to understand how these retardants interact with the decomposition process in cellulose to reduce its flammability. The present study seeks to develop a self-consistent model of the decomposition of cellulose and the effect of flame-retardant treatments. It reviews current theories of cellulose decomposition, including the Parker-Lipska model, ~~previously developed by one of the authors.~~ New data are presented and used to test the capability of the current theoretical models to predict the pyrolytic behavior of cellulose.

### The Findings

A significant finding of <sup>the</sup> ~~this~~ research is that the specially purified cellulose, a commercial filter paper, used in contemporary studies in other laboratories behaves in isothermal pyrolysis in a manner similar to that of acid-salt-treated alpha cellulose used in <sup>the author's</sup> ~~this~~ laboratory. This finding suggests that the specially purified material, known to have been treated with strong acids in the purification process, is substantially degraded by the purification process in a manner resembling the degradation induced by the addition of acids or salts of weak bases to alpha cellulose. With this in mind, it is reasonable to attribute at least part of the differences in mechanisms of decomposition of cellulose

to varying procedures used in the preparation of the material as well as to their residual mineral content. Molecular weight determinations of the acid-purified filter paper offer further evidence of the validity of this explanation.

The second highly significant finding of the current experimental work deals with the important effect of low concentrations of oxygen on the rate of decomposition of cellulose. Comparative measurements of rates of decomposition of thick and thin samples indicate no effect of sample thickness if oxygen is carefully excluded. On the other hand, surface adsorption of low concentrations of oxygen appears to increase the rate of decomposition in the initial phase of pyrolysis of the thin (0.0043-in.) samples by a factor of three, whereas no appreciable effect was noted in the case of thick (0.030-in.) samples. The results (1) suggest that the previously observed initial rapid decomposition phase is caused, at least in part, by effects of surface-absorbed oxygen and (2) indicate that there is no appreciable surface effect resulting from interaction between the particles of the fluidized bed and the surface of the cellulose, thereby proving the effectiveness of the fluidized-bed technique for isothermal-kinetic studies.

The experimental results further indicate that the overall pattern for the weight and monomer loss of neutral-salt-treated cellulose is similar to that of untreated samples, but with the rates of weight and monomer loss being, respectively, 25.8 and 25.2 times faster than the untreated samples. Observed rates of weight loss agree well with values predicted by the Parker-Lipska model.<sup>1</sup> Molecular-weight measurements of the neutral-salt-treated cellulose combined with the corresponding data on monomer loss suggest that the dominant reaction that governs the decomposition is simultaneous unzipping of the majority of the molecules.

Rates of weight loss for the acidic-salt-treated samples are often

orders of magnitude faster than those of untreated samples; for example, the whole degradation process is finished after 1 minute at a temperature of 276°C in cellulose containing small amounts of ammonium sulfate. In contrast to untreated cellulose, weight loss is not linear with time over most of the duration of active pyrolysis, similar to the case for acid-purified cellulose. Monomer loss is also changed, asymptotically approaching a limiting value rather than suffering depletion in value with the length of pyrolysis as with neutral and basic retardants. Molecular-weight measurements of the acid-salt-treated cellulose show a rapid decrease in the degree of polymerization at the beginning of pyrolysis, asymptotically approaching a  $\overline{DP}$  value of 10 with subsequent heating. This suggests that acidic salts increase the rate of degradation through hydronium-ion-catalyzed hydrolysis. This hydrolytic effect seems to be the primary reason for the failure of the Parker-Lipska model to predict effectively the rates of weight loss of cellulose treated with acid retardants.

The pattern for the rates of weight and monomer loss of basic-salt-treated cellulose is similar to that of the untreated cellulose, but with rates of weight and monomer loss being 19 and 50.05 times faster, respectively, than for the untreated samples. Results of the molecular weight measurements show a rapid drop in the average degree of polymerization after the initial heating, and, just as in KBr-treated samples, a slow progressive decrease in the length of the molecules on subsequent heating.

Degradation products from acid-, neutral-, and basic-salt-treated cellulose were analyzed with the gc/ms combination instrument and with an infrared spectrometer. Results indicated that the basic salt treatments eliminate the production of levoglucosan, whereas neutral and acidic salt additions decrease the amount of levoglucosan but do not eliminate it entirely. Acidic treatment significantly increases the amount of the furanose derivative, previously identified,<sup>1</sup> while decreasing the number

of degradation products. The neutral retardant increases the amount of water, furfural, 5-methyl-2-furfural, 5-hydroxymethylfurfural, and the furanose derivative and either eliminates or decreases all others. The basic retardant increases the amount of water, the furanose derivative, and both unsubstituted and substituted phenols.

These treatments also affect the carbon monoxide-carbon dioxide ratio. Its value of 1.14 in basic, 0.16 in neutral, and 0.33 in untreated samples has been reported by other researchers.<sup>2</sup> For a related acidic salt, the carbon monoxide-carbon dioxide ratio is 0.42.

The degradation products of pure levoglucosan are similar to those of untreated cellulose. Addition of a basic salt increases the total number of gc peaks as well as the amount of the furanose derivative. Acidic additives increase the amount of furanose derivative even more than basic ones and are most successful in decreasing the number of degradation products.

The furanose derivative degrades primarily into oxides of carbon, water, and char. Both basic and acidic additives increase the amount of water and char, which confirms SRI's earlier data. These findings, combined with those of the effects of additives on cellulose and levoglucosan, support the contention that the observed degradation products result from decomposition of these intermediate pyrolysis products of cellulose, and that the additional char from the retardant-treated cellulose is produced by the degradation of these products of cellulose decomposition rather than of the cellulose molecule itself.

Although the Parker-Lipska model represents a significant contribution to the state of the art, it has significant shortcomings that preclude its use for the prediction of ultimate improvement in fire and ignition retardance for cellulose. The most notable failing is its inability to predict char yields from readily characterizable properties

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of retardant molecules. However, it does provide some general guidance  
toward prescribing optimal retardance treatment. <sup>It was concluded that.</sup> Until further major  
advances are made in analytical models of cellulose pyrolysis, the Parker-  
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Appreciation is extended to David Fields for the glucose determinations in the pyrolyzed cellulose samples.

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Results are presented of a study of cellulose pyrolysis and the flame-retardant action of simple inorganic additives. The purpose of the study was to seek fundamental knowledge about chemical processes rather than to develop practical retardants. At the same time, it endeavored to provide guidance for prescribing the properties of materials in the formulation of improved fire retardants of practical value.

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## ADMINISTRATIVE INFORMATION

The purpose of this task order is to conclude the research conducted under Work Unit No. 2531C of Contract DAHC20-70-C-0219 at Stanford Research Institute since the closing of the Naval Radiological Defense Laboratory in 1969. The objective and scope of work as given in the pertinent research task order attached to that contract are as follows:

"OBJECTIVE: To increase the understanding of the fundamental aspects of fire while providing an improved data base for use in applied research.

"SCOPE OF WORK: An investigation should be continued into the basic physical and chemical mechanisms of suppression by solid, liquid, and gaseous suppressants of fires in wood, fabrics, and other critical urban fuels. The work will seek to describe the relevant processes in quantitative terms and will continue to depend heavily on laboratory measurements of changes in chemical and physical properties during exposure of cellulosic materials to external conditions representative of thermal and fire environments."

Based on the task order quoted above, a Work Plan, dated 1 August 1970, was prepared, containing a list of milestones and an anticipated schedule for completion of these. This Work Plan was approved by cognizant representatives of the Office of Civil Defense.

With the publication and distribution of this report, all contractual requirements have been satisfied. In every respect, the objectives and scope of the contracted work, as further detailed in the approved Work Plan, have been successfully accomplished and completed on schedule.

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## I INTRODUCTION

It has been known for some time that the nature of the pyrolysis reaction in cellulosic materials can be altered by different treatment and that this alteration in the pyrolysis process affects the flammability of the material. In relatively recent times, it has also been demonstrated that the susceptibility to ignition is similarly reduced or affected by such treatment. These facts carry considerable potential in relation to the development of countermeasures to thermal radiation and fire effects of nuclear detonations. In spite of their importance, the responsible chemical mechanisms have not been clearly delineated, as they should be to provide a basis for further advances in passive defenses against the incendiary hazards of nuclear attack.

### A. Theoretical Background

A number of highly qualitative theories, based to a large extent on experimental data acquired at low temperatures or low rates of heating, have been advanced to explain the action of a given treatment, or at most a limited class of retardant compounds, but these theories are inadequate to provide a systematic approach to improve retardant performance. Their limitation is principally their inability to provide a quantitative basis for predicting the result of any treatment that has not already been tried. These theories are generally based on the observations that (1) when cellulose is heated slowly, (2) when it has a significant natural mineral content, or (3) when it has been treated with flame retardants, a large fraction of its original weight remains as carbonaceous char following the evolution of highly oxygenated products such as water and carbon dioxide as contrasted with situations of rapid heating, particularly of mineral-free or additive-free cellulose, which leaves less char, and, as

a consequence, produces more flammable, more carbon-rich volatile products.

Some investigators postulate the existence of two competitive mechanisms of cellulose decomposition at temperatures of about 250<sup>o</sup>C and above. As a basis for explaining the action of retardant additives, they further postulate that one of these reactions is catalyzed by the additive. On the basis of experimental evidence, one of these reactions is thought to be depolymerization to levoglucosan (that is, 1,6-anhydro- $\beta$ -D-glucopyranose) while the other is broadly described as char formation. These postulates are supported by the large yields of levoglucosan that have been recovered from high temperature pyrolysis of purified cellulose in vacuo and conversely by the large char yields and poor yields of levoglucosan formed at low temperatures, or at high temperatures in mineral-treated cellulose. This evidence cannot be regarded as a proof of the competitive-mechanism hypothesis, nor is it all the evidence that can be given in its support. A comprehensive review of the relevant information to 1968 is given by Shafizadeh.<sup>3</sup>

The study of ignition of cellulose and its associated pyrolysis that was pursued for many years at the Naval Radiological Defense Laboratory not only accomplished a successful correlation of radiant ignition behavior, but also contributed substantially to the technology of cellulose pyrolysis. This work included measurement of decomposition rates and products, initially under the transient heating conditions approximating those of exposure to nuclear detonations and, more recently, isothermal conditions in the temperature range of 250 to 350<sup>o</sup>C. The results of the transient heating experiments have been summarized by Martin.<sup>4</sup> The results of the isothermal work have been described and interpreted by Parker and Lipska.<sup>5</sup>

Isothermal measurements can provide important clues about the nature of the pyrolysis process. The isothermal heating technique developed at

NRDL and now used at SRI is unique in its ability to achieve isothermal conditions. Results of previous attempts at isothermal pyrolysis have often been clouded by the inability to achieve isothermal conditions in a very short time, but also by small temperature variations following heat-up, by sample impurity, or by traces of oxygen in the inerting atmosphere. All of these factors can have a large effect on the outcome. At temperatures approaching 300°C where the decomposition is rapid, substantial decomposition will occur with conventional methods of heating before the isothermal condition is achieved. This can cause changes in the cellulose that will modify, or even preclude, subsequent reactions. Moreover, the original isothermal data obtained at NRDL clearly indicated an initial rapid reaction, which kinetic measurements using conventional heating methods would miss. If this early-time reaction is important to the interpretation of the rest of the experimental evidence, the lost information might be critical. The importance of the other factors, notably impurities in cellulose, is well established.

On the basis of their own isothermal data, supplemented with data acquired from a comprehensive search of the literature, Parker and Lipska<sup>1</sup> proposed a model of high temperature cellulose pyrolysis that appears to be capable of quantitatively accounting for the bulk of the relevant data, including data on the effects of impurities and additives. The model is a remarkably simple one in its essentials and does not purport to describe the chemical mechanisms in detail. The basic hypothesis is that, in the range of temperature above 275°C, cellulose decomposes through the simultaneous unzipping (that is, progressive depolymerization of glucosan monomers along the molecule) of all cellulose molecules, thus accounting for the constant rate of decomposition that is consistent with a zero-order process. The initial rapid reaction is postulated to entail breaking of the original cellulose molecules at weak links (possibly at amorphous sites) into shorter cellulose molecules with a degree of polymerization of about 500.

Subsequently, the monomeric fragments are assumed either to convert to levoglucosan or to agglomerate and condense to form char. The principal feature of this model is that there is only one controlling reaction, namely the unzipping, as opposed to the independently proposed scheme of competing reactions.

There are now data that contradict the Parker-Lipska model. To a large extent, these results have been acquired using specially purified acid-treated and hardened paper (Whatman Filter Paper), and are dominated by data acquired by nonisothermal procedures or, when acceptably isothermal, at temperatures below 275<sup>o</sup>C. A distinctive feature of these results is their better fit to first-order than to zero-order kinetics. These contradictory data are interpreted as evidence that the reactions entail a competition between unzipping to the monomer, on the one hand, and intramolecular dehydration, which ultimately leads to the production of char, on the other. The specific arguments of these investigators and the supporting data are reported in References 7, 8, and 9.

Recent experimental measurements, including the research reported here, have turned up some significant inconsistencies and inadequacies in the Parker-Lipska model. For example, the model does not anticipate the extremely rapid rates of decomposition observed with certain additives. Additionally, the negative-valence parachor may be criticized as being contrived, and, as more additives are tested, the contrivances needed to obtain agreement between measured and predicted effects have rendered the concept progressively less credible. It is time to critically examine and revise the Parker-Lipska model, or, if necessary, to replace it.

#### B. Objectives and Approach of the Current Research

In quite general terms, the objectives of the research reported here were to test the validity of the Parker-Lipska model by further experimental investigation of certain key elements treated by the model and to

propose changes in the model wherever such modification appears to be needed. More specifically, the following objectives are enumerated as a formal statement of the goals of the current research and as a background rationale for the approach taken. The specific objectives were:

1. To investigate possible causes of conflicting data concerning the pyrolysis of cellulose
2. To verify the utility and efficacy of the fluidized-bed technique as a factor of critical importance to the validity of results of OCD-supported research on cellulose pyrolysis
3. To further explore the nature and importance of the initial rapid-decomposition phase of cellulose pyrolysis
4. To expand the variety of types of additives chosen for study of additive influence on cellulose pyrolysis, seeking a critical test of the Parker-Lipska model's capability to predict additive effects and additional insight into the mechanisms of such effects
5. To further investigate the importance of molecular oxygen on the mechanisms and kinetics of cellulose pyrolysis
6. To elucidate further the basic causes of fire retardance imparted by various additives and substituents as well as the role in thermal degradation of cellulose of such reaction products as levoglucosan and the furanose derivative previously isolated and identified by one of the present authors.

To accomplish these objectives, the following experimental approach was taken:

1. Conflicting data concerning cellulose pyrolysis may be due to (1) differences in experimental conditions or (2) differences in the sources and pretreatment of specimens. Pertinent to the latter, a substantial portion of the data recently generated in other laboratories has been acquired with an acid-treated cellulose (Whatman Filter Paper) whose origins and method of preparation and purification may be sufficiently different

from the  $\alpha$ -cellulose used in this OCD-sponsored research to account for some, if not all, of the differences in behavior. Accordingly, we have conducted a direct experimental comparison of the pyrolysis of the two celluloses.

2. Another explanation for the differences deals with the totally dissimilar methods of heating used by different investigators. Of central importance to the OCD program is the fluidized-bed technique employed for many years as a means of achieving isothermal conditions. Although at the time the technique was first introduced its efficacy as a medium for isothermal pyrolysis of cellulose was demonstrated convincingly, recurrent doubts have persisted about the rigorous absence of catalytic effects of the sand particles, analogous to the effects of inorganic additives. Since such effects would be limited to the surface of the specimens and would, therefore, be proportionately increased in thin specimens, a careful comparison of the rates of degradation of thick and thin samples was undertaken as a final, unequivocal demonstration of the existence and magnitude, or the absence, of this effect.
3. The foregoing comparisons of thick and thin samples also offer an opportunity to further evaluate the rapid initial phase of pyrolysis because evidence of its dependence on specimen thickness, and therefore its existence as a possible consequence of surface effects, should be revealed by these experiments if such effects are large.
4. In an attempt to find clear, unambiguous evidence of failure of the Parker-Lipska prediction capability, and thereby to point up needed modifications in the theory on which the model is based, a wide variety of inorganic compounds was added to the cellulose in small amounts, and the resulting specimens were pyrolyzed to ascertain effects on rates of decomposition, production of char, reduction in degree of polymerization of pyrolyzed cellulose, and the distribution of the evolved products of pyrolysis. Earlier studies had suggested that "acidic" additives, notably the salts of weak bases, were responsible for unexpectedly large rates of pyrolysis which might result from hydrolysis either preceding or accompanying pyrolysis. For this reason, many of the salts used here were chosen because of their known hydrolytic

reactions,\* and even an inorganic acid,  $H_3PO_4$ , was used as an additive in anticipation of dramatic increases in pyrolytic rates. In a similar vein, phosphotungstic acid was chosen, not because it is an acid, but because of its very large content of oxygen atoms per molecule, which, according to the Parker-Lipska model, should exhibit unusually large char yields in cellulose to which it has been added. Additionally, consideration was given in the choice of inorganic compounds to their demonstrated effectiveness (or lack thereof) as a flame retardant. A complete list of additives used includes:  $NH_4H_2PO_4$ ,  $H_3PO_4$ ,  $KBr$ ,  $KHCO_3$ ,  $Na_2B_4O_7$ ,  $K_2CO_3$ ,  $NaH_2PO_4$ ,  $NH_4C_2H_3O_2$ ,  $20WO_3 \cdot 2H_3PO_4 \cdot 25H_2O$ ,  $ZnSO_4 \cdot 7H_2O$ ,  $(NH_4)_2SO_4$ , and  $MgSO_4 \cdot 7H_2O$ .

5. Although it had been intended to formally investigate the effects of oxygen on pyrolysis, an inadvertent discovery in the course of the experimental work provided the missing information and an unexpected revelation. Accordingly, no additional effort was expended along this avenue of inquiry.
6. In search of further mechanistic insight into the chemical reactions of pyrolysis and the perturbing effects underlying fire retardance, detailed analyses were conducted of the pyrolytic effluent from levoglucosan and from the furanose derivative, both of them as purified reagents on the one hand, and admixed with different salts on the other. These analyses are ultimately expected to offer clues about whether levoglucosan and the furanose derivative are important intermediates in the chemical sequence or are simply products subject to secondary decomposition.

The report that follows describes these experimental procedures and measurements, their results, and the conclusions drawn from them.

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\* Unfortunately, the choices typically led to ambiguous situations due to instability at elevated temperatures. The ammonium salts are good cases in point. Only  $ZnSO_4$ , chosen near the end of the project term, was sufficiently stable and had adequately known hydrolytic properties to be used with some degree of confidence in evaluating the perturbation due to hydrolysis.

