

The Effect of Inorganic Additives on the Formation, Composition, and Combustion of Cellulosic Char

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Synopsis

At temperatures above 300°C the glycosyl units of cellulose are simultaneously depolymerized to a tar and decomposed to a char by evolution of H₂O, CO, and CO₂. When the glycosyl units are depleted, a stable char is formed containing about 30% aliphatic and 70% aromatic components. The aliphatic component is formed first, but on further heating is converted to polycyclic aromatic structures. The chars formed at lower temperatures are more combustible because the aliphatic component of the char is highly pyrophoric and is oxidized almost at the same temperature at which it is formed (~360°C). The aromatic component, however, is less reactive and is oxidized at ~520°C. Consequently, the chars formed at higher temperatures are less combustible. It has been shown that (NH₄)₂HPO₄, which is a well-known flame retardant and smoldering inhibitor, lowers the pyrolysis temperature and increases the char yield by accelerating the decomposition reactions. This affects the composition of the intermediate chars but the final products have about the same composition irrespective of additives. (NH₄)₂HPO₄ also lowers the rate of oxidation of the aromatic component and the corresponding heat release. NaCl, which is an enhancer of smoldering combustion, has a slight stabilizing effect on pyrolysis of cellulose. It lowers the oxidation temperature of the aromatic component and dramatically increases its rate. The corresponding heat release is also increased due to complete oxidation to CO₂. The rate of oxidation calculated from the dynamic thermal analysis data is more than tripled by NaCl and significantly reduced by (NH₄)₂HPO₄.

INTRODUCTION

A variety of inorganic materials are used for suppression of flaming and smoldering combustion of cellulosic materials. Flaming combustion involves gas phase oxidation of the volatile pyrolysis products, and smoldering combustion involves solid phase oxidation of chars remaining after evaporation of the volatile products. Both of these processes involve complex interactions between chemical reactions and heat, and mass transport. The nature and rates of the chemical reactions change with the temperature and are also affected by inorganic catalysts or additives. Pyrolysis of cellulose proceeds by two alternative pathways, involving decomposition of the glycosyl units to char, which dominates at lower temperatures, and depolymerization of these units to volatile tarry products containing levoglucosan, which dominates at higher temperatures.¹⁻⁴ Flame retardants enhance the dehydration, rearrangement, decarboxylation, and decarbonylation which produce water, carbon monoxide, carbon dioxide, and char at the expense of the combustion volatiles. Thus, they reduce the amount of fuel available in the gas phase as well as its heat of combustion or flammability.⁵⁻⁷

The effects of inorganic additives on smoldering combustion, however, is quite different and more complex, particularly in view of the fact that some of the flame

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retardants and inorganic materials in general enhance while others suppress this process. Therefore, mechanisms of the enhancement or suppression of smoldering combustion are not well established. So far it has been shown that smoldering combustion of cellulosic materials involves pyrolysis of the substrate to form a highly reactive char, characterized by a large surface area and high concentration of free radicals; chemisorption of oxygen on the reactive sites of the char which is highly exothermic takes place at relatively low temperatures; and gasification or decomposition of the surface oxides to form CO and CO₂ generate new reactive sites for propagation of the combustion process. Propagation is highly sensitive to the rate of heat release that provides the required driving force.⁶⁻¹⁰ An exact definition of the chemical reactions, however, has proven to be more difficult because composition and reactivity of the charred material involved in these reactions are affected by the prevailing time and temperature profile and the presence of inorganic additives.

In the previous articles in this series it was shown that during pyrolysis, decomposition of the glycosyl units in cellulose provides aliphatic and aromatic groups. The aliphatic groups consist of paraffinic, carbonyl, and carboxyl functionalities. As the pyrolysis proceeds, the concentration of glycosyl units is gradually reduced to zero, forming the aliphatic and aromatic components. On further heating, the aliphatic groups, which are less stable than the aromatic groups, are preferentially decomposed, and condensation and crosslinking of the residue forms a char composed predominantly of polycyclic aromatic structures, carrying a high concentration of resonance stabilized free radicals.^{11,12}

A combination of thermal, chemical, and spectroscopic investigation of chars formed at different temperatures and having differing proportions of aliphatic and aromatic structures indicated that they are oxidized at two distinct exothermic stages. The first exotherm at about 360°C corresponds with oxidation of the aliphatic components, and the second exotherm at about 520°C corresponds with the oxidation of the more stable aromatic structures.¹³

This article shows the effect of inorganic additives on the formation, structure, and reactivity of cellulosic chars, particularly the effect of inorganic materials on the rate of oxidation of the aliphatic and aromatic components of cellulosic chars. This in turn indicates the effect of inorganic additives on the enhancement or suppression of smoldering combustion of cellulosic materials.

EXPERIMENTAL

Acid-washed cellulose powder (Whatman CF-11) was used as the substrate. Pyrolysis was carried out in a preheated furnace for 5 min at temperatures ranging from 325°C to 600°C, under flowing nitrogen (60 mL/min), following the procedure described in a previous paper¹¹ from our laboratory. The cellulose powder was treated to a level of 1.0 mol additives [NaCl or (NH₄)₂HPO₄]/100 mol anhydroglucose units by suspension in aqueous solution. This suspension was dried slowly in a stream of air while agitating. When the majority of water was removed, the pastelike sample was dried overnight at 60°C under vacuum. After drying, the treated sample was ground by pestle and mortar and redried under vacuum at 60°C for 3 h. The chars prepared at 350°C and 500°C in N₂ were also treated and dried using the same procedure described above, except for the concentration of additives (8% of char weight).