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## II EXPERIMENTAL PROCEDURE

### A. Comparative Measurements of Rates of Decomposition of Whatman Filter Paper and $\alpha$ -Cellulose

The isothermal-pyrolysis chamber (a nitrogen-fluidized sand bed) used in the kinetics studies has been described in an earlier publication.<sup>10</sup>

White  $\alpha$ -cellulose sheets 0.004 in. thick and Whatman 541 Filter Paper 0.005 in. thick were cut into disks (2.0 cm in diameter). The samples were then evacuated for 30 minutes, dried to a constant weight in nitrogen in the presence of phosphorus pentoxide transferred in a covered tared weighing bottle to the loading chamber, and then inserted into the reaction chamber.

It is within the present capability of the equipment to lower the oxygen content in the loading chamber to  $< 10\%$  by displacing much of the air in the chamber with liquid nitrogen boil-off. In most of the experiments reported here, this was done to reduce the amount of oxygen available to be absorbed on the surface of the samples during the transfer process.

The samples were all pyrolyzed at  $315^{\circ}\text{C}$ . This temperature was chosen because at higher temperatures the rate of degradation is too rapid for detailed kinetic studies and because of temperatures significantly less than  $276^{\circ}\text{C}$ , the kinetic behavior is not representative of high temperature pyrolysis. At the end of each run, the sample residue was removed from the reaction chamber, returned to its weighing bottle, desiccated, and reweighed to obtain the amount of sample converted into volatiles.

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B. Comparative Measurements of Rates of Decomposition of Thick and Thin  $\alpha$ -Cellulose

The comparative rate measurements served a twofold purpose: (1) to validate the effectiveness of the fluidized bed for isothermal kinetic studies and (2) to investigate the effect of oxygen adsorbed on the surface of the sample on the rate of decomposition. To accomplish the first objective, 0.030-in.-thick  $\alpha$ -cellulose samples were pyrolyzed under the same conditions as in the foregoing experiments. The rates of decomposition were compared with those of the 0.004-in.-thick samples. The second objective was achieved by pyrolyzing the thick and thin samples in nitrogen at 315<sup>o</sup>C and leaving the oxygen content in the loading chamber at 20.9%. As in part A, the residues of all the samples were returned to the weighing bottles, desiccated, and weighed to determine the amount of cellulose changed into volatiles. The rates of decomposition of the cellulose contaminated by the surface-adsorbed oxygen were compared with those of the uncontaminated samples.

C. Effect of Basic, Neutral, and Acidic Additives on Thermal Degradation Processes of  $\alpha$ -Cellulose

1. Effect of Additives on the Kinetics of Weight and Monomer Loss

Alpha-cellulose sheets (0.030 in. thick) were soaked for 2.0 seconds in 2% aqueous solutions of KBr,  $K_2CO_3 \cdot 1-1/2 H_2O$ , and  $(NH_4)_2SO_4$ , and then air-dried for five days. The treatment resulted in the following percent add-on weights: 3.03% KBr, 2.93%  $K_2CO_3 \cdot 1-1/2 H_2O$ , and 3.13%  $(NH_4)_2SO_4$ . The sheets were cut into 2.0-cm-wide disks, prepared as in foregoing experiments and pyrolyzed at 276<sup>o</sup>C.

After the weight loss was determined, each pyrolyzed sample was soaked in 25 ml of  $H_2O$  for at least 12 hours to measure the amount of nonvolatile, water-soluble decomposition products, dried to a constant weight, and reweighed. The remaining solid residue was subjected to

Saeman's<sup>11</sup> hydrolysis followed by Mendel's<sup>12</sup> glucose determination. The amount of glucose observed was compared with that obtained from unpyrolyzed cellulose samples to determine the percentage of residual or undecomposed cellulose remaining in the pyrolyzed specimens.

Subsequent to these experiments, additional cellulose samples were treated with  $ZnSO_4$  solution to evaluate hydrolytic effects, using a salt that is stable at the temperatures of cellulose pyrolysis and whose hydrolytic properties (i.e., the dissociation constant for  $ZnOH^+$ ) are known. Disks (2.0 cm wide) were injected with 0.25 ml of 0.1M  $ZnSO_4$  solution with a syringe; the samples were dried and then pyrolyzed at 276°C. Only weight-loss measurements were made in this case.

2. Effect of Additives on Changes in Viscosity Average Molecular Weight with the Length of Heating

Cellulose samples containing either 3.03% (by weight) KBr, 2.93%  $K_2CO_3 \cdot 1-1/2 H_2O$ , or 3.13%  $(NH_4)_2SO_4$  were pyrolyzed at 276°C for various predetermined periods of time, and residual cellulose, estimated as glucosan, was determined as described above. The results were correlated with previously obtained glucosan-loss measurements to determine the actual amount of undecomposed cellulose left in the pyrolyzed sample. Cadoxen [tris (ethylene diamine) cadmium dihydroxide] was chosen as a solvent for the samples since it is known to dissolve high-molecular-weight cellulose ( $Mwt > 10^6$ ) and to cause negligible oxidative degradation of the dissolved polymer. The solvent was prepared according to W. Brown.<sup>13</sup>

1. A 28% by weight aqueous solution of fresh ethylenediamine (redistilled) was cooled to 0°C.
2. With vigorous stirring, 90 g of CdO were slowly added to 910 g of the aqueous mixture. Stirring was continued at 0°C until the mixture was white.

3. The mixture was refrigerated overnight, decanted from the excess CdO, and filtered with a filter aid.
4. To each 625 ml of this solution a refrigerated mixture of the following was added: 39.5 ml ethylenediamine, 101.9 ml H<sub>2</sub>O, and 9.2 g NaOH.
5. The solvent (density = 1.0824 g/cm<sup>3</sup>) was stored in a refrigerator.

To a 5.0-ml volumetric flask 0.125 g of finely divided cellulose sample (the 0.0125 g was the actual amount of cellulose remaining in the residue) and 5.0 ml of Cadoxen were added. The flask with the mixture was first shaken for 15 minutes at room temperature and then kept in a refrigerator for 1 hour at 0°C. The viscosities were then measured at 25 ± 0.05°C in calibrated Cannon-Ubbelohde viscometers. All solutions were filtered at least twice through a medium sintered-glass funnel before measurement.

### 3. Effect of Additives on Increase of Char

Cellulose disks (2.0 cm wide) were saturated with various concentrations of aqueous solutions of a variety of inorganic additives. An aliquot of solution (0.25 ml) was introduced into the sample with a syringe, and the disks were allowed to air-dry to a constant weight. Each sample was sandwiched between two index cards and wrapped with aluminum foil to minimize air oxidation. The index cards protected the samples from possible detrimental effects of direct contact with the aluminum foil. Each treated sample and a control untreated sample were pyrolyzed in a muffle oven at 600°C for 12.0 minutes.

### 4. Effect of Additives on Degradation Products

The pyrolysis products (Mwt < 150) of 3.03% KBr-treated, 2.93% K<sub>2</sub>CO<sub>3</sub> · 1-1/2 H<sub>2</sub>O-treated, and 3.13% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-treated cellulose samples were analyzed with a gas-chromatograph/mass-spectrometer combination instrument. A Beckman G.C.-4 analytical gas chromatograph was linked

with a Bendix G.C./M.S.-interface system to a modified Bendix time-of-flight mass spectrometer.

The treated cellulose sheets were rolled into cylinders and burned in air. The degradation products formed at about 400°C by this process were collected by placing one end of the cylinder in a liquid nitrogen-cooled centrifuge tube and igniting the other. This method allows the volatile pyrolysis products to flow down the center of the cylinder and condense out on the bottom of the centrifuge tube. Aliquots of 10 µl were injected with a syringe onto a 10 ft by 0.25-in.-o.d. stainless-steel column packed with 10% by weight of Carbowax-20M on Chromosorb-T 40-60 mesh. The column was ballistically temperature-programmed from 90 to 220°C.<sup>2</sup> In 40 minutes, the helium flow rate was 60 cc/min, the therm conductivity detector oven was maintained at 225°C, and both the injection port and the interface system were held at 220°C.

The effect of basic, neutral, and acidic treatments on the production of levoglucosan was investigated with a Perkin Elmer Model 221 infrared spectrophotometer. An NaCl window was coated with approximately 0.25 µl of the tarry mixture, and the spectrum was examined for those group frequencies that characterize levoglucosan.

D. Effect of Basic and Acidic Additives on the Pyrolysis Products of Levoglucosan

Levoglucosan, both in the neat form and treated with acidic and basic additives, was thermally degraded in a Packard Curie-Point pyrolyzer, and the resulting products were analyzed with the gc/ms combination instrument. A looped iron-nickel wire with a 480°C Curie-Point temperature was coated with a saturated methanolic solution of levoglucosan. The wire supported approximately 10 µg of levoglucosan when dried. When additives were included, levoglucosan and the salt were first dissolved in methanol, and the wire was then coated with the resulting mixture. The coated wire was placed in the pyrolyzer and pyrolyzed for

10 seconds in a 200°C preheated helium stream. The degradation products were introduced directly onto the Carbowax 20-M on Chromosorb-T 40-60 mesh column and, with the exception of a higher filament current (350 milliamperes), were analyzed under similar conditions to those used for the identification of the degradation products of cellulose.

E. Effect of Basic, Neutral, and Acidic Additives on the Pyrolysis Products of 1,5-Anhydro-2,3-Deoxy-β-D-Pent-2-Eno-Furanose

The furanose derivative was prepared by pyrolyzing fire-retardant-treated cellulose and separating the derivative from the rest of the components by means of preparative gas chromatography. A sample of approximately 17 g of shredded cellulose containing 6%  $\text{NH}_4\text{H}_2\text{PO}_4$  was heated with a Bunsen burner in a 125-ml distillation flask. The pyrolyzate was collected in a 15-ml liquid nitrogen-cooled centrifuge tube. The pyrolysis was continued until the cellulose was completely charred and there was no evidence of further generation of condensable products. The tube was then allowed to warm to room temperature, and a 3.0-ml aliquot was injected with a syringe onto a 7-1/2-ft x 3/4-in. column packed with 10% Carbowax 20-M on 80-100 mesh Chromosorb. With a helium rate of 330 ml/min, the temperature of the column was ballistically programmed from 100 to 200°C. The injection port and the buffer zone were maintained at 250°C, the detector block was held at 230°C, and the temperature of the exit manifold was maintained at 225°C. A thermoconductivity detector operated at 150 milliamperes provided the signal recorded as the chromatogram. A series of glass traps attached to the manifold and submerged in an ice bath was used to collect the compounds contained in the mixture.

The isolated furanose derivative, both in the neat form and when mixed with acidic and basic retardants, was pyrolyzed at 480°C in the Curie-Point pyrolyzer. The degradation products were analyzed with the

gc/ms combination instrument under conditions similar to those used in the levoglucosan study.

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### III RESULTS AND DISCUSSION

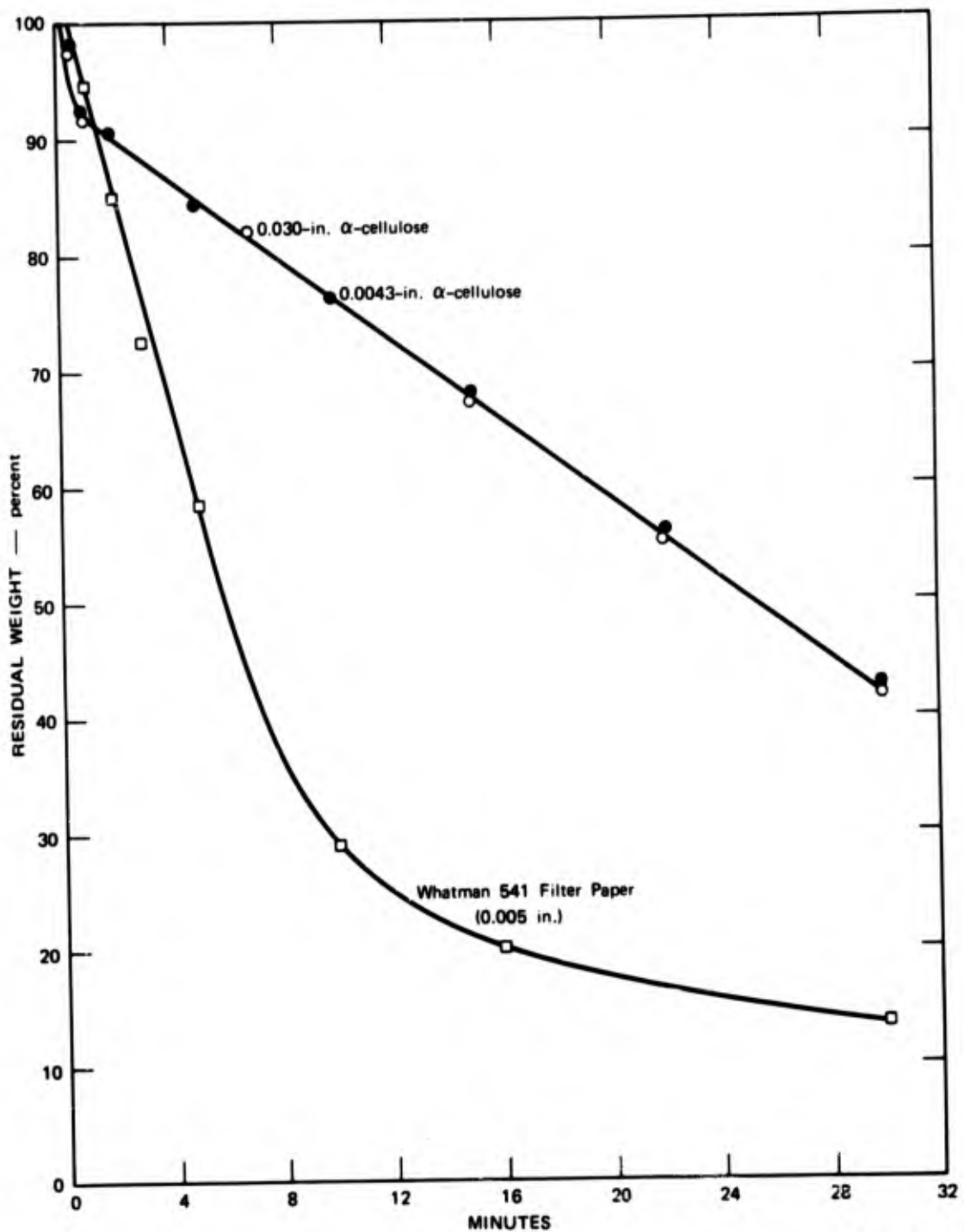
#### A. Comparative Measurements of Rates of Decomposition of Whatman 541 Filter Paper and $\alpha$ -Cellulose

The results of the pyrolysis experiments are summarized in Table 1. Residual weights are expressed as percentages of the original dry samples. Figure 1 compares the remaining weights of Whatman 541 Filter Paper (0.005 in. thick) with  $\alpha$ -cellulose (0.0043 in. and 0.030 in. thick) as function of time. The same weight-loss rates for both thin and thick  $\alpha$ -cellulose samples validate the use of the fluidized bed in the isothermal kinetic studies and negate the possibility that the higher weight-loss rates of the filter paper are simply the result of the different thicknesses of the two materials. Careful examination of the curves show that during the first 10 minutes of pyrolysis, the rate of weight loss of the filter paper is 2.6 times as high as that of the  $\alpha$ -cellulose samples, whereas in the short linear region, the weight-loss rate is 4.2 times as high as that of the cellulose samples. The overall pattern of the weight-loss curve of the Whatman paper resembles that of the acid-salt-treated cellulose (Figure 2) and suggests that the greater part of degradation occurs by a more nearly first-order than zero-order reaction, as reported by other researchers who used Whatman 541 Filter Paper in their studies.<sup>8,9</sup> Since the paper was double-washed in hydrochloric and hydrofluoric acids by the manufacturers, it is not surprising perhaps that such treatment induces changes in the degradation process similar to the acid-salt-treated  $\alpha$ -cellulose. It is therefore reasonable to attribute at least a part of the differences in the mechanism of decomposition of cellulose to the different procedures used in the preparation of the above samples. The authors' molecular-weight determination of the residues of pyrolyzed and acid-treated cellulose further substantiates the validity of this explanation.