The cross polarization/magic angle spinning (CP/MAS) ^{13}C -NMR spectroscopy was carried out at 37.7 MHz with a Nicolet NT-150 Spectrometer, a home-built CP/MAS probe, using 0.4 cc of powdered sample. A pulse repetition time of 1.0 sec and contact time of 1 ms were used, and 5000–15,000 scans were accumulated. Experimental details are described in the previous paper.¹²

Thermogravimetry (TG) was carried out using a Cahn R-100 Electric Balance equipped with a time derivative computer. Samples (1.7 mg) were heated at a rate of 10°C/min under flowing air or nitrogen (25 mL/min). A DuPont Model 990 Thermal Analyzer was used for temperature control of the TG furnace and for differential scanning calorimetry (DSC) under the same conditions.

Infrared spectra were recorded on a Nicolet MX-1 Fourier Transform Infrared Spectrometer (FTIR) using potassium bromide discs containing 1% (w/w) of the sample.

RESULTS AND DISCUSSION

The Effects of Inorganics on Char Formation

Investigation into the mechanism and kinetics of the pyrolysis of cellulose clearly indicates the operation of alternative pathways. The first pathway, which dominates at temperatures below 300°C, involves dehydration, rearrangement, formation of carboxyl and carbonyl groups, evolution of carbon monoxide and carbon dioxide, and formation of a carbonaceous residue.^{1,2} These reactions involve an initial induction period and are accelerated in the presence of air and with the addition of a variety of inorganic materials, particularly Lewis acids, which catalyze the dehydration reactions. The second pathway, which starts at about 300°C and overshadows the first pathway at the higher temperatures, involves cleavage of the glycosyl units by intramolecular transglycosylation and formation of anhydrosugars which evaporate. Consequently, the kinetics of pyrolysis and char formation can be expressed by a model involving the simultaneous decomposition to char, water, carbon monoxide, and carbon dioxide and depolymerization to tarry volatiles containing levoglucosan and other anhydrosugar derivatives.^{3,4} The char formed after complete disappearance of the glycosyl units (at about 400°C) is relatively stable and contains ~30% aliphatic and ~70% aromatic components. On further heating, the less stable aliphatic groups are preferentially decomposed, presumably through homolytic cleavage of C—C and C—H bonds. Combination of some of the resulting free radicals gives a highly condensed and crosslinked carbonaceous material composed mainly of polycyclic aromatic groups.^{11,12} The course of the above reaction can be followed by TG that shows the weight loss due to rapid conversion and decomposition of the glycosyl units to anhydrosugars and char, respectively, followed by gradual condensation of the residue to polycyclic aromatic compounds.

It has been shown that flame-retardant salts lower the decomposition temperature of cellulose and enhance char formation by catalyzing the dehydration and decomposition reactions.⁵⁻⁷ In this study the effects of $(\text{NH}_4)_2\text{HPO}_4$, which is a well-known flame retardant and smoldering inhibitor, have been compared with the effects of NaCl which acts as a strong smoldering enhancer. Figure 1 shows the TG in N_2 of cellulose samples before and after treatment with these salts. The sample containing $(\text{NH}_4)_2\text{HPO}_4$ is decomposed at lower temperatures

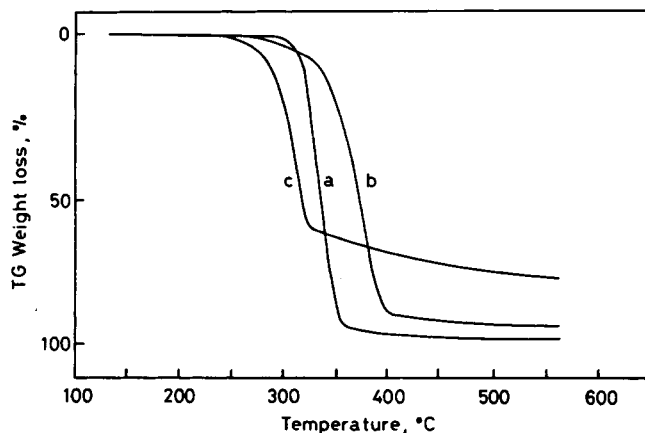


Fig. 1. Thermal analysis in N_2 of cellulose treated with: (a) none; (b) NaCl; (c) $(NH_4)_2HPO_4$.

than pure cellulose and leaves more char. This occurs because $(NH_4)_2HPO_4$ is decomposed to NH_3 , $(NH_4)H_2PO_4$, and H_3PO_4 on heating.^{14,15} The highly acidic reagents which result catalyze hydrolysis and decomposition of the cellulose. The NH_3 facilitates decomposition by reacting with intermediate carbonyl compounds to form glycosylamines or Schiff bases, that are readily dehydrated by a β -elimination process.^{16,17} Addition of NaCl which is a neutral salt, however, slightly increases the decomposition temperature and the char yield, as compared to pure cellulose. As the decomposition proceeds, the elemental composition of the residue changes, and becomes more carbonaceous. The yields and composition of the charred residues are given in Table I for dif-