Table 1

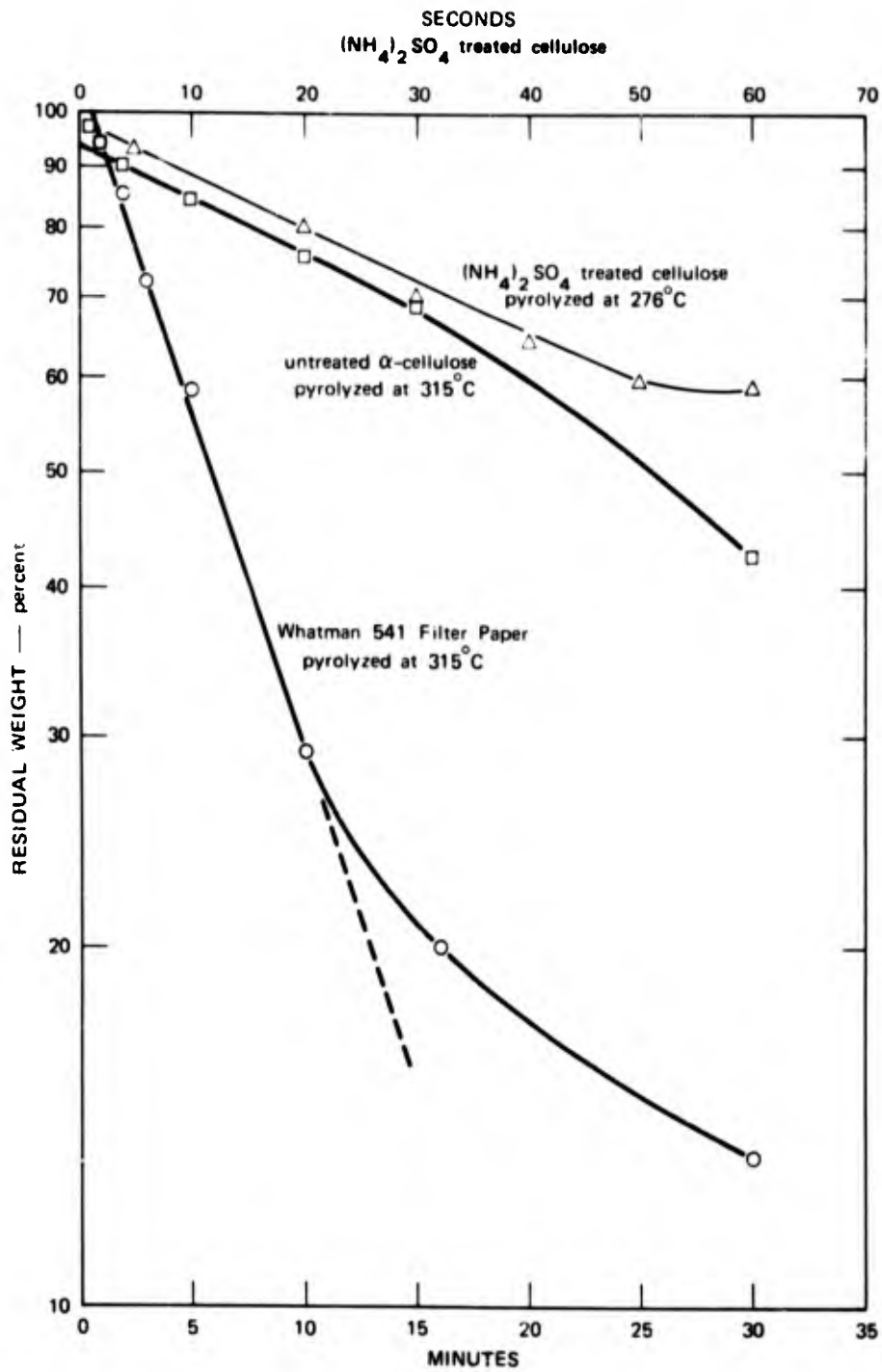
COMPARISON OF WEIGHT LOSS OF  $\alpha$ -CELLULOSE WITH WHATMAN 541 FILTER PAPER  
IN N<sub>2</sub> AT 315°C WITH VARIED O<sub>2</sub> CONCENTRATIONS IN THE HOLDING CHAMBER

SAMPLE DESCRIPTION	DURATION (min)	DRY WEIGHT OF ORIGINAL SAMPLE (g)	RESIDUAL WEIGHT OF PYROLYZED SAMPLE (%)
0.005-in.-thick Whatman Filter Paper  Oxygen content in outer chamber < 10%	1.0	0.0275	94.54
	2.0	0.0285	85.26
	3.0	0.0293	72.01
	5.0	0.0288	58.68
	10.0	0.0261	29.11
	16.0	0.0290	20.00
	30.0	0.0245	13.46
0.0043-in.-thick cellulose  Oxygen content in outer chamber < 10%	0.5	0.0303	97.02
	1.0	0.0303	94.38
	2.0	0.0296	90.87
	5.0	0.0276	84.42
	10.0	0.0324	75.92
	15.0	0.0312	68.91
	30.0	0.0321	42.50
0.030-in.-thick cellulose  Oxygen content in outer chamber < 10%	0.5	0.1825	97.50
	1.0	0.1981	94.97
	7.0	0.1483	82.13
	10.0	0.1676	74.22
	15.0	0.1399	67.69
	22.0	0.1753	56.58
	30.0	0.1811	42.52
0.0043-in.-thick cellulose  Oxygen content in outer chamber > 10%	0.5	0.0311	88.10
	1.0	0.0345	85.21
	3.0	0.0331	80.96
	5.0	0.0326	75.15
	10.0	0.0340	68.8
	16.0	0.0313	58.46
	30.0	0.0312	33.65
0.030-in.-thick cellulose  Oxygen content in outer chamber > 10%	0.5	0.1825	97.58
	2.0	0.1872	92.62
	7.0	0.1850	82.11
	10.5	0.1775	75.77
	15.0	0.1823	67.69
	22.0	0.1753	56.58
	30.0	0.1811	42.40



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FIGURE 1 COMPARISON OF WEIGHT LOSS OF WHATMAN 541 FILTER PAPER AND  $\alpha$ -CELLULOSE IN  $N_2$  AT  $315^\circ C$  WITH  $O_2$  CONTENT IN THE HOLDING CHAMBER OF LESS THAN 10%



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FIGURE 2 COMPARISON OF RESIDUAL WEIGHTS OF WHATMAN 541 FILTER PAPER WITH UNTREATED α-CELLULOSE PYROLYZED AT 315°C AND 3.13% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-TREATED CELLULOSE PYROLYZED AT 276°C

B. Comparative Measurements of Rates of Decomposition of Thick and Thin  $\alpha$ -Cellulose

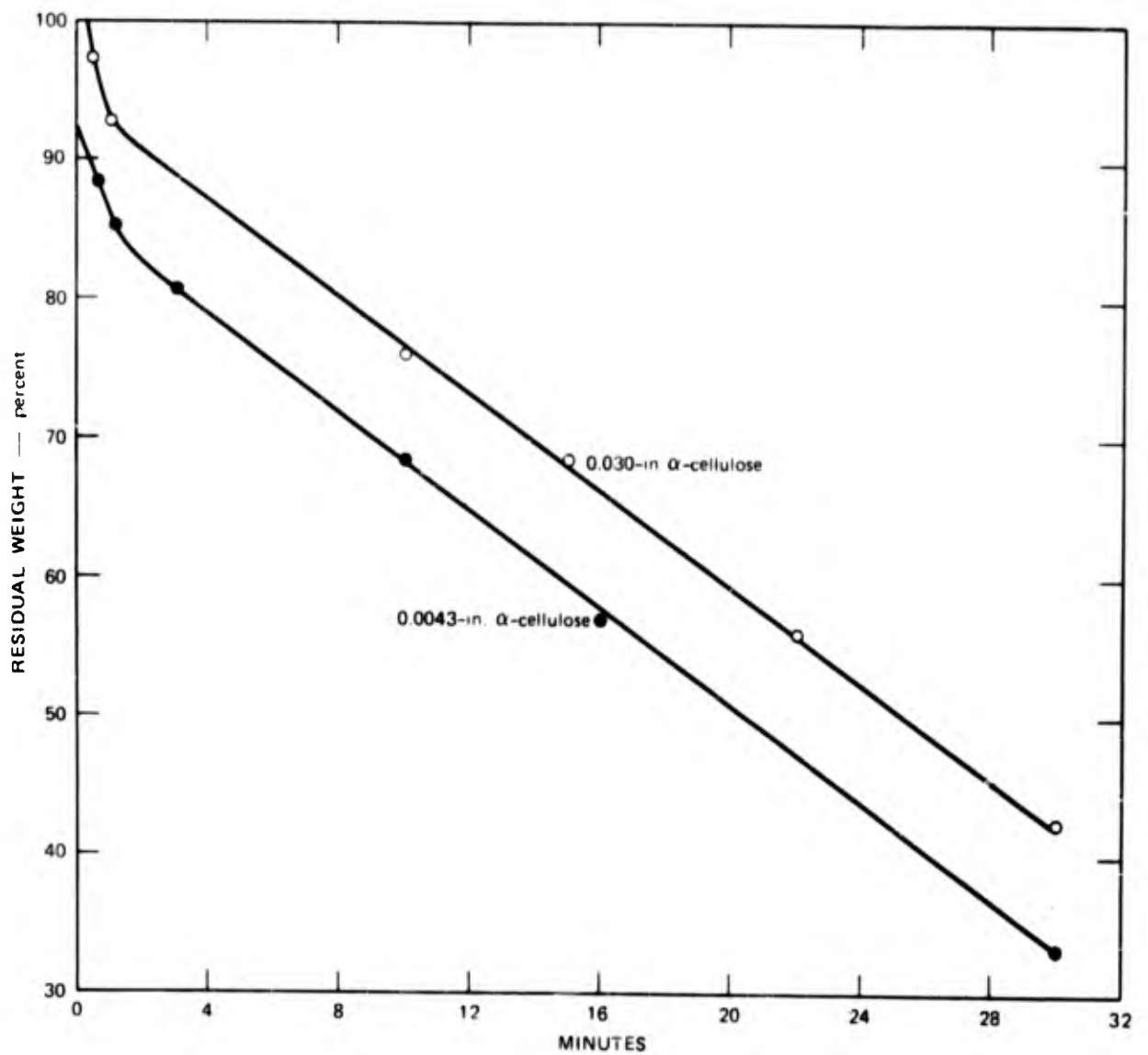
The rates of weight loss of the thin and thick  $\alpha$ -cellulose samples under carefully controlled anaerobic conditions are shown in Figure 1. Results indicate that the sample thickness does not affect the rate of degradation, provided that oxygen is excluded from the environment. This observation further verifies the absence of interfering reactions caused by interaction between the sand particles and the surface of the cellulose samples and thereby validates the efficacy of the fluidized-bed technique for isothermal kinetic studies.

For some time, the authors have recognized the possibility that oxygen adsorbed on the surface of the cellulose samples could be responsible for increasing the rate of decomposition in the initial period of pyrolysis. Such an effect would be especially pronounced in the thin samples where the bulk surface-to-volume ratio is much greater than in the thick samples. The results shown in Figure 3 are consistent with this effect. This finding suggests that the previously reported initial rapid pyrolysis phase resulted, at least partly, from oxidation by surface-adsorbed oxygen. To clarify the nature of this initial rapid weight-loss behavior, the degradation process of cellulose should be investigated directly in the time-of-flight mass spectrometer where effects of atmospheric oxygen can be totally excluded.

C. Effect of Basic, Neutral, and Acidic Additives on Thermal Degradation Processes of Cellulose

1. Effect of Additives on Weight and Monomer Loss

The results of the pyrolysis experiments are summarized in Table 2. The amount of unhydrolyzable material in the treated samples was measured by weighing the dried residue after hydrolysis of the pyrolyzed sample. The unhydrolyzable material for the untreated cellulose was obtained by taking the difference between column 3 and the sum of columns 4 and 5.



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FIGURE 3 COMPARISON OF WEIGHT LOSS OF 0.0043-INCH-THICK  $\alpha$ -CELLULOSE WITH 0.030-INCH-THICK  $\alpha$ -CELLULOSE IN  $N_2$  AT  $315^\circ C$  WITH  $O_2$  CONCENTRATION OF 20.9% IN THE HOLDING CHAMBER

Table 2  
EFFECT OF ADDITIVES ON WEIGHT LOSS AND MONOMER LOSS OF  $\alpha$ -CELLULOSE PYROLYZED IN N<sub>2</sub> AT 276°C\*

SAMPLE DESCRIPTION	DURATION	RESIDUAL WT OF PYROLYZED SAMPLE (%)	WATER SOLUBLE MATERIAL (%)	RESIDUAL CELLULOSE (%)	UNHYDROLYZABLE MATERIAL (%)
0.030-in.-thick cellulose 3.03% KBr-treated	30 sec	98.19	1.43	94.26	2.50
	2.0 min	94.35	2.38	87.46	4.51
	3.5 min	91.25	4.73	80.10	6.42
	5.0 min	85.51	4.01	66.14	15.36
	7.0 min	82.11	4.70	61.5	15.91
	10.0 min	74.87	4.11	46.19	24.57
0.030-in.-thick cellulose 3.3% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> -treated	16.0 min	60.03	2.88	23.87	33.28
	18.0 min	55.85	4.22	21.5	30.13
	20.0 min	47.78	0	13.96	33.82
	25.0 min	37.87	0	2.13	35.74
	5 sec	93.0	3.94	89.50	0
	20 sec	80.02	6.22	47.40	26.40-
0.030-in.-thick cellulose 2.93% K <sub>2</sub> CO <sub>3</sub> .1-1/2 H <sub>2</sub> O- treated	30 sec	69.84	3.38	29.10	37.36
	40 sec	64.3	0.56	15.50-	48.24
	50 sec	59.95	0.42	3.35	51.17
	60 sec	58.54	0	7.00	51.54
	30 sec	96.50	0.70	94.8	0
	2.0 min	85.47	3.25	72.00	10.22
0.030-in.-thick cellulose lose, untreated†	3.5 min	81.74	2.40	55.8	23.54
	6.0 min	75.47	2.24	43.8	29.43
	10.0 min	69.33	2.00	36.50	30.80
	16.0 min	59.51	0.06	28.70	28.75
	25.0 min	54.36	0.41	22.72	31.23
	10 min	96.42	0.86	89.95	5.61§
0.030-in.-thick cellulose 4.0% ZnSO <sub>4</sub> -treated	20 min	95.72	0.44	88.82	6.46
	40 min	92.30	0.71	83.73	7.86
	1 hr	90.14	--	80.00	10.14
	2 hr	85.86	0.54	68.12	17.20
	4 hr	74.17	0.44	55.33	18.40
	8 hr	54.16	--	27.23	26.93
0.030-in.-thick cellulose	13 hr	37.48	--	7.90	29.58
	17 hr	27.16	--	--	27.16
	22 hr	20.82	--	--	20.82
	26 hr	18.90	--	--	18.90
	32 hr	17.58	--	--	17.58
	0.5 min	83.64			
1.0 min	75.03				
2.0 min	56.23				
4.0 min	51.40				
9.5 min	45.02				

\* All percentages refer to the original weight of dry cellulose.

† Lipka, A. E., and W. J. Parker, "Kinetics of the Pyrolysis of Cellulose in the Temperature Range 250-300°C, J. Appl. Polym. Sci. 10, 1439 (1966).

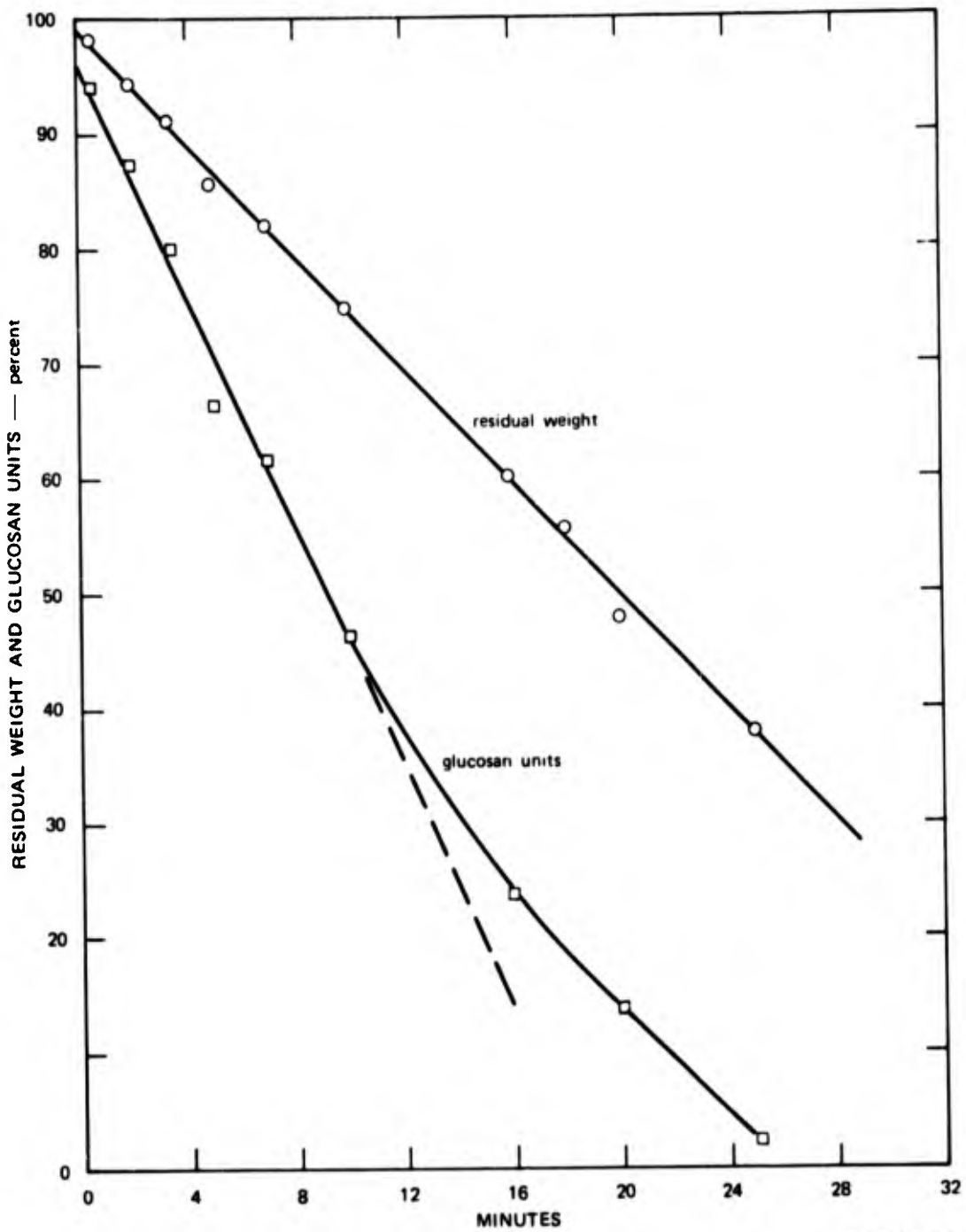
§ The percentage of the unhydrolyzable material for the untreated cellulose was obtained by taking the difference between column 3 and the sum of columns 4 and 5.

The amount of water-soluble material rises to a maximum in all the treated samples when about 20% of the sample has volatilized, then progressively decreases with subsequent heating. The aqueous solutions showed absence of carbohydrates when tested with the Anthrone reagent. No other test was performed at this time. The amount of unhydrolyzable material in all three treatments increases progressively with the length of heating. Furthermore, all three treatments increase the amounts of both water-soluble material and unhydrolyzable material over those obtained from the untreated samples.

Figure 4 shows the residual weight and monomer units of 3.03% KBr-treated cellulose pyrolyzed at 276<sup>o</sup>C. The overall pattern of the treated cellulose is similar to the untreated samples (Figure 5), with the rate of weight loss of the KBr-treated samples being 25.8 times faster than the untreated. The increase in rate predicted by the Parker-Lipska model is 21.5.

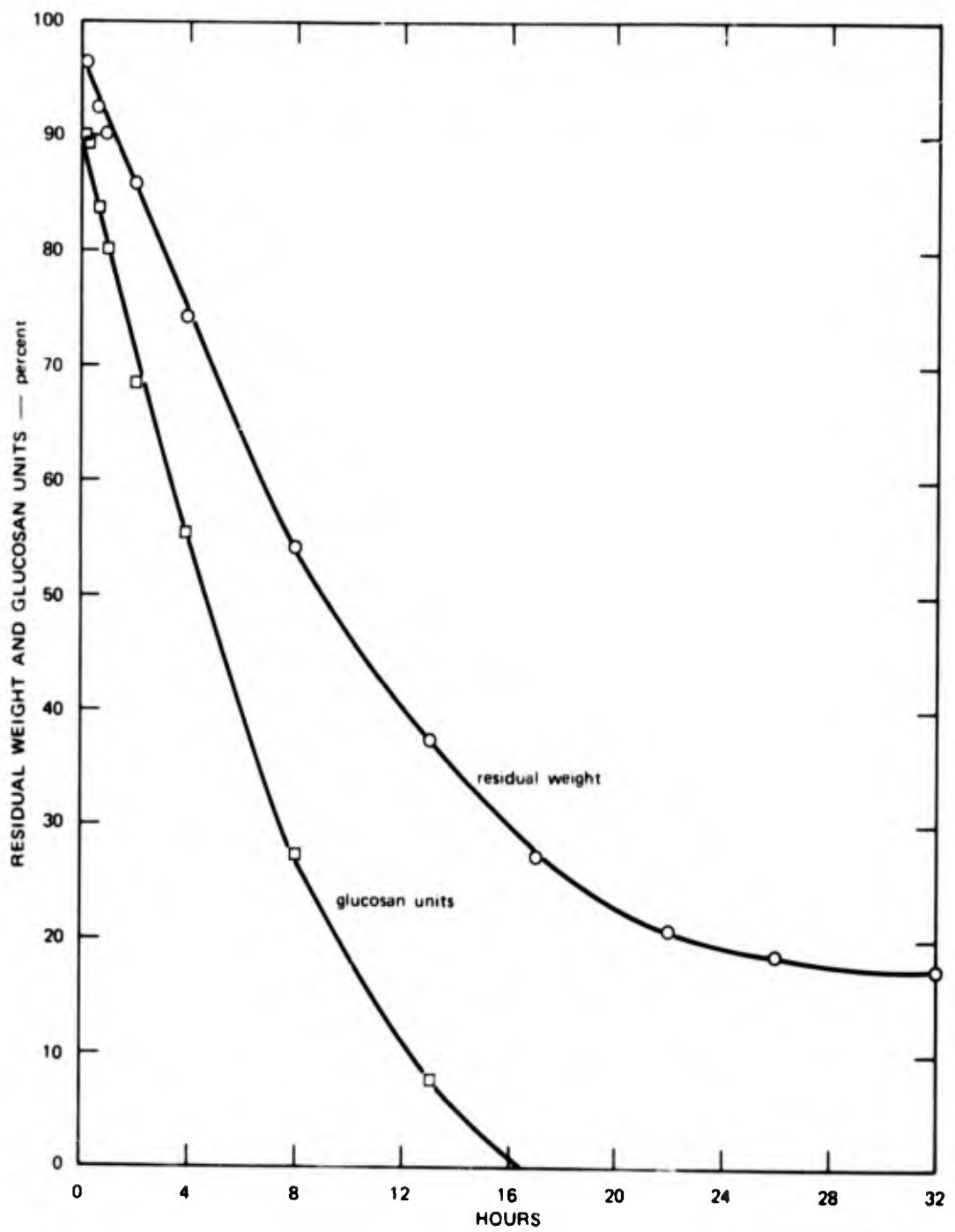
Figure 6 shows the decrease in weight and monomer units with time of 2.93%  $K_2CO_3 \cdot 1-1/2 H_2O$ -treated cellulose. The overall pattern of the curves resembles that of the untreated samples more than that of the acid-treated samples. However, the extent of the linear region in both the weight and monomer-loss curves is considerably shortened, emphasizing the complexity of the entire decomposition process. The observed increased weight-loss rate in the linear region is 19, and the predicted rate increase is 18. It therefore appears that salts of strong bases and weak acids, as well as the neutral salts of strong acids and strong bases, give rates of decomposition that are predictable by the Parker-Lipska model.

Figure 7 depicts the loss in weight and monomer units with time of 3.13%  $(NH_4)_2SO_4$ -treated cellulose. The rate of weight loss is between 2 and 3 orders of magnitude faster than that of untreated samples, the whole degradation process being finished after 1 minute, and nearly 30 times faster than the value predicted by the Parker-Lipska model. Moreover,



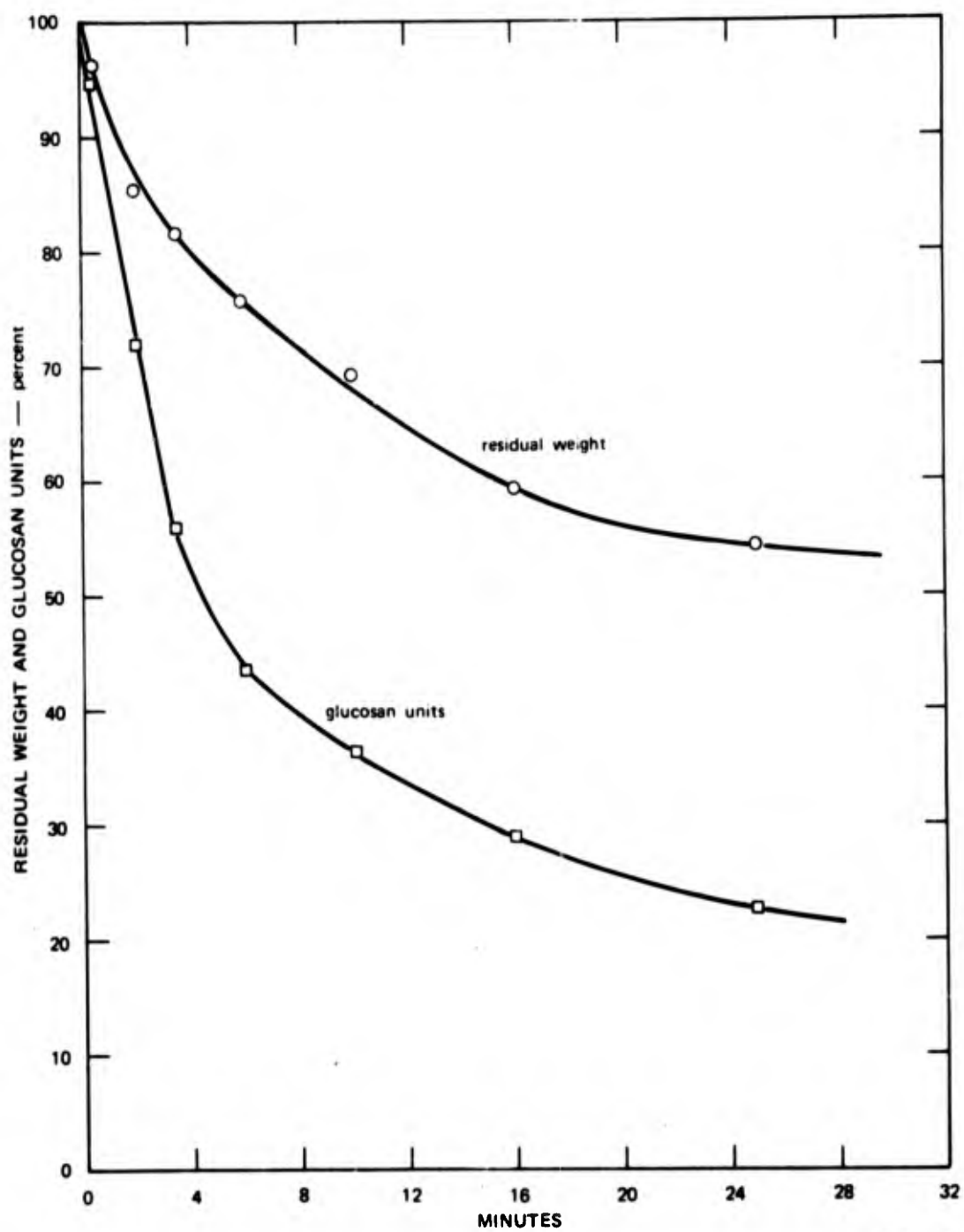
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FIGURE 4 RESIDUAL WEIGHT AND GLUCOSAN UNITS OF 3.03% KBr-TREATED CELLULOSE PYROLYZED IN N<sub>2</sub> AT 276°C



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FIGURE 5 RESIDUAL WEIGHT AND GLUCOSAN UNITS OF UNTREATED CELLULOSE PYROLYZED IN N<sub>2</sub> AT 276°C



TA-8150-161

FIGURE 6 RESIDUAL WEIGHT AND GLUCOSAN UNITS OF 2.93%  $K_2CO_3 \cdot 1-1/2 H_2O$ -TREATED CELLULOSE PYROLYZED IN  $N_2$  AT  $276^\circ C$

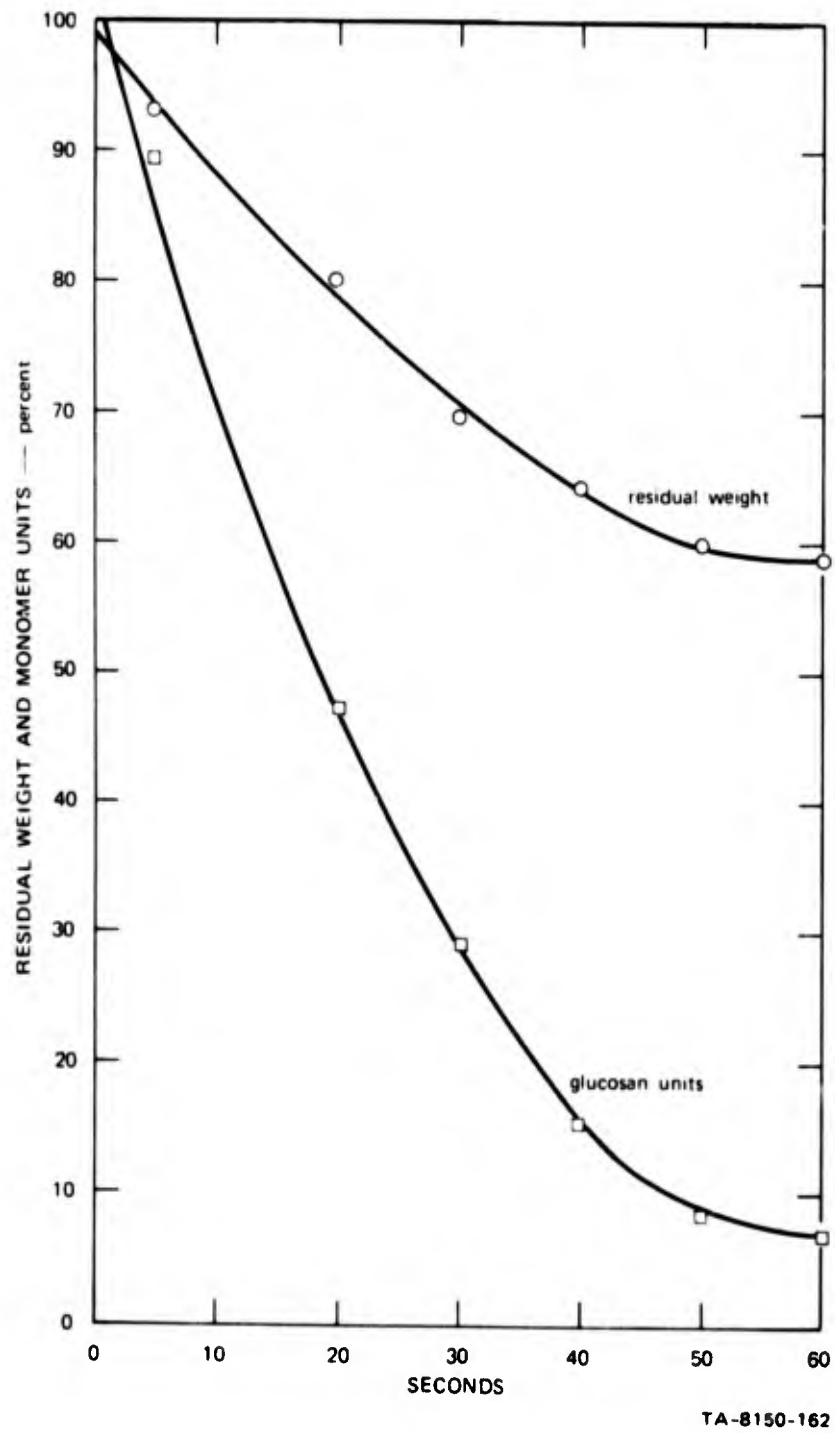


FIGURE 7 RESIDUAL WEIGHT AND GLUCOSAN UNITS OF 3.13%  $(\text{NH}_4)_2\text{SO}_4$ -TREATED CELLULOSE PYROLYZED IN  $\text{N}_2$  AT  $276^\circ\text{C}$

in contrast to that for the untreated cellulose, the weight-loss curve is not linear over most of the duration of active pyrolysis. The monomer loss curve is also changed, asymptotically approaching a limiting value rather than suffering depletion in value with length of pyrolysis as in the case of neutral retardants.

The weight and monomer-loss measurements of the acidic-salt-treated samples indicate that the treatment causes cellulose to be lost by a more nearly first-order than zero-order process. However, it is not apparent from these data why the acid treatment increases the rate of degradation.

## 2. Effect of Additives on Changes in Viscosity-Average Molecular Weights with the Length of Heating

Table 3 summarizes the relative and specific viscosity values used in obtaining the intrinsic viscosity  $[\eta]$ . These values are ultimately used in calculating the viscosity-average molecular-weight values. The intrinsic viscosity  $[\eta]$  is usually determined by extrapolating the reduced viscosity ( $\eta_{sp}/c$ , where  $\eta_{sp}$  is the viscosity, and  $c$  is the concentration) to infinite dilution and to zero velocity gradient. However, since the slopes of the linear plots of  $\eta_{sp}/c$  versus  $c$  depend on the molecular weight, the error in estimation of  $M$  from the efflux time ( $\eta_{sp}/c$ ) will vary and will increase with increase of  $M$ . It is therefore important to be able to calculate  $[\eta]$  for a measurement of the efflux time of one concentration. In this study, the Schulz-Blaschke<sup>14</sup> empirical equation

$$[\eta] = \frac{\eta_{sp}/c}{1 + k\eta_{sp}}$$

was used to calculate the value of  $[\eta]$ . The constant  $k$

has a value of 0.29 for cellulose dissolved in Cadoxen.<sup>14</sup> The average degree of polymerization ( $\overline{DP}$ ) of the pyrolyzed samples was calculated according to Brown and Wikström's equation:<sup>15</sup>  $[\eta] = k \overline{DP}^a$ , where  $k$  and  $a$  are empirical constants, and for cellulose dissolved in Cadoxen,  $k$  has a value of  $1.84 \times 10^{-2}$  and  $a$  is 0.71.

Table 3  
INTRINSIC VISCOSITY OF TREATED  $\alpha$ -CELLULOSE AS A FUNCTION OF LENGTH OF PYROLYSIS AT 276°C.

SAMPLE DESCRIPTION	LENGTH OF HEATING	CONCENTRATION (g/100 ml)	$\eta_{rel}$	$\eta_{sp}$	$\eta_{sp}/c$	$[\eta]$
0.030-in. 2.93% K <sub>2</sub> CO <sub>3</sub> -1-1-2 H <sub>2</sub> O- treated cellulose	0.5 min	0.250	1.4766	0.4766	1.9064	1.6749
	2.0 min	0.250	1.3614	0.3614	1.4450	1.308
	3.5 min	0.250	1.3123	0.3123	1.2491	1.1453
	10.0 min	0.250	1.2343	0.2343	0.937	0.8774
	17.5 min	0.250	1.1077	0.1077	0.431	0.4179
25.0 min	0.250	1.0839	0.0839	0.335	0.3270	
0.030-in. 3.03% KBr- treated cellulose	0	0.250	2.1990	1.1990	4.7960	3.560
	0.5 min	0.250	1.5520	0.5520	2.2080	1.9030
	2.0 min	0.250	1.2750	0.2750	1.1000	1.0187
	5.5 min	0.250	1.1820	0.1820	0.7280	0.7808
	15.0 min	0.250	1.0858	0.0858	0.3432	0.3347
22.5 min	0.250	1.0461	0.0461	0.1990	0.1964	
0.030-in. 3.13% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> -treated cellulose	0	0.250	1.9156	0.9156	3.6624	2.8940
	2.5 sec	0.250	1.3187	0.3187	1.2784	1.1669
	12.5 sec	0.250	1.0394	0.0894	0.3570	0.2835
	20.0 sec	0.250	1.0243	0.0243	0.0972	0.1872
30.0 sec	0.250	1.0240	0.0240	0.0970	0.1872	

Figure 8 shows the  $\overline{DP}$  of untreated and treated cellulose as a function of residual glucosan units. All samples show a rapid drop in  $\overline{DP}$  after the heating, and all except the  $(\text{NH}_4)_2\text{SO}_4$ -treated samples show a progressive decrease in the length of molecules on subsequent heating. The average lengths remain roughly proportional to the residual fraction of undecomposed cellulose. This further supports the contention of the Parker-Lipska model that the principal mechanism of cellulose decomposition is a zero-order elimination of monomer units.

The  $(\text{NH}_4)_2\text{SO}_4$ -treated samples display a different mode of decomposition, asymptotically approaching a limiting value of  $10 \overline{DP}$  after the initial heating. For a given percentage of residual glucosan units, the acid-salt-treated samples show the lowest degree of polymerization and the  $\text{K}_2\text{CO}_3 \cdot 1\frac{1}{2} \text{H}_2\text{O}$ -treated samples display the highest degree of polymerization. This observation is closely paralleled by rates of decomposition with the highest rates of decomposition occurring in the acid-salt-treated samples and the lowest in the basic-salt-treated samples. It is a well-established fact that in the presence of hydronium ions, cellulose undergoes cleavage of the 1,4-glucosidic bonds, producing molecules of lower average  $\overline{DP}$ . The rate at which this hydrolysis occurs undoubtedly depends on the hydrolyzing acid, its concentration, and the temperature of the reaction. The morphology of the cellulose may also play a considerable role in the hydrolytic process, and the possibility that, in the case of the acidic-salt treatment, hydrolysis might occur during the soaking and drying period as well as subsequently during heating, should not be overlooked. The Parker-Lipska model neglects any such hydrolytic effects.