TABLE I
Char Yield and Its Elemental Composition

Additives	Temp (°C)	Char yield (wt %)	Composition (wt %)			H/C (Atomic ratio)	O/C (Atomic ratio)
			C	H	O ^a		
Cellulose	—	—	42.8 ^b	6.5 ^b	50.7 ^b	1.82	0.88
None	300	89.4	44.0	6.4	49.6	1.74	0.84
None	325	63.3	47.9	6.0	46.1	1.50	0.72
None	350	33.1	61.3	4.8	33.9	1.03	0.43
None	400	16.7	73.5	4.6	21.9	0.73	0.18
None	450	10.5	78.8	4.3	16.9	0.65	0.17
None	500	8.7	80.4	3.6	16.1	0.53	0.15
ZnCl ₂	275	73.6	50.0	5.5	44.0	1.30	0.67
ZnCl ₂	290	49.7	57.2	4.7	38.1	0.98	0.57
ZnCl ₂	325	38.1	64.1	4.2	31.7	0.78	0.37
$(NH_4)_2HPO_4$	275	74.0	50.6	5.6	43.8	1.32	0.65
$(NH_4)_2HPO_4$	290	58.0	55.9	4.9	39.2	1.05	0.53
$(NH_4)_2HPO_4$	325	40.2	67.2	4.0	28.8	0.72	0.32
$(NH_4)_2HPO_4$	400	28.9	72.2	4.1	23.7	0.68	0.22
$(NH_4)_2HPO_4$	450	25.7	79.4	3.3	17.3	0.50	0.17
$(NH_4)_2HPO_4$	500	22.8	83.1	3.2	13.7	0.45	0.13
NaCl	290	92.8	45.9	6.0	48.1	1.56	0.79
NaCl	325	60.7	53.4	5.5	41.1	1.24	0.58
NaCl	350	35.6	59.3	5.1	35.6	1.03	0.43
NaCl	400	17.5	74.9	4.5	20.6	0.72	0.21

^a By difference.

^b Theoretical values.

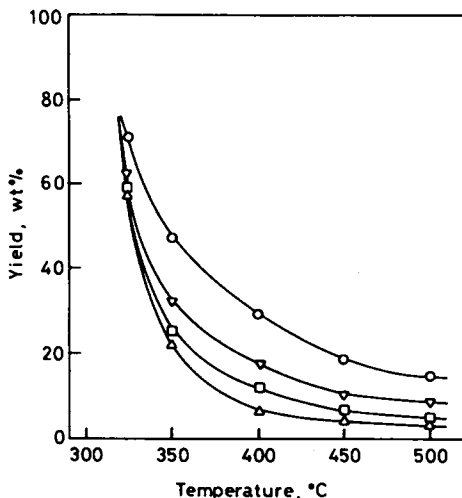


Fig. 2. Variation of char yield and its consisting elements produced from pure cellulose pyrolysis at different temperatures: (∇) char; (\circ) carbon; (\square) hydrogen; (Δ) oxygen.

ferent temperatures and additives. Figure 2 shows the loss of the elemental components at different stages of pyrolysis, compared to the total weight loss. The differences in this figure are due to loss of H_2O , CO , CO_2 , and H_2 at different stages of pyrolysis, which change the ratio of H/C and O/C. These ratios are calculated from the analyses of chars formed from cellulose with and without inorganic salts at different temperatures, and the results are plotted in Figure 3 along with theoretical lines formed by straight dehydration. These data show three different trends during the char formation. First, there is a straight line due to decomposition, predominantly by dehydration reactions. This is followed by an increased loss of oxygen due to evolution of CO and CO_2 at the middle stage and finally a third stage showing an increased loss of hydrogen due to decomposition of the aliphatic groups and condensation to polycyclic aromatic compounds. The dehydration process proceeds much faster with samples containing $(\text{NH}_4)_2\text{HPO}_4$ and ZnCl_2 ¹⁸ than with either pure cellulose or cellulose containing

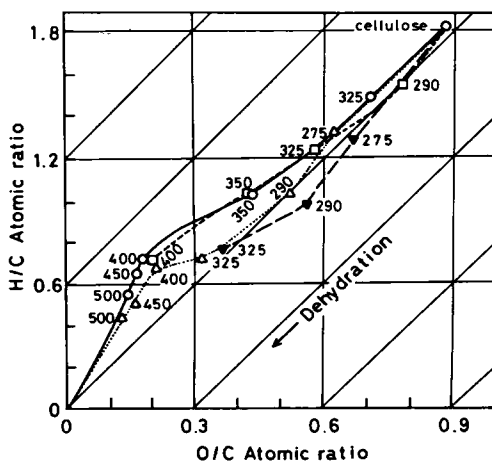


Fig. 3. Relationship between H/C and O/C atomic ratio of chars prepared from treated and untreated cellulose in N_2 at temperatures noted: (\circ) none; (\square) NaCl ; (Δ) $(\text{NH}_4)_2\text{HPO}_4$; (\blacktriangledown) ZnCl_2 .

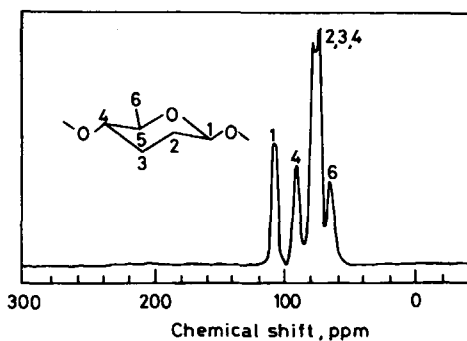


Fig. 4. CP/MAS ^{13}C -NMR spectrum of pure cellulose.

NaCl. It can be seen from Figure 3 that towards the end of the pyrolysis composition of the chars become similar, irrespective of the additives.