The present evaluation of the possible effects of hydrolysis focuses on the early period of pyrolysis, postulating that sufficient water is produced during this early stage of pyrolysis to provide an aqueous environment. The approach is based on the assumptions that hydrolysis

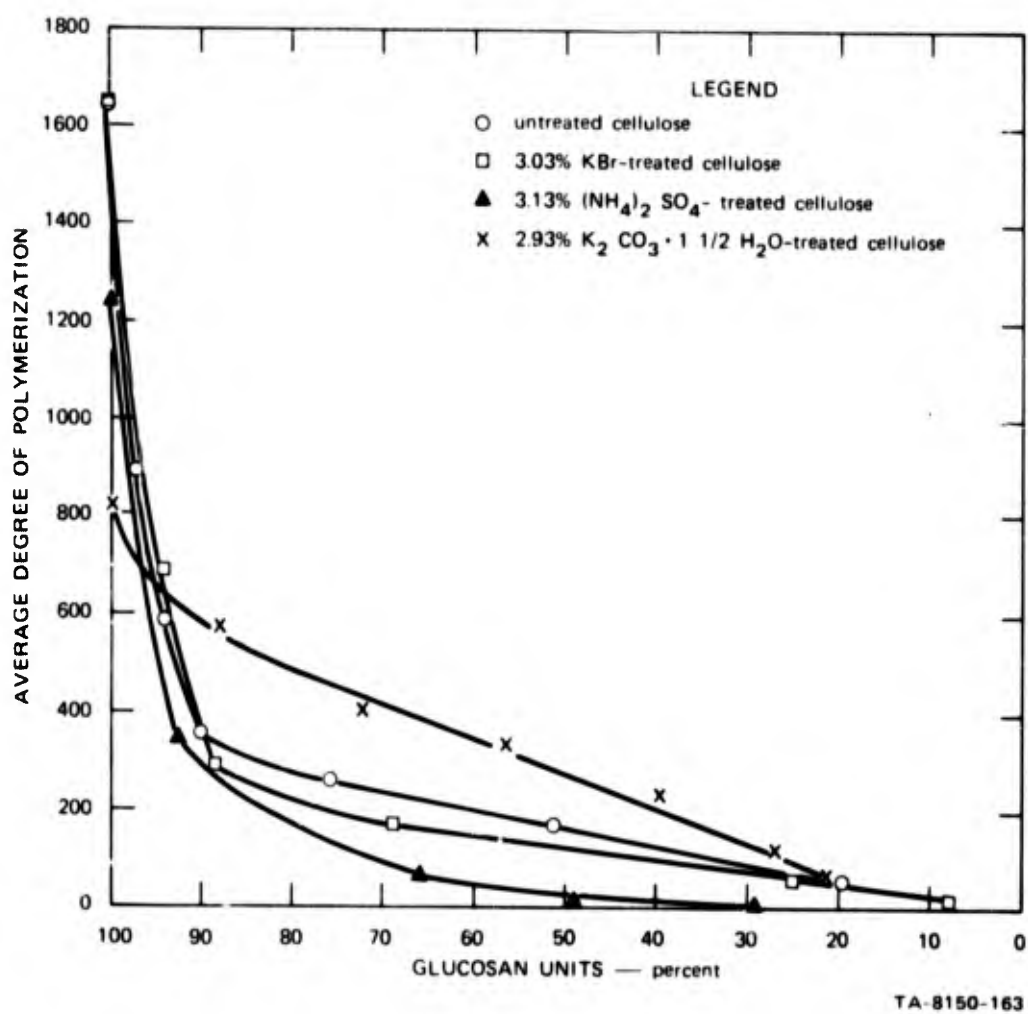


FIGURE 8 DEGREE OF POLYMERIZATION OF UNTREATED AND TREATED CELLULOSE AS A FUNCTION OF RESIDUAL GLUCOSAN UNITS

reduces some of the large cellulose chains to a larger number of relatively shorter ones and that the resulting rate of pyrolysis is increased in proportion to the concentration of hydronium ions contributed by those additives that are either acids or salts of weak bases. Unfortunately, the effect cannot be rigorously evaluated for several reasons. For example, many of the salts of weak bases are thermally unstable and are subject to poorly defined changes in composition throughout the period of their potential activity. More important, however, the definition of aqueous concentration as it applies to such a system is ambiguous. Also, virtually nothing is known for certain of the kinetics of cellulose hydrolysis or of the relevant acid-base equilibria at the temperature of pyrolysis. Nevertheless, the authors have attempted a preliminary evaluation of the possible role of hydrolysis in the kinetics of cellulose pyrolysis.

The approach taken contemplates a multiplicative factor, whose value is proportional to the hydrogen-ion concentration,  $[H^+]$ , that may be applied to the Parker-Lipska method of calculating enhanced rates of decomposition. It is reasonable to expect that this factor would have the form

$$F = \frac{[H^+]}{\sqrt{k_w}}$$

where  $k_w$  is the ionization constant for water. Thus, for such neutral salts as KBr, the value of F would be unity, whereas F could range from unity to values over several orders of magnitude above unity for acids and salts of acidic hydrolytic reaction.

The results are summarized in Tables 4 and 5. Table 4 compares the experimental data of increased rates of degradation and char values of treated cellulose with the predicted values as calculated by the original Parker-Lipska method. With the exception of samples treated with acid or salts of weak bases, the predicted values are in reasonably

Table 4

(COMPARISON OF DATA ON PYROLYSIS RATES AND CHAR YIELDS WITH VALUES PREDICTED FROM THE PARKER-LIPSKA MODEL)

ADDITIVE	MOLECULAR WEIGHT, M (g mol <sup>-1</sup> )	FRACTIONAL ADD-ON WEIGHT, W (dimensionless)	OBSERVED		OBSERVED $\Delta C/\Delta R$	POSSIBLE FORMS AT PYROLYSIS TEMPERATURE	W/M (mols g <sup>-1</sup> )	CALCULATED (P-L)	
			H/R <sub>0</sub>	$\Delta C$ (%)				R/R <sub>0</sub>	$\Delta C$ (%)
KBr	119.0	0.0089	--	5.8	--	KBr	7.47 x 10 <sup>-5</sup>	--	0.35
			19.0	9.6	0.53		14.60	0.80	
			25.0	11.2	0.47		21.41	1.20	
			--	18.3	--		--	2.02	
Al <sub>2</sub> O <sub>3</sub>	101.9	0.004	--	17.6	--	Al <sub>2</sub> O <sub>3</sub>	8.56 x 10 <sup>-4</sup>	--	4.08
			5.5	--	4.2		--		
KHCO <sub>3</sub>	100.1	0.02	7.0	12.3	2.05	KHCO <sub>3</sub> K <sub>2</sub> CO <sub>3</sub> K <sub>2</sub> O K <sub>2</sub> CO <sub>3</sub> · 2H <sub>2</sub> O	2.00 x 10 <sup>-4</sup>	17.2	11.75*
			--	--	--		9.1	5.87*	
			--	--	--		9.1	1.96*	
			--	--	--		9.1	9.80*	
K <sub>2</sub> CO <sub>3</sub>	138.2	0.014	7.0	--	--	K <sub>2</sub> CO <sub>3</sub> K <sub>2</sub> O	1.01 x 10 <sup>-4</sup>	9.2	5.87*
			--	--	9.2		1.96*		
K <sub>2</sub> CO <sub>3</sub> · 1½ H <sub>2</sub> O	165.2	0.029	19.0	12.9	0.716	K <sub>2</sub> CO <sub>3</sub> · 1½ H <sub>2</sub> O K <sub>2</sub> CO <sub>3</sub>	1.76 x 10 <sup>-4</sup>	15.2	5.90
			--	--	--		15.4	5.20	
Na <sub>2</sub> F <sub>4</sub> O <sub>7</sub> · 10 H <sub>2</sub> O	381.4	0.02	1.5	12.6	25.2	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10 H <sub>2</sub> O Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 2 H <sub>2</sub> O Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	5.24 x 10 <sup>-5</sup>	5.2	9.16*
			--	--	--		5.2	4.50*	
			--	--	--		5.2	3.53*	
			--	--	--		--	--	
AlCl <sub>3</sub> · 6 H <sub>2</sub> O	241.4	0.02	--	19.04	--	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10 H <sub>2</sub> O Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 2 H <sub>2</sub> O Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	2.13 x 10 <sup>-4</sup>	--	34.80
			--	--	--		--	18.40	
			--	--	--		--	14.12	
			--	--	--		--	--	
NaH <sub>2</sub> PO <sub>4</sub> · H <sub>2</sub> O	137.9	0.02	--	24.74	--	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10 H <sub>2</sub> O Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 2 H <sub>2</sub> O Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	3.59 x 10 <sup>-4</sup>	--	58.50
			--	--	--		--	31.90	
			--	--	--		--	24.10	
			--	--	--		--	--	
AlCl <sub>3</sub> · 6 H <sub>2</sub> O	241.4	0.02	5.5	3.6	0.8	AlCl <sub>3</sub> · 6 H <sub>2</sub> O AlCl <sub>3</sub> Al <sub>2</sub> O <sub>3</sub>	8.30 x 10 <sup>-5</sup>	7.7	12.2*
			--	--	--		7.7	2.44*	
			--	--	--		4.39	2.44*	
			--	--	--		--	--	
NaH <sub>2</sub> PO <sub>4</sub> · H <sub>2</sub> O	137.9	0.02	5.2	12.1	2.89	Na <sub>2</sub> H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> NaH <sub>2</sub> PO <sub>4</sub> · H <sub>2</sub> O NaH <sub>2</sub> PO <sub>4</sub> NaPO <sub>3</sub>	0.72 x 10 <sup>-4</sup>	6.83	6.80
			--	--	--		12.70	9.05	
			--	--	--		12.70	7.67	
			--	--	--		12.70	6.25	

Table 4 (Concluded)

ADDITIVE	MOLECULAR WEIGHT, M (g mol <sup>-1</sup> )	FRACTIONAL ADD-ON WEIGHT, W (dimensionless)	OBSERVED		OBSERVED $\Delta C/\Delta R$	POSSIBLE FORMS AT PYROLYSIS TEMPERATURE	W/M (mole g <sup>-1</sup> )	CALCULATED (P-L)																					
			R/R <sub>0</sub>	$\Delta C$ (%)				R/R <sub>0</sub>	$\Delta C$ (%)																				
NaH <sub>2</sub> PO <sub>4</sub> · H <sub>2</sub> O (continued)		0.05	--	18.3	--	Na <sub>2</sub> H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> NaH <sub>2</sub> PO <sub>4</sub> · H <sub>2</sub> O NaH <sub>2</sub> PO <sub>4</sub> NaPO <sub>3</sub>	1.80 × 10 <sup>-4</sup> 3.60 × 10 <sup>-4</sup> 3.60 × 10 <sup>-4</sup> 3.60 × 10 <sup>-4</sup>	--	17.25 22.50 19.20 15.55																				
										NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	115.0	0.02	8.0	18.3	2.61	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> H <sub>3</sub> PO <sub>4</sub> H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 0.87 × 10 <sup>-4</sup>	15.0 15.0 8.05	18.79* 18.79* 16.98*										
																				ZnSO <sub>4</sub> · 7H <sub>2</sub> O	287.6	0.04	117.0	10.9	0.094	ZnSO <sub>4</sub> ZnSO <sub>4</sub> · 7H <sub>2</sub> O	1.39 × 10 <sup>-4</sup> 1.39 × 10 <sup>-4</sup>	12.30 12.30	6.69 15.32
20MO <sub>3</sub> · 2H <sub>3</sub> PO <sub>4</sub> · 25H <sub>2</sub> O	5282.0	0.012	--	5.11	--	20MO <sub>3</sub> · 2H <sub>3</sub> PO <sub>4</sub> · 25H <sub>2</sub> O 20MO <sub>3</sub> · 2H <sub>3</sub> PO <sub>4</sub>	2.27 × 10 <sup>-6</sup> 2.27 × 10 <sup>-6</sup>	--	2.54 1.88																				
										H <sub>3</sub> PO <sub>4</sub>	0.05	--	24.56	--	H <sub>3</sub> PO <sub>4</sub> H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> P <sub>2</sub> O <sub>5</sub>	5.1 × 10 <sup>-4</sup> 2.55 × 10 <sup>-4</sup> 2.55 × 10 <sup>-4</sup>	--	27.0 24.5 24.5											
																			(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132	0.023	362.0	11.9	3.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup>	15.1 15.1 8.35	8.35 8.35 8.35	
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	246.5	0.016	--	4.31	--	MgSO <sub>4</sub> · 7H <sub>2</sub> O MgSO <sub>4</sub>	6.50 × 10 <sup>-5</sup>	--											7.49 3.12
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	580.0	0.013	580.0	13.5	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup>	20.2 20.2 20.2	11.38 11.38 11.38																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	900.0	0.05	900.0	20.9	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup>	31.7 31.7 31.7	18.2 18.2 18.2										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132	0.023	362.0	11.9	3.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup>	15.1 15.1 8.35	8.35 8.35 8.35																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	246.5	0.016	--	4.31	--	MgSO <sub>4</sub> · 7H <sub>2</sub> O MgSO <sub>4</sub>	6.50 × 10 <sup>-5</sup>	--	7.49 3.12										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	580.0	0.013	580.0	13.5	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup>	20.2 20.2 20.2	11.38 11.38 11.38																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	900.0	0.05	900.0	20.9	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup>	31.7 31.7 31.7	18.2 18.2 18.2										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132	0.023	362.0	11.9	3.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup>	15.1 15.1 8.35	8.35 8.35 8.35																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	246.5	0.016	--	4.31	--	MgSO <sub>4</sub> · 7H <sub>2</sub> O MgSO <sub>4</sub>	6.50 × 10 <sup>-5</sup>	--	7.49 3.12										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	580.0	0.013	580.0	13.5	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup>	20.2 20.2 20.2	11.38 11.38 11.38																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	900.0	0.05	900.0	20.9	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup>	31.7 31.7 31.7	18.2 18.2 18.2										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132	0.023	362.0	11.9	3.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup>	15.1 15.1 8.35	8.35 8.35 8.35																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	246.5	0.016	--	4.31	--	MgSO <sub>4</sub> · 7H <sub>2</sub> O MgSO <sub>4</sub>	6.50 × 10 <sup>-5</sup>	--	7.49 3.12										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	580.0	0.013	580.0	13.5	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup>	20.2 20.2 20.2	11.38 11.38 11.38																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	900.0	0.05	900.0	20.9	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup>	31.7 31.7 31.7	18.2 18.2 18.2										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132	0.023	362.0	11.9	3.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup>	15.1 15.1 8.35	8.35 8.35 8.35																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	246.5	0.016	--	4.31	--	MgSO <sub>4</sub> · 7H <sub>2</sub> O MgSO <sub>4</sub>	6.50 × 10 <sup>-5</sup>	--	7.49 3.12										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	580.0	0.013	580.0	13.5	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup>	20.2 20.2 20.2	11.38 11.38 11.38																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	900.0	0.05	900.0	20.9	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup>	31.7 31.7 31.7	18.2 18.2 18.2										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132	0.023	362.0	11.9	3.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup>	15.1 15.1 8.35	8.35 8.35 8.35																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	246.5	0.016	--	4.31	--	MgSO <sub>4</sub> · 7H <sub>2</sub> O MgSO <sub>4</sub>	6.50 × 10 <sup>-5</sup>	--	7.49 3.12										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	580.0	0.013	580.0	13.5	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup>	20.2 20.2 20.2	11.38 11.38 11.38																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	900.0	0.05	900.0	20.9	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup>	31.7 31.7 31.7	18.2 18.2 18.2										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132	0.023	362.0	11.9	3.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup>	15.1 15.1 8.35	8.35 8.35 8.35																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	246.5	0.016	--	4.31	--	MgSO <sub>4</sub> · 7H <sub>2</sub> O MgSO <sub>4</sub>	6.50 × 10 <sup>-5</sup>	--	7.49 3.12										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	580.0	0.013	580.0	13.5	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup>	20.2 20.2 20.2	11.38 11.38 11.38																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	900.0	0.05	900.0	20.9	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup>	31.7 31.7 31.7	18.2 18.2 18.2										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132	0.023	362.0	11.9	3.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup>	15.1 15.1 8.35	8.35 8.35 8.35																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	246.5	0.016	--	4.31	--	MgSO <sub>4</sub> · 7H <sub>2</sub> O MgSO <sub>4</sub>	6.50 × 10 <sup>-5</sup>	--	7.49 3.12										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	580.0	0.013	580.0	13.5	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup>	20.2 20.2 20.2	11.38 11.38 11.38																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	900.0	0.05	900.0	20.9	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup>	31.7 31.7 31.7	18.2 18.2 18.2										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132	0.023	362.0	11.9	3.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup>	15.1 15.1 8.35	8.35 8.35 8.35																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	246.5	0.016	--	4.31	--	MgSO <sub>4</sub> · 7H <sub>2</sub> O MgSO <sub>4</sub>	6.50 × 10 <sup>-5</sup>	--	7.49 3.12										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	580.0	0.013	580.0	13.5	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup>	20.2 20.2 20.2	11.38 11.38 11.38																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	900.0	0.05	900.0	20.9	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup> 3.79 × 10 <sup>-4</sup>	31.7 31.7 31.7	18.2 18.2 18.2										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132	0.023	362.0	11.9	3.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup> 1.74 × 10 <sup>-4</sup>	15.1 15.1 8.35	8.35 8.35 8.35																				
										MgSO <sub>4</sub> · 7H <sub>2</sub> O	246.5	0.016	--	4.31	--	MgSO <sub>4</sub> · 7H <sub>2</sub> O MgSO <sub>4</sub>	6.50 × 10 <sup>-5</sup>	--	7.49 3.12										
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	580.0	0.013	580.0	13.5	2.3 × 10 <sup>-2</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup> 2.37 × 10 <sup>-4</sup>	20.2 20.2 20.2	11.38 11.38 1																				

Table 5  
 PREDICTIONS OF THE INCREASED RATES OF PYROLYSIS OF CELLULOSE CONTAINING EITHER  
 ACIDS OR SALTS OF WEAK BASES, REVISED TO ACCOUNT FOR HYDROLYSIS

ADDITIVE	POSSIBLE FORMS AT PYROLYSIS TEMPERATURE	$\frac{W}{M}$ (l) (mols g <sup>-1</sup> )	R/R <sub>0</sub> (observed)	R/R <sub>0</sub> (P-L) (calculated)	Approx. [H <sup>+</sup> ] (mols liter <sup>-1</sup> )	F([H <sup>+</sup> ])	F · R/R <sub>0</sub> (P-L)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> HSO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	1.74 × 10 <sup>-4</sup>	362.0	15.1	2.06 × 10 <sup>-6</sup>	20.67	312.5
		1.74 × 10 <sup>-4</sup>			4.74 × 10 <sup>-3</sup>	47,447.40	717,102.8
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> HSO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	2.37 × 10 <sup>-4</sup>	580.0	13.5	2.40 × 10 <sup>-6</sup>	26.92	483.9
		3.79 × 10 <sup>-4</sup>			5.56 × 10 <sup>-5</sup>	59,660.0	1,205,538.6
ZnSO <sub>4</sub> · 7H <sub>2</sub> O	ZnSO <sub>4</sub> · 7H <sub>2</sub> O	1.39 × 10 <sup>-4</sup>	900.00	20.9	3.00 × 10 <sup>-6</sup>	30.01	950.8
		1.39 × 10 <sup>-4</sup>			8.31 × 10 <sup>-3</sup>	83,146.18	2,634,222.1
H <sub>3</sub> PO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub> H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> P <sub>2</sub> O <sub>5</sub>	2.04 × 10 <sup>-4</sup>	117.0	12.30	9.3 × 10 <sup>-7</sup>	9.34	114.53
		1.02 × 10 <sup>-4</sup>			1.02 × 10 <sup>-6</sup>	11.75	205.97
AlCl <sub>3</sub> · 6H <sub>2</sub> O	AlCl <sub>3</sub> · 6H <sub>2</sub> O	8.30 × 10 <sup>-5</sup>	253.0	17.50	1.02 × 10 <sup>-6</sup>	1.0	9.43
		4.15 × 10 <sup>-5</sup>			1.0 × 10 <sup>-4</sup>	10 <sup>3</sup>	7.7 × 10 <sup>3</sup>
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> H <sub>3</sub> PO <sub>4</sub> H <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	1.74 × 10 <sup>-4</sup>	5.5	7.70	1 × 10 <sup>-7</sup>	1.0	4.39
		0.87 × 10 <sup>-4</sup>			1.63 × 10 <sup>-4</sup>	163.26	2,463.14
NaH <sub>2</sub> PO <sub>4</sub> · H <sub>2</sub> O	Na <sub>2</sub> H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> NaH <sub>2</sub> PO <sub>4</sub>	0.72 × 10 <sup>-4</sup>	8.0	15.00	1.0 × 10 <sup>-7</sup>	1.0	8.04
		1.45 × 10 <sup>-4</sup>			6.83	60.5	770.89
			5.2	12.70	1.37 × 10 <sup>-5</sup>	136.7	1,742.95

good agreement with the experimental results. The effect of the multiplicative factor on the predicted degradation rates of samples treated with acids or salts of weak bases is shown in Table 5. Since the form the additive will take and its aqueous concentration in the pyrolyzing cellulose are not known, it was necessary in making such calculations to consider several likely forms of each additive and to use, as a working value, an aqueous concentration that is proportional to the add-on weight. The proportionality constant was based on experimentally obtained pH values of various concentration of  $ZnSO_4$  solution. This attempt to account for hydronium-ion hydrolysis, as a possible revision to the Parker-Lipska method, brought about closer agreement between predicted and experimentally obtained values in cases where the total hydrogen ion concentration did not exceed about  $10^{-5}$  mols/liter. Higher  $[H^+]$  increased the calculated estimates of the degradation rates several orders of magnitude more than the actual experimental measurements indicated. In cases where the additive is alkaline, the multiplicative factors are not meant to apply. Since for most of these cases the calculated values by the original Parker-Lipska method agree reasonably well with the observed values, no comparable correction for alkaline hydrolysis appears to be needed.

These calculations show that hydronium-ion hydrolysis is an entirely plausible mechanism for the much more rapid decomposition rates of cellulose in the presence of acids or salts of weak bases, but a practical modification to the Parker-Lipska model, based on this mechanism, remains to be discovered.

### 3. Effect of Additives on Increase of Char Production

A novel concept contained in the Parker-Lipska model relating to char yield is that the characteristic of the additive that determines char production is the total negative valence of the additive molecule. No fundamental reason has been proposed for such a proposition; it was

deduced on a purely empirical basis. Subsequent attempts to verify or refute this concept have been inconclusive, principally because of the inability to specify unambiguously the form of the additive molecules at the pyrolysis temperature. This thermal instability is a common characteristic of ammonium salts, hydrogen-containing anions of salts of polybasic acids such as bicarbonate ion and dihydrogen phosphate ion, and salts of organic acids, all of which have figured prominently among fire retardants.

The mathematical expression originally developed by Parker and Lipska relates the increase in char to the concentration of the salt and its total negative valence, as given by the following relationship:

$$\Delta C = k \frac{W}{M} \sum_i N_i V_i \%$$

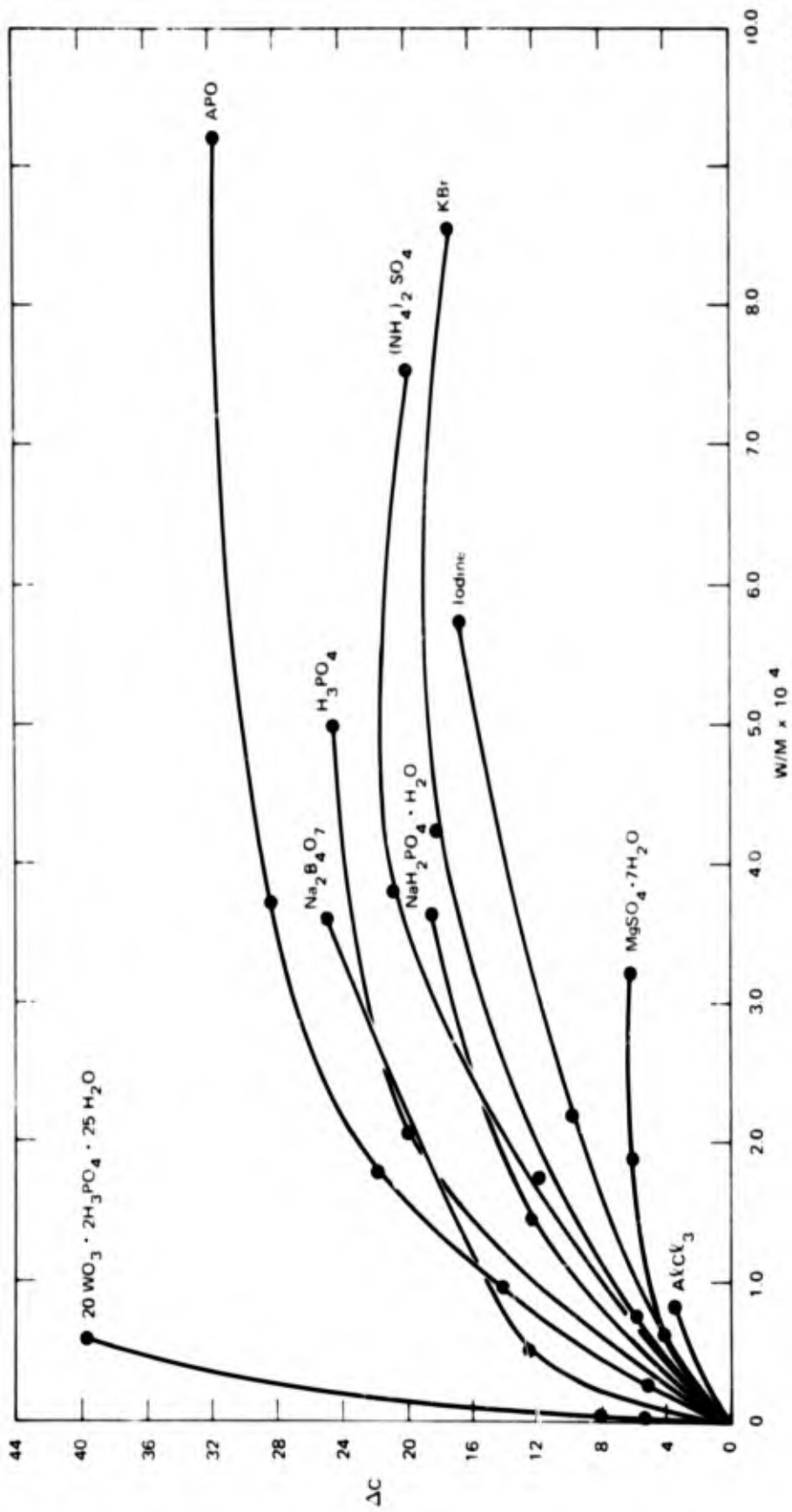
where W equals the add-on weight of the retardant, M is the molecular weight of the molecule as retained during pyrolysis, and the  $\Sigma$  quantity is the total negative valence of the retained molecule. In the Parker-Lipska model, the coefficient k is given the value 48, corresponding to the formula weight of the four carbon atoms that were postulated to remain as char from each molecule of levoglucosan that contributed to the final char. In calculating the intermediate char (that is, the char yield under circumstances of heating that incompletely rid the residue of its volatile content), Parker and Lipska assigned k the value 98, interpreted by them as corresponding to an intermediate compound formed from one molecule of levoglucosan, which, upon polymerization, contributes to the formation of intermediate char. Contrary to chemical convention, however, the method of assigning negative valence to the elements in the formula does not necessarily balance the positive valence in the compound. The special rules applied to this correlation were that whereas hydrogen is always taken to be positive, carbon can be either positive or negative, and any element having both positive and negative valence is always

assigned its most common negative valence, as given in lists of chemical valences.

Although no reference was made to it in the original work, ammonium ion, because of its chemical analogy to metallic ions in aqueous systems, is treated as a single entity; that is, in this one instance the nitrogen atom is not assigned a negative valence.

Data for increased yields of final and intermediate char are listed in Table 4. Calculated values are based on the total negative valence of the undecomposed additive as well as on the total negative valence of its possible alternative forms at pyrolysis temperatures. The majority of both the calculated and observed char yield increases pertain to the final char. Values for samples treated with  $\text{KHCO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$  are taken from the literature and refer to the intermediate char in both the case of observed data and the calculated values. With the exception of samples treated with KBr, there is satisfactory agreement between the calculated and observed values of  $\Delta C$ . No logical explanation for the discrepancy between the calculated and observed char yields for the KBr-treated samples can be offered at this time. On the whole, the calculated  $\Delta C$  for the most plausible form of the salt at pyrolysis temperature is lower than the observed  $\Delta C$ . Since the observed  $\Delta C$  includes residues from the additives, this discrepancy may be attributed to the residue from the additives remaining in the samples. However, direct estimates of the residual amounts have not been made.

Figure 9 shows how increases in char yield depend on concentrations of additives. The overall trend in char production increases initially in direct proportion to concentration, but rapidly approaches a limit. This accounts for the discrepancies between predicted and observed  $\Delta C$ 's at high additive concentration. In general, it appears that the initial slope in each of the  $\Delta C$ -versus-additive-concentration curves is roughly



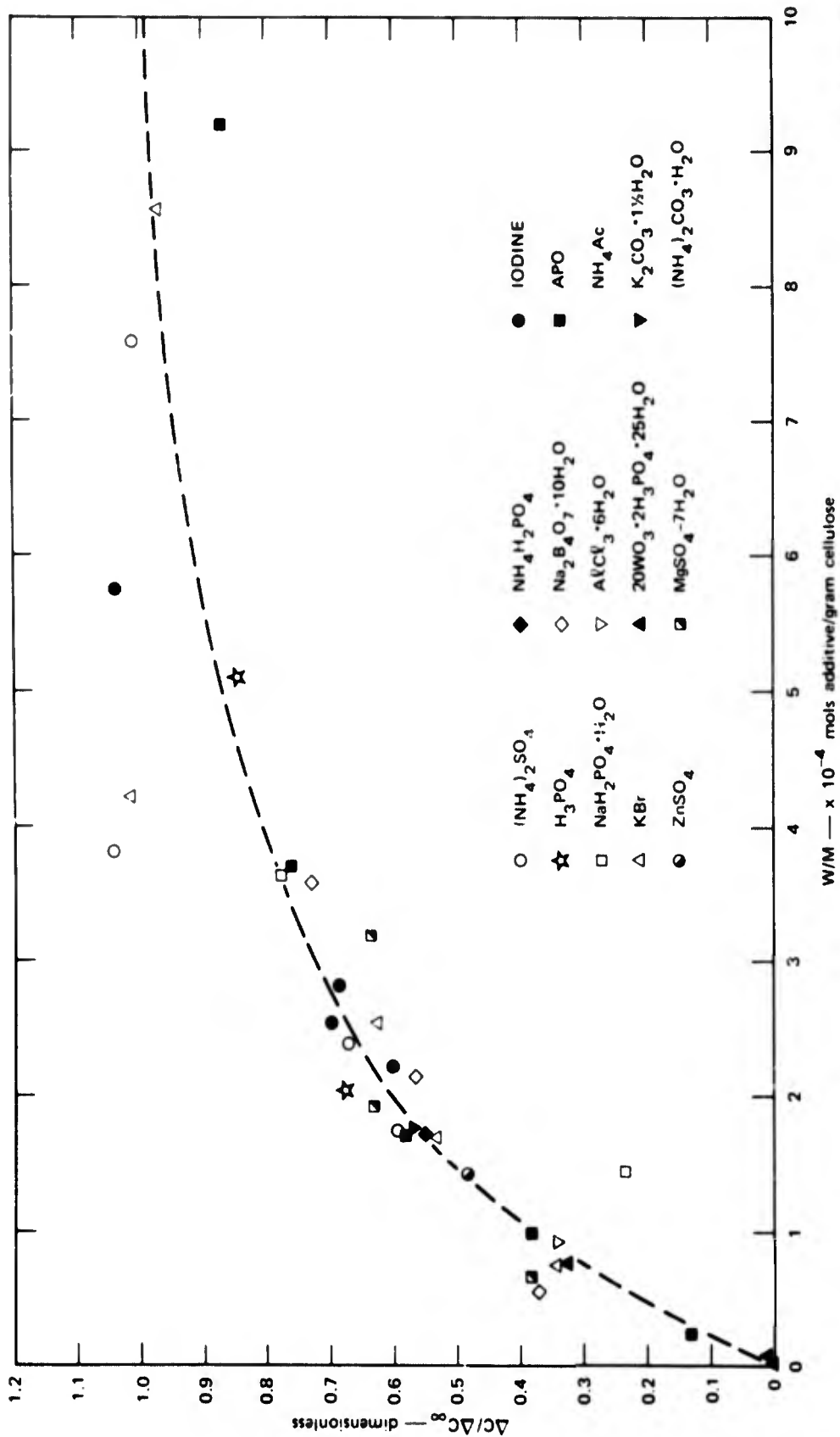
TA-B150-164

FIGURE 9 THE EFFECT OF CONCENTRATION OF ADDITIVES ON CHAR PRODUCTION

proportional to the asymptotic limit of that curve for each of these additives. This observation suggests that the individual  $\Delta C$ -versus-concentration curves might be correlated with one another if appropriate coordinate parameters were chosen. An example correlation is shown in Figure 10. In this case, wherever values of the asymptotic limit could not be estimated directly from the data, arbitrary values were chosen to provide the best fit of the existing data. The resulting correlation is reasonably good. Although there is considerable scatter to the points, it appears justifiable to conclude that the parameter  $\Delta C/\Delta C_{\infty}$  can be expressed as a single function of the concentration evaluated as  $W/M$ .

From such a relationship, it is possible to relate directly the  $\Delta C_{\infty}$  values to the total negative valence quantity in the Parker-Lipska relationship and thereby to test whether a meaningful correlation exists between the increase in char and total negative valence. This has been done in Table 6. It can readily be seen that there is, at best, a poor correlation between the estimates of  $\Delta C_{\infty}$  and the total negative valences of those additives included to date. There is a similarly poor correlation with molecular weight. No alternative basis for prediction can be offered at this time, however.

The correlation of Figure 10 is of practical value in addition to use in testing the predictability of char production. The correlation indicates that the optimal add-on values for all fire retardants are in the neighborhood of  $2 \times 10^{-4}$  mols of additive/g of cellulose. At this point, nearly two-thirds of the potential char increase has been obtained, and further addition of an additive provides decreasingly small returns in added char. If the basic premise that increased char results in decreased flammability is valid, the quantity of material applied should not exceed a value of about  $2 \times 10^{-4}$  mols/g of cellulose to achieve optimal retardance without excessive add-on of fire-retardant material.



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FIGURE 10 CORRELATION OF CHAR INCREASE WITH CONCENTRATION OF ADDITIVES

Table 6

CORRELATION OF INCREASED CHAR YIELDS  
WITH CONCENTRATION OF ADDITIVES

Additive	MW	$\sum \frac{N}{i} \frac{V}{i}$	$\Delta C_{\infty}$ in % by wt
$20\text{WO}_3 \cdot 2\text{H}_3\text{PO}_4 \cdot 25\text{H}_2\text{O}$	5282	192	120
APO (substituted (cellulose))	173	-	37
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	387.4	34 <sup>(14)*</sup>	34
$\text{NH}_4\text{H}_2\text{PO}_4$	115	11 <sup>(20)*</sup>	33
$\text{H}_3\text{PO}_4$	98	11	29
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	137.9	13 <sup>(11)*</sup>	23.4
$\text{K}_2\text{CO}_3 \cdot 1-1/2 \text{H}_2\text{O}$	165.2	7	22.5
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	287.5	24 <sup>(10)*</sup>	22.3
$(\text{NH}_4)_2\text{SO}_4$	132	10	20.0
KBr	119	1	18.0
Iodine	109	-	16.0
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	246.5	24 <sup>(10)*</sup>	11.0
$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	241	15 <sup>(3)*</sup>	10.5
$\text{NH}_4\text{Ac}$	77	3	1.0
$(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$	114	8	0

\* Value in parenthesis is representative of extreme variation in factor for the likely alternative forms at pyrolysis temperatures.

Thus, it appears that low molecular-weight additives would have a weight advantage over high molecular-weight additives; however, high molecular-weight materials may tend to produce the largest values of  $\Delta C_{\infty}$ . This does not necessarily mean that there is a good correlation between molecular weight and char increase, but from the few examples in hand, an extreme case of high molecular weight resulted in the extreme value of  $\Delta C_{\infty}$ . The value  $2 \times 10^{-4}$  mols of additive/g of cellulose corresponds to about 0.03 mols/mol of glucosan units or about 30 glucosan units per additive molecule. In view of the fact that salts typically form crystals, and many salt molecules are accordingly compacted into a small spatial volume, inorganic salts appear to be highly effective catalysts of cellulose pyrolysis.

Little additional guidance can be given at this time in the matter of selecting optimal fire-retardant agents for cellulose. It appears to be desirable to maximize the char production while minimizing the rate of decomposition<sup>\*</sup> within the constraint that the molecular weight should be kept as small as practical. Acidic retardants--that is, acids and salts of weak bases--cause excessively high rates of decomposition, and since their increased production of char is not similarly large, they are not among the best candidates for fire retardancy by these criteria. On the other hand, some of the basic retardants--that is, salts of weak acids (notably the alkali carbonates)--do produce acceptably large char yields, while rates of decomposition remain relatively low. The large value of the ratio  $\Delta C/\Delta R$  for  $\text{Na}_2\text{B}_4\text{O}_7$  in Table 4 suggests that this salt should be an effective retardant. At this time, however, there is no certain means of selecting retardants with the optimal characteristics. For example,

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\* One figure of merit is the ratio  $\Delta C/\Delta R$ , where  $\Delta R = R/R_0 - 1$  is the relative incremental increase in rate of decomposition<sup>o</sup> caused by an additive. The Parker-Lipska model proposes that each of the quantities forming the ratio is proportional to W/M. Accordingly, their ratio is independent of W/M and therefore of concentration.

the property of an additive that causes it to produce large values of char yield is not known. It appears that some property other than the negative valence parachor must be sought. This property appears to relate to the capability of certain elements of the additive molecule to form coordination complexes. It may be related to the Lewis acid-base characteristics of the material, but the fundamental cause-and-effect relationships are not known at this time.