The Effects of Inorganics on Char Composition

The inorganic additives affect not only the decomposition temperature and char yield but also the composition of the intermediate chars. The latter effects have been studied by CP/MAS ^{13}C -NMR of chars prepared at different temperatures (Figs. 4–9). Figure 4 shows the spectrum of original cellulose. It

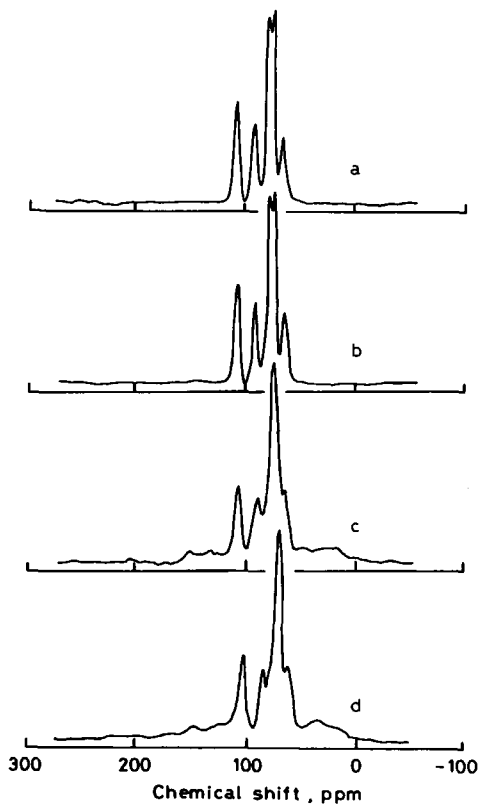


Fig. 5. CP/MAS ^{13}C -NMR spectra of chars prepared at 275°C in N_2 from cellulose treated with: (a) none; (b) NaCl; (c) $(\text{NH}_4)_2\text{HPO}_4$; (d) ZnCl_2 .

consists of several resonance peaks at 60–110 ppm associated with the carbon chain of glycosyl units. The carbons at positions 1, 4, and 6 show distinct peaks, and those at 2, 3, and 5 show larger overlapping peaks.¹²

On heating at 275°C, untreated and NaCl-treated cellulose samples showed little weight loss (by TG) and indicated no changes in the NMR spectra (Fig. 5). However, the ZnCl₂- and (NH₄)₂HPO₄-treated cellulose samples showed a large weight loss of about 25% (see Table I), and the NMR spectra revealed broad peaks at 0–60 ppm and 110–210 ppm, on both sides of the glycosyl units corresponding to newly formed functionalities, which will be described later. These peaks became more pronounced on further heating.

On heating at 290°C the untreated and NaCl-treated samples gave 10% weight loss. However, the concentration of new functionalities formed from decomposition of the glycosyl units was not sufficient to show discernable changes in the NMR spectra of the residues (see Fig. 6). The ZnCl₂- and (NH₄)₂HPO₄-treated cellulose showed 50% and 42% weight losses, respectively. Furthermore, their NMR spectra contained distinct resonance peaks at 0–60, 110–190, and 170–220 ppm for paraffinic, aromatic, and oxygenated (—CO and —COO—) groups, respectively. At this stage the residues contained about 44% glycosyl groups, 25% aliphatic, 25% aromatic, and 6% oxygenated groups.

On heating at 325°C the untreated and NaCl-treated cellulose samples lost 37% and 39% of their weight, respectively, and their NMR spectra showed two minor new peaks due to decomposition products, similar to those in the spectra

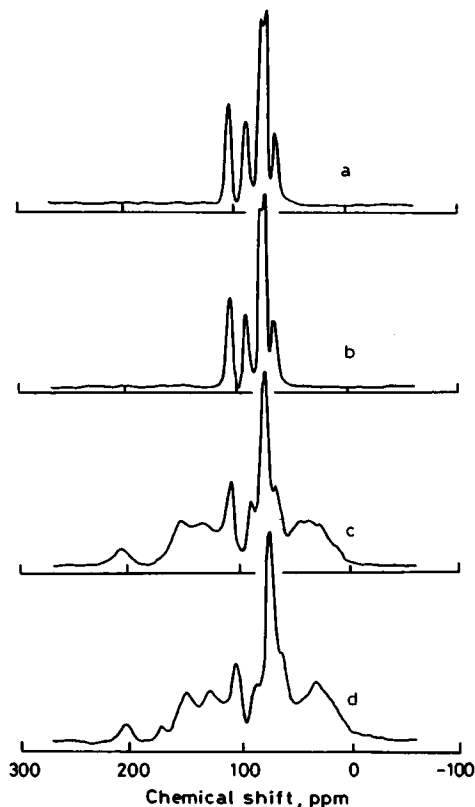


Fig. 6. CP/MAS ¹³C-NMR spectra of chars prepared at 290°C in N₂ from cellulose treated with: (a) none; (b) NaCl; (c) (NH₄)₂HPO₄; (d) ZnCl₂.

of ZnCl_2 - and $(\text{NH}_4)_2\text{HPO}_4$ -treated samples after heating at 275°C . On the other hand, the ZnCl_2 - and $(\text{NH}_4)_2\text{HPO}_4$ -treated samples showed 60% weight loss, and the NMR spectra of the residual chars showed only 10–20% glycosyl units but 30% paraffinic, 45% aromatic, and 10% oxygenated functional groups (Fig. 7 and Table II).

As shown in Tables I and II, this trend continued on heating at 350°C (Fig. 8) when the glycosyl units of the sample containing $(\text{NH}_4)_2\text{HPO}_4$ were almost depleted, whereas pure cellulose and the sample treated with NaCl contained 31% and 52% glycosyl units, respectively. The higher glycosyl content of the latter sample confirms the stabilization effect of NaCl discussed before. NaCl also shows unusual effects during oxidation of the char discussed later and in the formation of hydroxybenzene compounds on pyrolysis under vacuum.¹⁹

On further heating at 400°C , the char from the $(\text{NH}_4)_2\text{HPO}_4$ -treated sample showed relatively little change. The char from pure and NaCl -treated samples, however, showed a major change and the composition of all these chars eventually becomes similar (see Fig. 9). The changes in composition of chars prepared with and without additives at different temperatures are shown in Figure 10. These data show that the inorganic additives affect the decomposition range of the sample as well as the composition of the intermediate chars. However, there is little or no discernible difference in the chemical composition of the final products.

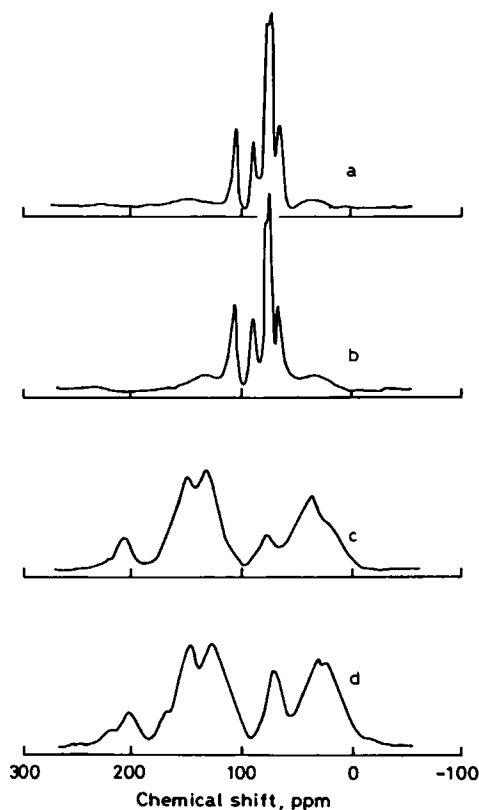


Fig. 7. CP/MAS ^{13}C -NMR spectra of chars prepared at 325°C in N_2 from cellulose treated with: (a) none; (b) NaCl ; (c) $(\text{NH}_4)_2\text{HPO}_4$; (d) ZnCl_2 .

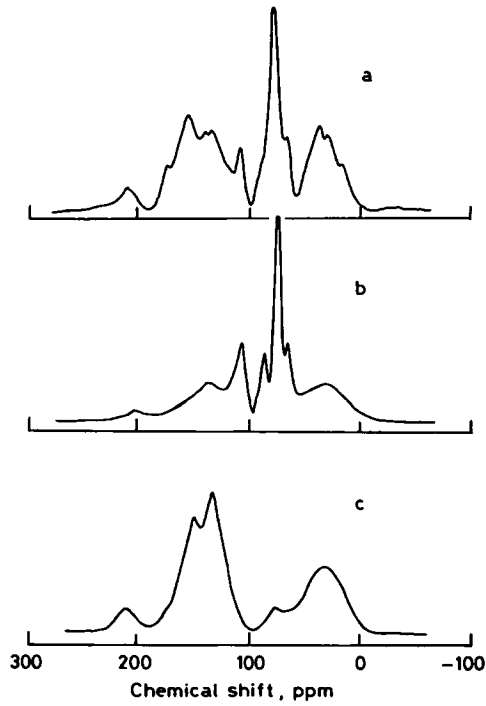


Fig. 8. CP/MAS ^{13}C -NMR spectra of chars prepared at 350°C in N_2 from cellulose treated with: (a) none; (b) NaCl; (c) $(\text{NH}_4)_2\text{HPO}_4$.

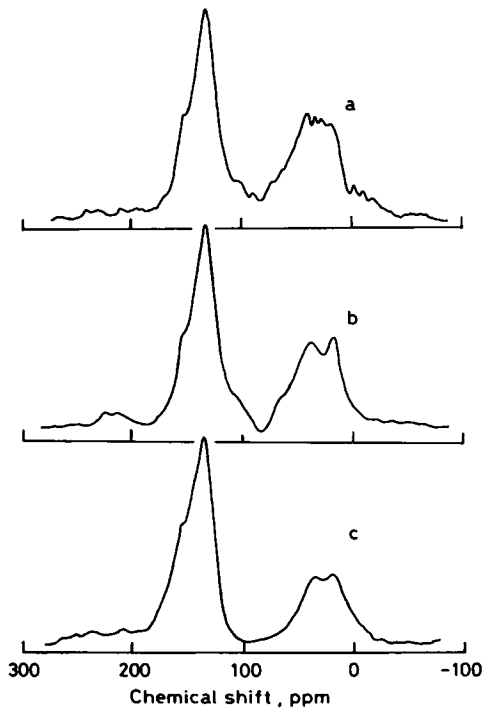


Fig. 9. CP/MAS ^{13}C -NMR spectra of chars prepared at 400°C in N_2 from cellulose treated with: (a) none; (b) NaCl; (c) $(\text{NH}_4)_2\text{HPO}_4$.