#### 4. The Effect of Additives on Degradation Products

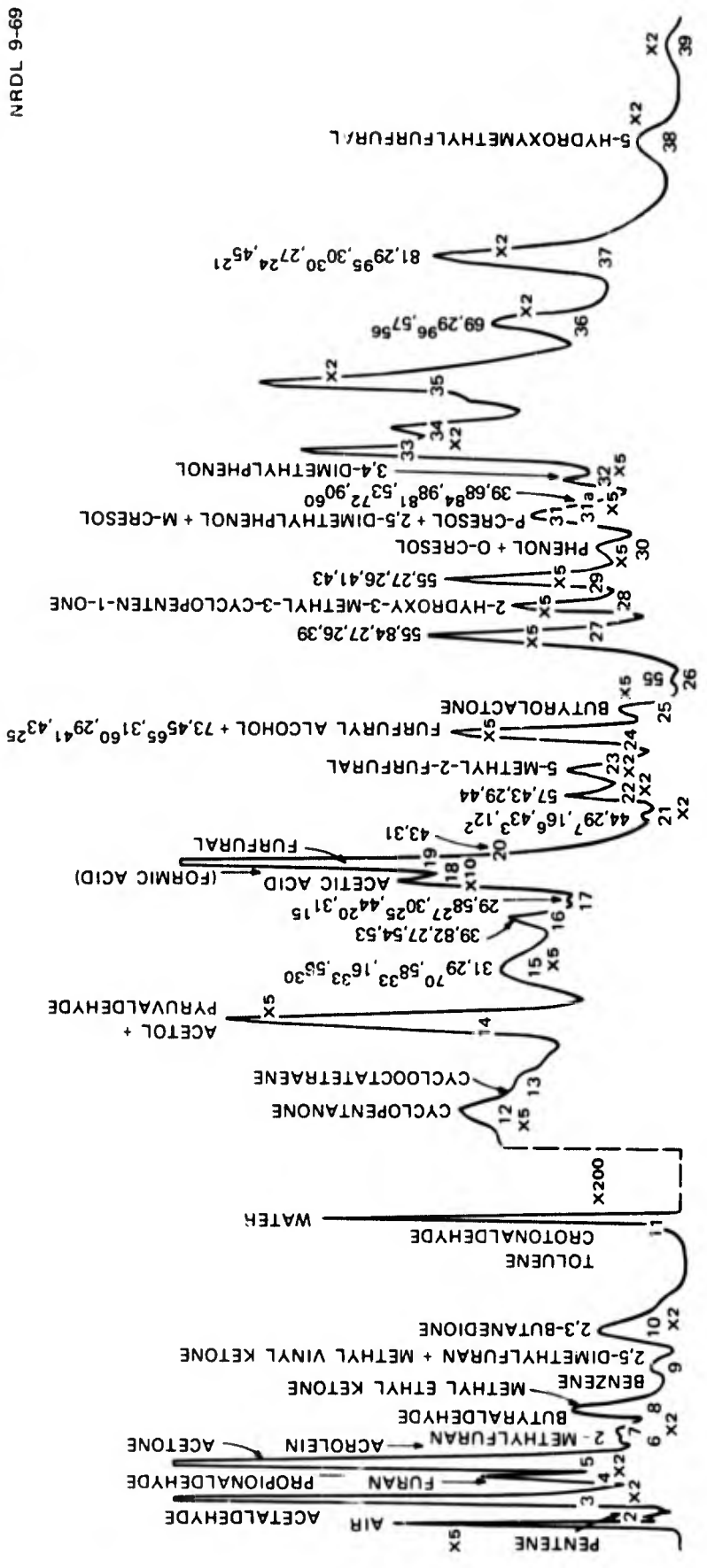
Figure 11 a-d compares chromatograms of the degradation products of untreated cellulose with basic, neutral, and acidic retardants. A typical chromatogram of the degradation products of untreated cellulose consists of 39 peaks that represent at least 59 compounds as analyzed by the time-of-flight mass spectrometer. Since no silyl derivatives were prepared for the identification of higher molecular-weight components, the gas chromatographic analysis includes only compounds with molecular weights less than about 150. The products formed from cellulose containing 2.93%  $K_2CO_3 \cdot 1\frac{1}{2} H_2O$  are similar to those from the untreated cellulose; however, peaks 25 (butyrolactone), 30 (phenol, O-cresol), and 31 (2,5-dimethylphenol + m-cresol + p-cresol) increase in the treated cellulose, while peaks 3 (acetaldehyde), 14 (acetol, pyruvaldehyde), 16 (unknown), 18 (acetic acid), and 19 (furfural) decrease. The IR spectrophotometric analysis shows an absence of levoglucosan. These findings are in good agreement with the project team's results on the 2%  $KHCO_3$ -treated sample as well as the work of others.<sup>2,16</sup> Although the ratio of CO to  $CO_2$  was not measured in the authors' experiments, Tsuchiya and Sumi<sup>2</sup> show that, at 320°C, the ratio of CO to  $CO_2$  in the  $K_2CO_3$ -treated material is 1.14 as opposed to 0.33 in the untreated cellulose at the same temperature.

The product mixture from the 3.03% KBr-treated cellulose shows a substantial increase in peak 31a (1,5-anhydro-2,3-deoxy-β-D-pent-2-enofuranose) as opposed to a trace in the untreated cellulose. Peaks 11 (water),

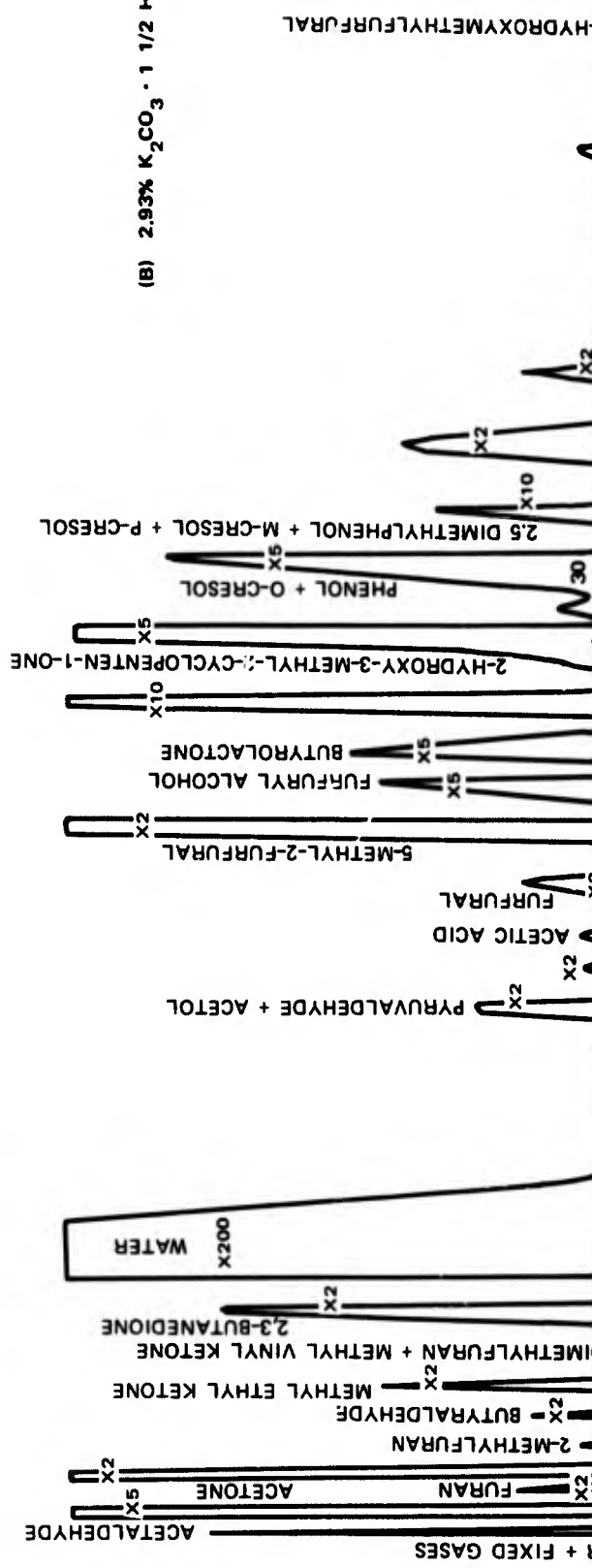
A

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(A) UNTREATED

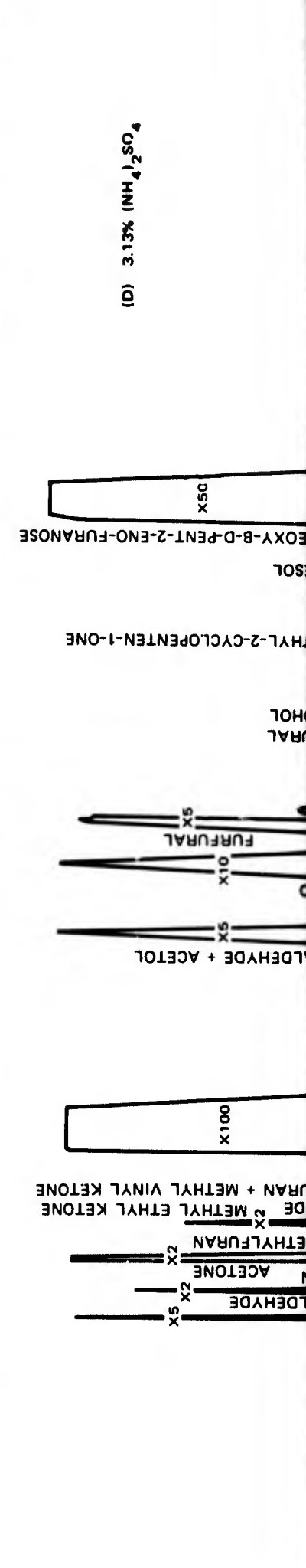
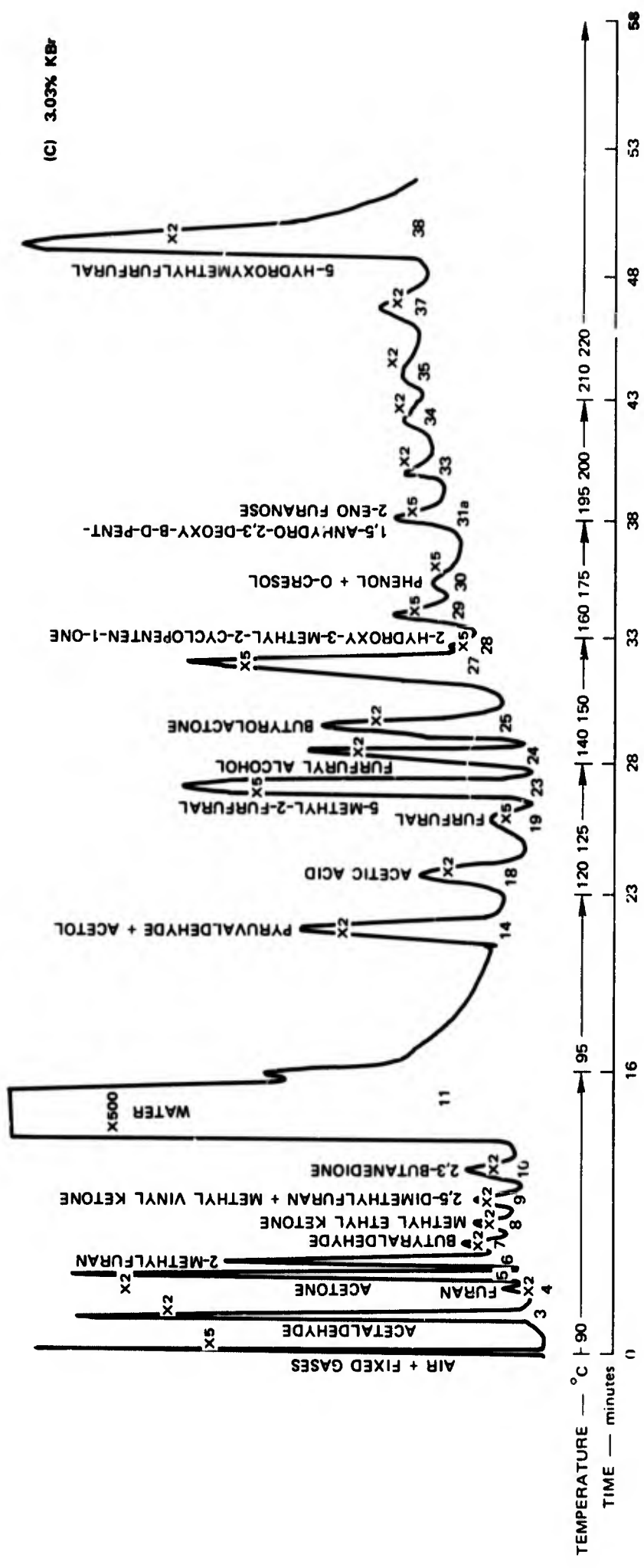
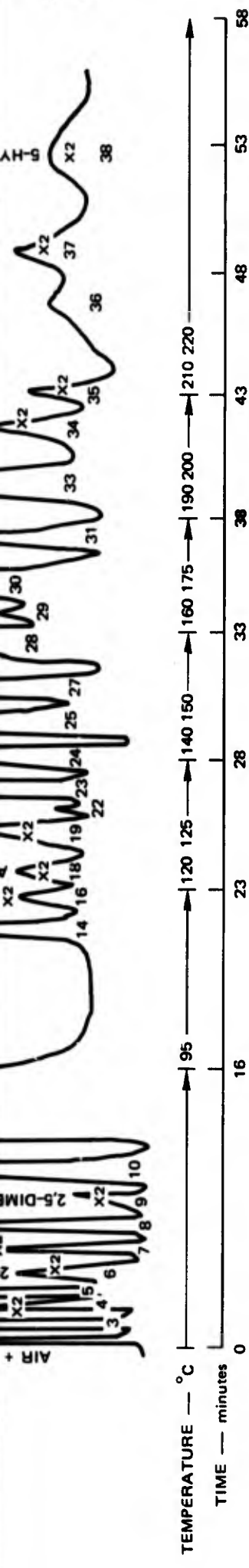


(B) 2.93% K<sub>2</sub>CO<sub>3</sub> · 1 1/2 H<sub>2</sub>O



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1 B



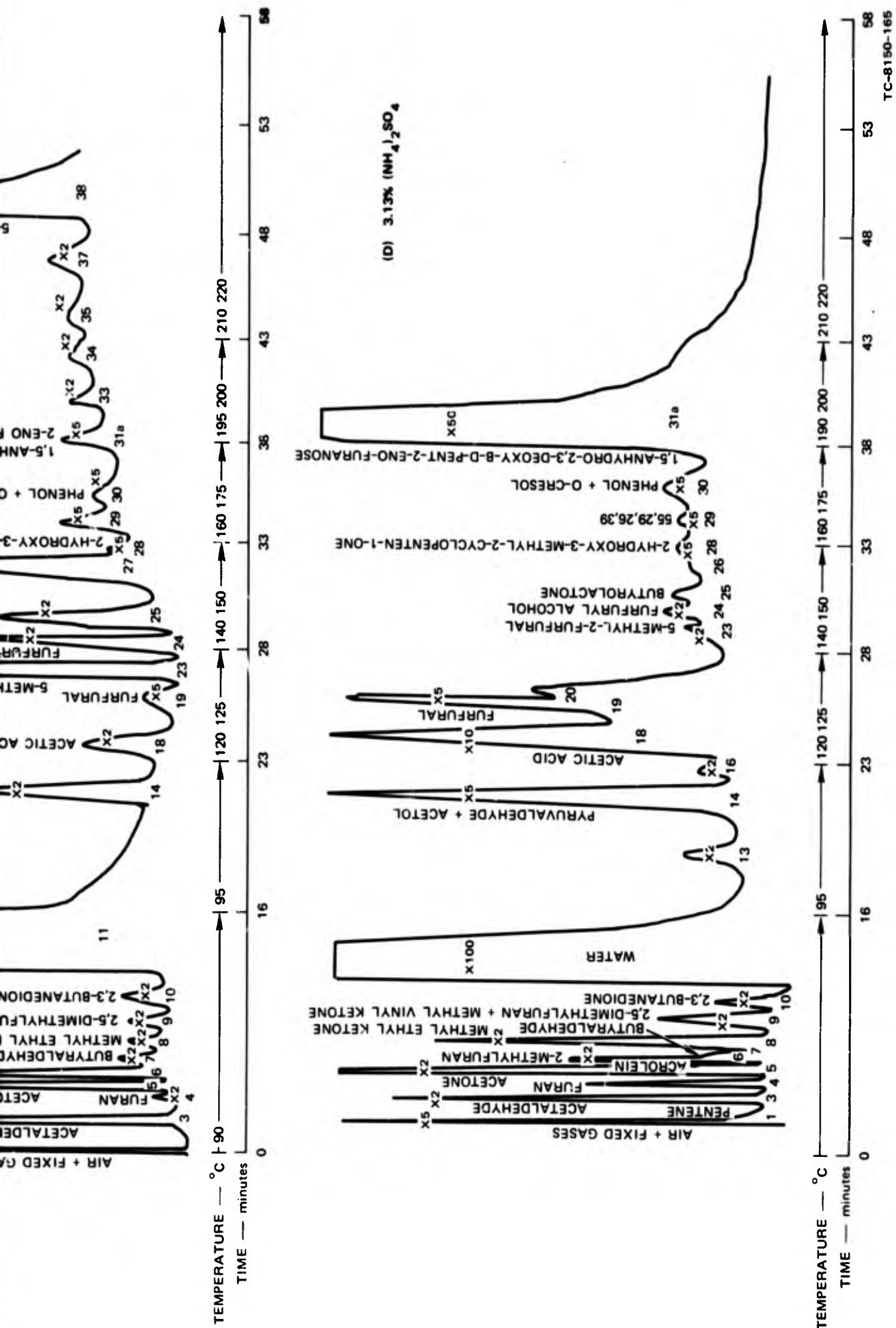


FIGURE 11 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS FROM THE PYROLYSIS OF UNTREATED AND BASIC, NEUTRAL, AND ACIDIC-SALTS-TREATED CELLULOSE