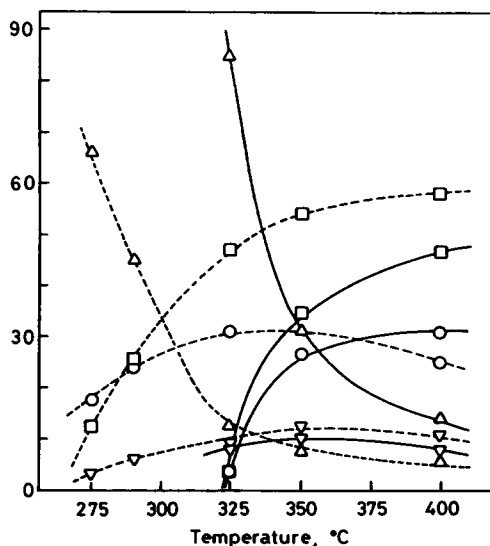


Fig. 10. Distribution of functionalities in chars prepared from cellulose treated with $(\text{NH}_4)_2\text{HPO}_4$ (---) and none (—): (Δ) glycosylic; (O) paraffinic; (\square) aromatic; (∇) C=O and COO.

Similar results were obtained by comparing the FTIR spectra of chars prepared from cellulose samples before and after treatment with $(\text{NH}_4)_2\text{HPO}_4$ at various temperatures. The IR spectra (Fig. 11) show absorption bands for OH at ~ 3500 , glycosyl C—O at 900, C=C at 1600, and C=O at 1700 cm^{-1} . These data indicate

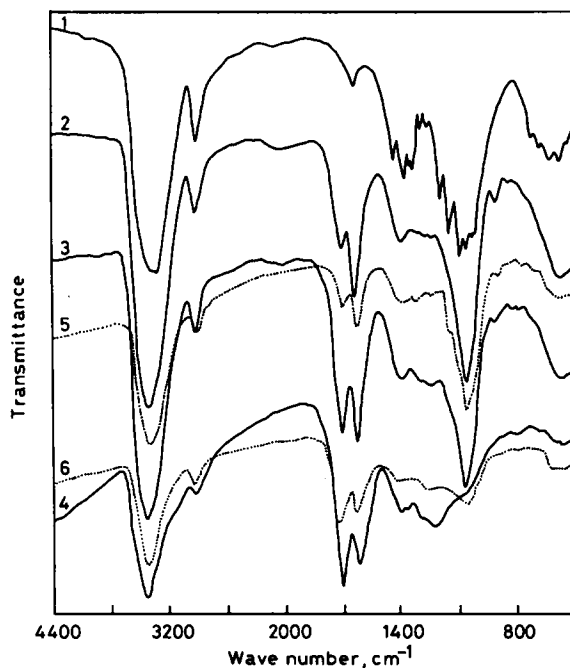


Fig. 11. FTIR spectra of chars in N_2 at (1) room temperature, (2) 275°C , (3) 290°C , and (4) 325°C from cellulose treated with $(\text{NH}_4)_2\text{HPO}_4$; (5) 325°C and (6) 350°C from untreated cellulose.

the gradual disappearance of the OH and C—O bands of the glycosyl units and the appearance of C=C and C=O bands of the decomposition products (since particle size affects the resolution of the spectra in the region of 2500–4000 cm^{-1} , the region in which the OH stretch occurs is somewhat obscured in the higher temperature samples). These spectra show that the state of decomposition of the treated sample at 275°C is similar to the state of decomposition of the untreated sample at 325°C (also see Figs. 5 and 7). However, the differences in the state of decomposition of the various char samples disappear at 400°C when all the glycosyl units are depleted, and a relatively “stable” char is formed that has approximately the same IR spectrum, irrespective of treatment with additives (see Fig. 12).

The Effect of Inorganics on Combustion

In the total combustion of cellulosic materials, the substrate is partially converted to volatiles that burn in the gas phase (flaming combustion) and partially converted to char that burns in the solid phase (smoldering or glowing combustion). The contributions to the latter process, before and after treatment with inorganic materials, can be studied by thermal analysis. Figure 13 shows the TG and DSC in flowing air of cellulose samples before and after treatment with $(\text{NH}_4)_2\text{HPO}_4$ and NaCl. TG curves show rapid weight loss due to evaporation of the pyrolysis products. This is superimposed upon and followed by a slower weight loss due to oxidation of the charred residues. The difference between pyrolytic and oxidation weight loss can be discerned by comparison with TG in flowing nitrogen (Fig. 1). The corresponding DSC curves show the heat release due to oxidative gasification of the chars as two exotherms. A combination of

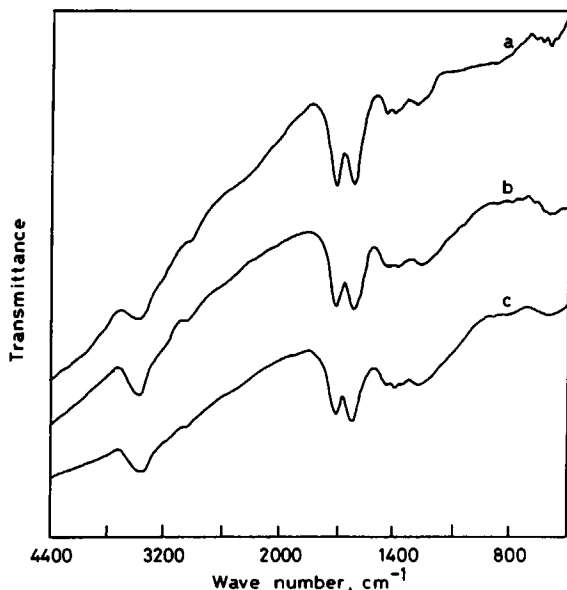


Fig. 12. FTIR spectra of chars prepared at 400°C in N_2 from cellulose treated with: (a) none; (b) NaCl; (c) $(\text{NH}_4)_2\text{HPO}_4$.

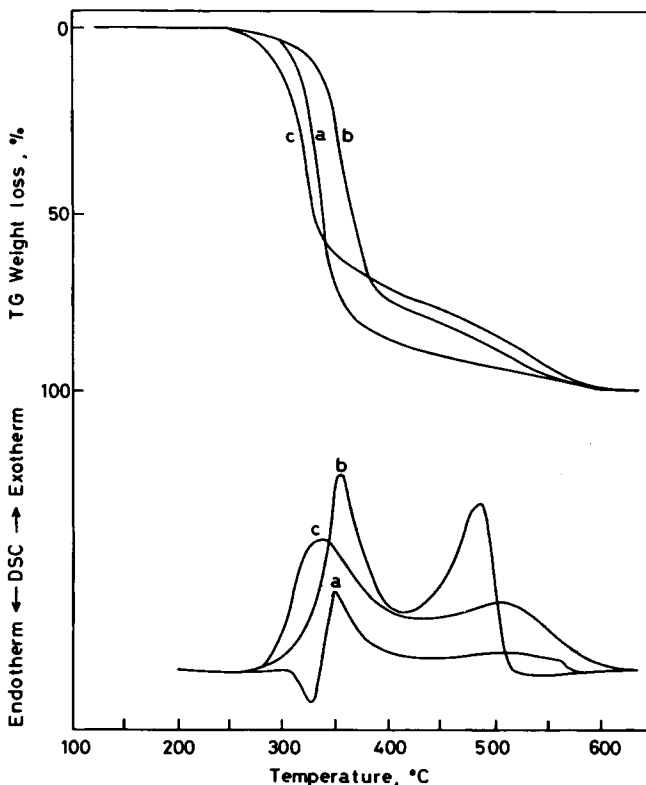


Fig. 13. Thermal analysis in air of cellulose treated with: (a) none; (b) NaCl; (c) $(\text{NH}_4)_2\text{HPO}_4$.

chemical, spectroscopic, and thermal analyses has shown that these exotherms which normally peak at about 360°C and 520°C are associated with combustion of the aliphatic and aromatic component of the char, respectively.¹³ Figure 13 shows that the inorganic additives affect the decomposition temperature and amount of char formed in air (TG curves), the distribution of the heats of combustion of the cellulosic materials between the gas phase (flaming) and solid phase (smoldering or glowing) combustion, and the combustion properties of the chars (DSC curves). Pure cellulose forms mostly combustible volatiles that contribute to the flaming combustion, and the small amount of char that is formed is oxidized mainly at the first exotherm. The sample containing $(\text{NH}_4)_2\text{HPO}_4$ is decomposed at lower temperatures and forms more char. The chars that are formed start to oxidize immediately, and thus the combustion and heat release start earlier. The rate of oxidation, however, is slower, and the heat release is distributed between two broad peaks covering a wide area. The situation is quite different for the sample containing NaCl. It is decomposed at slightly higher temperatures; but the rate of oxidation is much faster, and the heat release is distributed between two sharp and closely spaced exotherms. The difference is particularly pronounced for the second exotherm, which is much sharper and peaks at a lower temperature than that of untreated and $(\text{NH}_4)_2\text{HPO}_4$ -treated samples.

In the previous studies derivative thermogravimetry (DTG) was used to show the effect of inorganics on the rates of weight loss.²⁰ These data showed two peaks. The first peak corresponds to the rate of weight loss due to both the evaporation of the volatiles and the almost simultaneous oxidation of the aliphatic components of the char. The second peak shows the rate of weight loss due to oxidation of the aromatic component of the char. The results clearly showed that the combustion process is affected differently by various additives, but a more precise interpretation of the results awaited the structural determination of the charred residue and DSC studies.

Since, as discussed already, the amounts of char formed from the cellulose samples vary according to the treatment to show the exact effect of the additives on combustion of the char, several experiments were carried out using the same amounts of char rather than the same amounts of cellulose. Thermal analysis during oxidation of char (prepared at 350°C) with and without the additives, is shown in Figure 14. This figure shows several effects. Total heat release is increased by addition of NaCl and reduced by addition of $(\text{NH}_4)_2\text{HPO}_4$, despite the fact that the same amount of char is used. This difference is due to oxidation of the char producing a mixture of CO and CO_2 . The heat of formation of CO_2 is -94.1 kcal/mol vs. -26.4 kcal/mol for CO.²⁰ NaCl, which is known to be a smoldering combustion enhancer, reduced the ratio of CO/ CO_2 , and this gen-

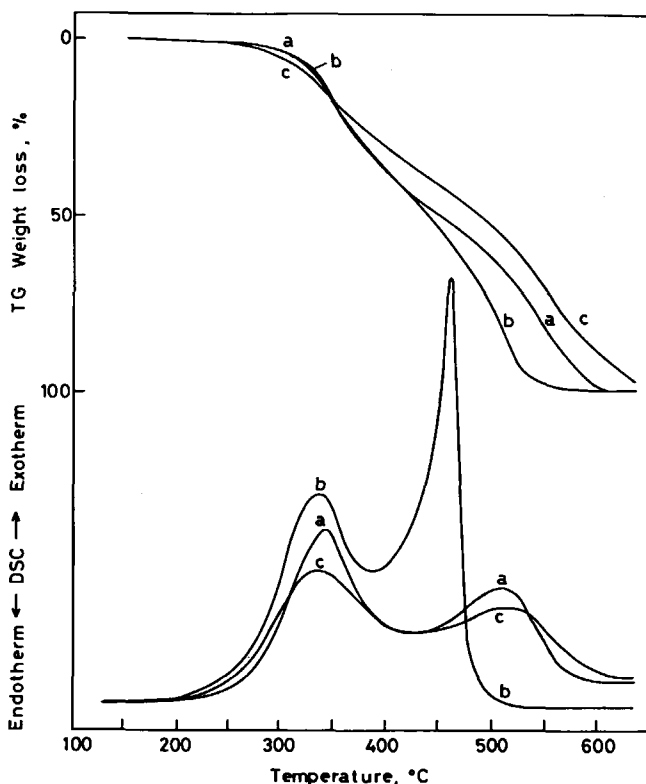


Fig. 14. Thermal analysis in air of chars prepared at 350°C in N_2 treated with: (a) none; (b) NaCl; (c) $(\text{NH}_4)_2\text{HPO}_4$.