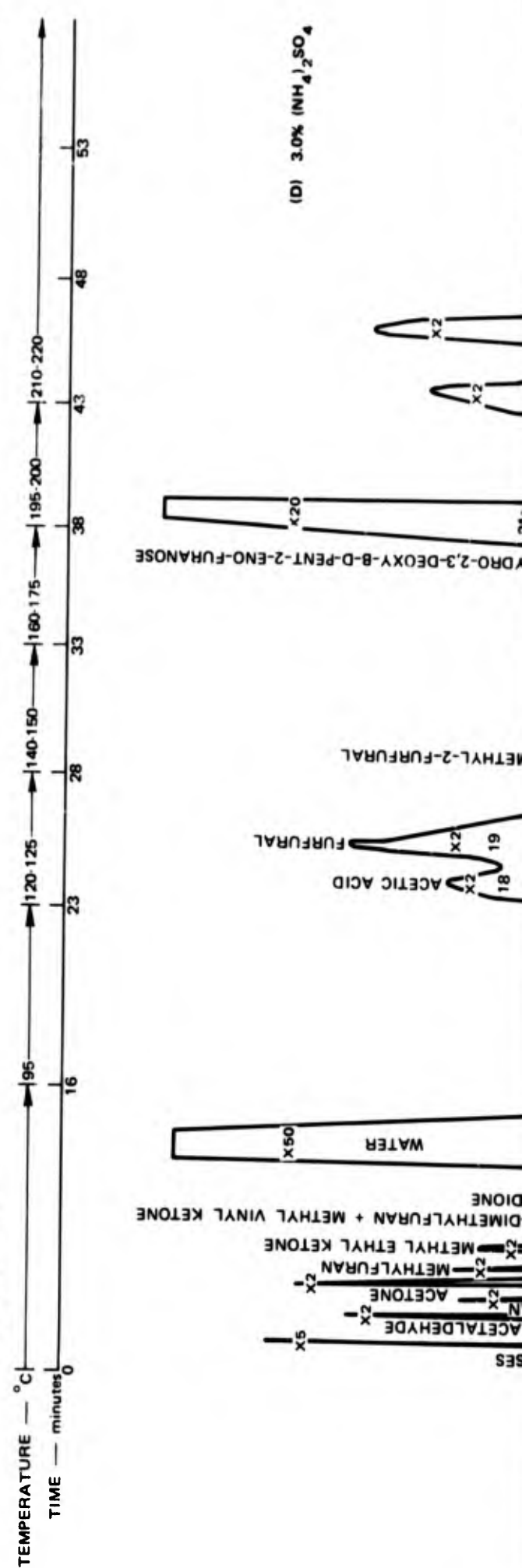
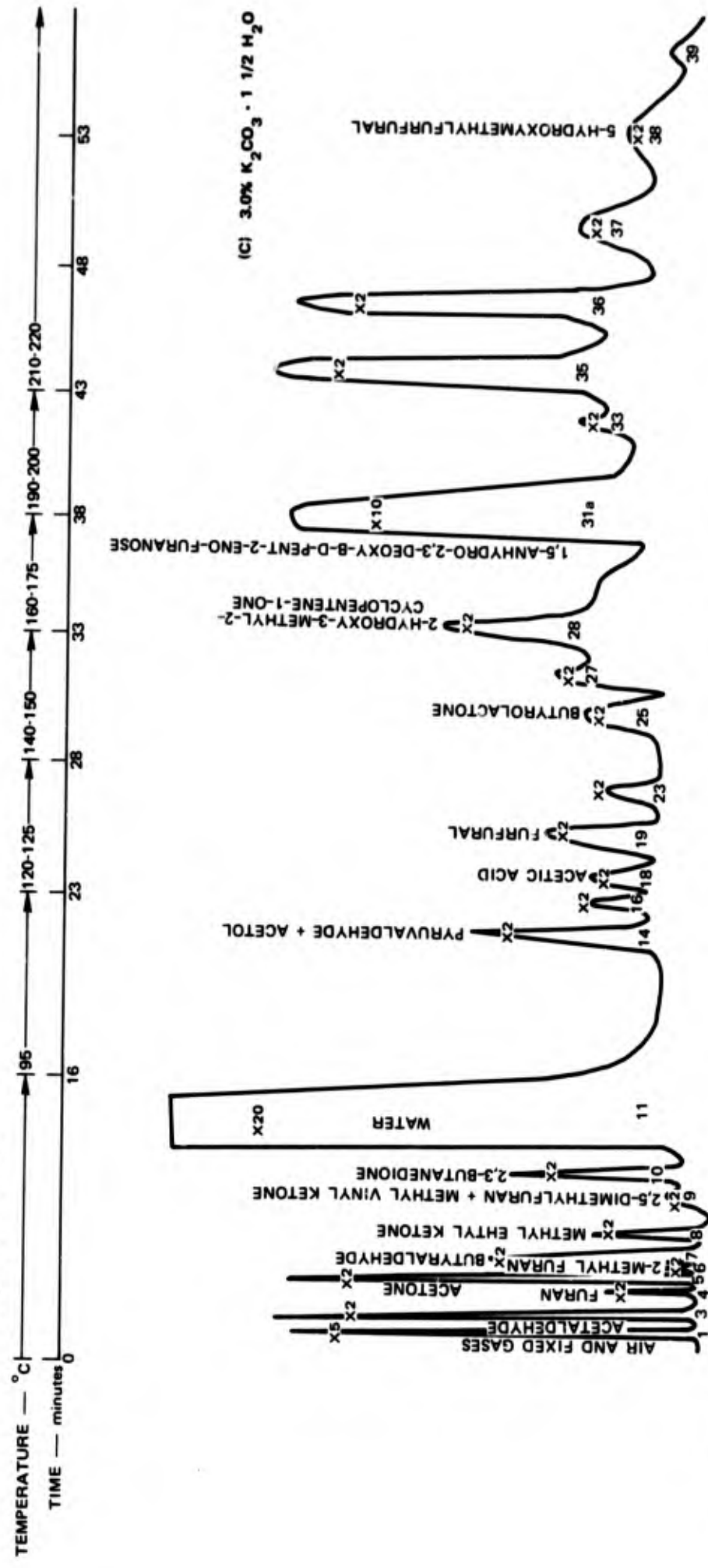
23 (5-methyl-2 furfural), and 38 (5-hydroxymethyl-furfural) also increase, while peaks 12 (cyclopentanone), 13 (cyclooctatetraene), 15, 16, 17, 21, 22, and 26 (all unidentified) are absent and all others decrease. The infrared spectrum of the tar reveals the presence of levoglucosan, but in much smaller amounts than in the products from the untreated cellulose. The CO to CO<sub>2</sub> ratio as reported by Tsuchiya and Sumi<sup>2</sup> at 320°C is 0.16 as opposed to 0.33 from the untreated samples.

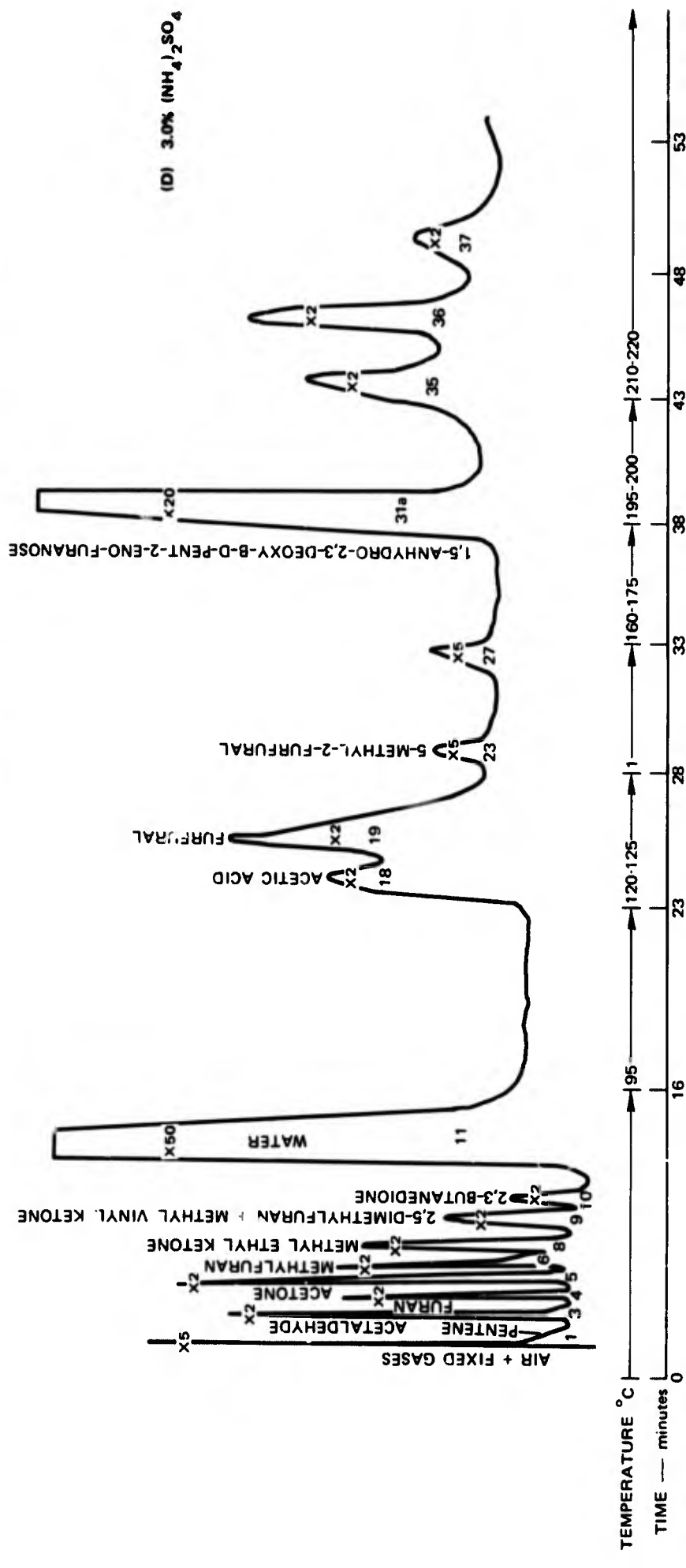
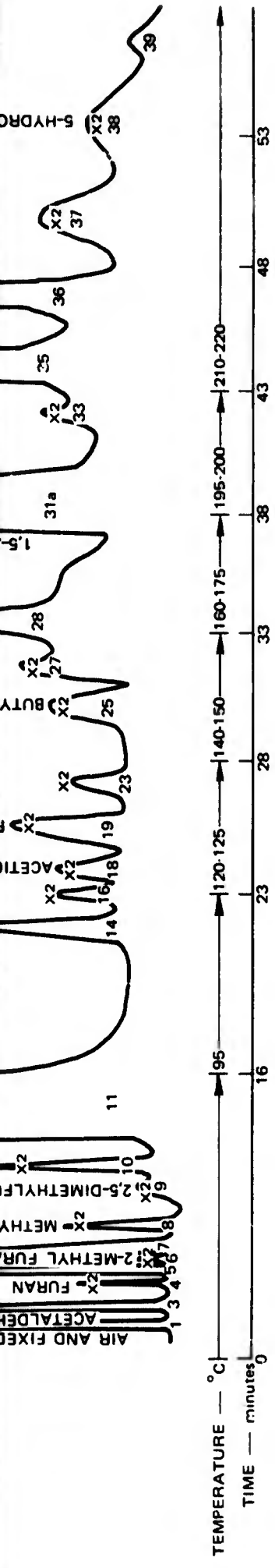
Of the three treatments tried, the 3.13% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> additive proved most effective in reducing the number of degradation products. Essentially, this treatment renders the following five dominant gc peaks: 11 (water), 14 (pyruvaldehyde + acetol), 18 (acetic acid), 19 (furfural), and 31a (the furanose derivative). Water and the furanose derivative are the most abundant. Levoglucosan has also been detected via infrared spectrophotometry, but in a smaller amount than from the untreated samples. These results are in excellent agreement with the previously reported work on NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>-treated samples, suggesting that the furanose derivative may be produced in substantial quantities in the presence of any acid types of additives.

D. Effect of Basic and Acidic Additives  
on the Pyrolysis Products of Levoglucosan

Figure 12 a-d shows chromatograms of the degradation products from untreated, 3.0% K<sub>2</sub>CO<sub>3</sub> · 1-1/2 H<sub>2</sub>O-treated, and 3.0% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-treated levoglucosan. For the sake of comparison, a chromatogram of the degradation products from untreated cellulose is included. The untreated cellulose renders more products than levoglucosan; however, the amount of the furanose derivative is substantially greater from the levoglucosan than from the cellulose. All products from the levoglucosan are also found among the products from cellulose. The K<sub>2</sub>CO<sub>3</sub> · 1-1/2 H<sub>2</sub>O-treated levoglucosan shows additional peaks, all of which are found among those from cellulose. These are peaks 18 (acetic acid), 25 (butyrolactone), 33 (unknown),







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FIGURE 12 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS FROM UNTREATED CELLULOSE, UNTREATED LEVOGLUCOSAN, AND BASIC AND ACIDIC-SALT-TREATED LEVOGLUCOSAN

38 (5-hydroxymethylfurfural), and 39 (unknown). The  $(\text{NH}_4)_2\text{SO}_4$ -treated levoglucosan produces the highest amount of the furanose derivative compared with the  $\text{K}_2\text{CO}_3 \cdot 1\frac{1}{2} \text{H}_2\text{O}$ -treated and the untreated levoglucosan. In addition, there is evidence of furfural and 5-methyl-2-furfural as well as compounds that are eluted off the chromatographic column before water.

These findings combined with the results of previous studies on the effects of retardants on the degradation of cellulose suggest that many of the observed degradation products result from decomposition of the primary and secondary pyrolysis products of cellulose. Furthermore, the possibility that retardants cause the levoglucosan to decompose rather than prevent its formation should not be overlooked.

E. The Effect of Basic and Acidic Additives on the Degradation of 1,5-Anhydro-2,3-Deoxy- $\beta$ -D-Pent-2-Eno-Furanose

The pyrolysis of the furanose derivative in He in both the neat form and in the presence of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{K}_2\text{CO}_3 \cdot 1\frac{1}{2} \text{H}_2\text{O}$  rendered similar results, confirming earlier reported findings that the compound degrades to water, char, oxides of carbon, and traces of acetaldehyde, acrolein, and acetone. Much of the compound remains undecomposed and is eluted off the column as such. The additives considerably increase the amounts of char and water and eliminate the lower organics. These results support the contention that the excess yield of char in retardant-treated cellulose is caused by the degradation of secondary products of cellulose decomposition rather than of the cellulose molecule itself.

#### IV CONCLUSIONS AND RECOMMENDATIONS

The conclusions of this study are as follows:

1. The differences in pyrolytic behavior of Whatman 541 Filter Paper and the cellulose used in this laboratory are caused at least in part by differing procedures used in the preparation of the material as well as by the residual mineral content. As a preliminary test of the breadth of applicability of the Parker-Lipska method in guiding the selection of fire retardants, comparative studies should be extended to include cotton and the most widely used synthetics.
2. The effectiveness of the fluidized-bed technique for isothermal kinetic studies was validated by identical degradation rates of 0.0043-in.- and 0.030-in.-thick cellulose samples at 315°C.
3. The presence of oxygen, even in low concentrations, will increase the rate of decomposition in the initial period of pyrolysis. To determine whether the previously reported initial rapid weight and monomer loss are caused by adsorbed oxygen on the surface of the samples, the degradation of cellulose should be investigated directly in the time-of-flight mass spectrometer where effects of atmospheric oxygen may be totally excluded. The importance of such oxidatively catalyzed pyrolysis reactions should be considered in all practical situations of ignition and combustion of cellulose.
4. Measurements of monomer loss, weight loss, and changes in the degree of polymerization in pyrolyzed cellulose treated with basic and neutral additives show that the overall pattern of decomposition is similar to that of the untreated samples. The pyrolytic decomposition of samples treated with acidic retardants takes on a different characteristic, where the cellulose is lost by a more nearly first-order than zero-order process. Furthermore, the results suggest that the extremely rapid decomposition rates of the acidic-salt-treated samples may be caused by combined effects of hydrolysis and pyrolysis. Modification of the mathematical expression used to calculate the increase in rate of degradation of cellulose treated with additives entails estimating hydronium-ion

concentrations, which, unfortunately, cannot be done in a rigorous theoretical way. The action of the basic, neutral, and acidic additives on cotton and synthetics should be investigated to determine whether the Parker-Lipska method of predicting the rates of degradation resulting from the action of retardants may be extended to materials other than cellulose.

5. Measurements relating to the effect of additives on char production show that each retardant has an optimal add-on weight of about  $2 \times 10^{-4}$  mols/g of cellulose. The total negative valence concept appears to be an approximate empirical device, at best, but no alternative basis for predicting char production can be offered at this time. The ratio  $\Delta C/\Delta R$  is proposed as an interim figure of merit of retardant performance.
6. Results of the gc/ms and IR analyses of the degradation products of the variously treated cellulose show that the acidic salt treatment was most effective in reducing the number of volatile products and in increasing the amount of the furanose derivative. Levoglucosan was absent from the degradation products of  $K_2CO_3 \cdot 1-1/2 H_2O$ -treated samples and substantially decreased in quantity in the KBr- and  $(NH_4)_2SO_4$ -treated samples. The CO/CO<sub>2</sub> ratio as reported by others<sup>2</sup> is 1.14 in the  $K_2CO_3 \cdot 1-1/2 H_2O$ -treated samples as opposed to 0.33 in the untreated samples and 0.16 in the KBr-treated samples. The CO/CO<sub>2</sub> ratio was not determined for the  $(NH_4)_2SO_4$ -treated samples, but the closely related  $NH_4H_2PO_4$  treatment resulted in a ratio of 0.42. Future emphasis should be placed on determination of the degradation products of untreated and retardant-treated cotton and synthetic materials.
7. The pyrolysis products of untreated and retardant-treated levoglucosan closely parallel those from untreated and retardant-treated cellulose. This suggests that many of the observed degradation products result from decomposition of the primary and secondary pyrolysis products of cellulose rather than direct decomposition of the cellulose molecule itself.
8. The furanose derivative degrades primarily into water, char, some lower organics, and oxides of carbon. Additives increase the amount of char and water and eliminate the

lower organics. These findings support the contention that the excess yield of char in retardant-treated cellulose results from the degradation of secondary products of cellulose decomposition rather than of the cellulose molecule itself.

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