erates more heat, while the reverse is true for $(\text{NH}_4)_2\text{HPO}_4$. This effect is more pronounced if one considers the volatiles formed from pyrolysis of the remaining glycosyl units in the chars, which are 52%, 31%, and 5% for the char containing NaCl, no additive, and $(\text{NH}_4)_2\text{HPO}_4$, respectively.

In earlier studies the first exotherm was assigned to combustion of the volatiles,^{2,21,22} before it was shown by CP/MAS ^{13}C -NMR studies that it is due to oxidation of the aliphatic components of the char. This conclusion was confirmed by comparing the DSC curves for cellulose (Fig. 13) and chars prepared at 350°C (Fig. 14) in the absence of additives. This comparison shows that the heat release at the first exotherm is proportional to the amount of the char (with its aliphatic components) rather than the volatiles formed by pyrolysis. Figure 14 also shows the strong catalytic effect of NaCl on combustion of the aromatic components of the char at the second exotherm, forming a very sharp peak centered at $\sim 450^\circ\text{C}$ instead of 520°C .

The above experiment was also carried out with chars prepared at 500°C , because the chars prepared at this temperature have a similar structure and are predominantly (90%) composed of polycyclic aromatic groups. Furthermore, since the temperature of the smoldering front is about 500°C , combustion of these chars provides a better simulation of the smoldering combustion. The results presented in Figure 15 indicate an absence of pyrolytic weight loss (decomposi-

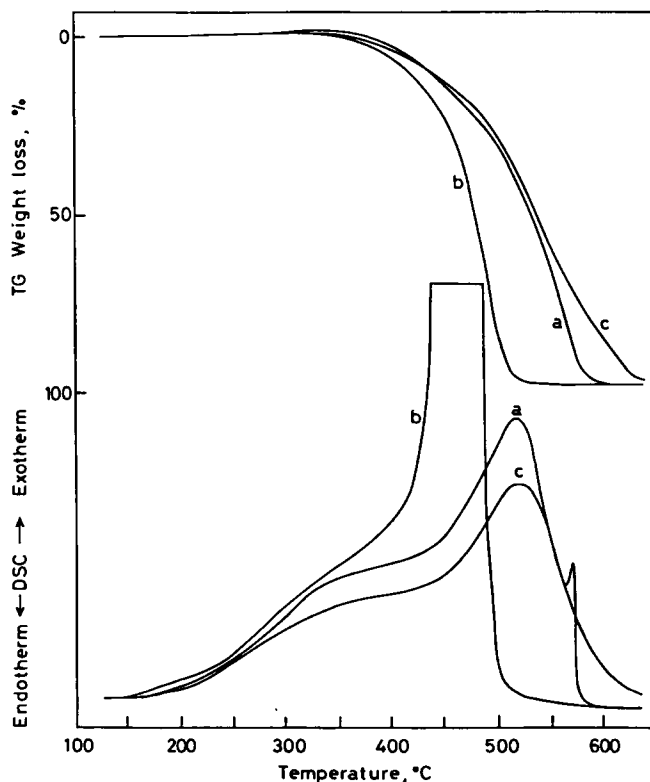


Fig. 15. Thermal analysis in air of chars prepared at 500°C in N_2 treated with: (a) none; (b) NaCl; (c) $(\text{NH}_4)_2\text{HPO}_4$.

tion of the glycosyl units). Furthermore, the first exotherm due to oxidation of the aliphatic components of the char appears merely as a shoulder, whereas the weight loss and exotherm due to oxidation of aromatic components, which form the bulk of these chars, are proportionately more pronounced.

For the char from untreated cellulose this exotherm is centered at 520°C. In addition to this, this sample also exhibits a small but sharp exotherm at about 560°C. This exotherm is probably due to accumulated impurities contained in the original cellulose, because it disappears on washing with 10% HCl solution. For chars prepared at temperatures between 600°C and 800°C the first exotherm completely disappears even as a shoulder and the second exotherm shifts to slightly higher temperatures.⁸ This shows that the reactivity of the chars is reduced as their production temperatures are increased. The sample containing NaCl gives a larger and very sharp exotherm centered at about 450°C, indicating that NaCl has lowered the combustion temperature and has increased both the rate and the amount of heat release. This increased rate of oxidation and weight loss is also apparent from the TG curve. The exotherm and weight loss of the (NH₄)₂HPO₄-treated sample are very similar to those of the untreated samples except that the rate of oxidation and the amount of heat release is considerably lower.

The variation in the amount of heat release as mentioned before is due to the changes in the ratio of CO:CO₂ as the combustion products. It has already been shown that during smoldering of samples of cotton linters containing NaCl, (NH₄)₂HPO₄, and no additive, at 450°C, the ratios of CO to CO₂ evolved as oxidation products are 0.7, 1.71 and 1.01, respectively. Similarly, the rate of production of CO + CO₂ are 13.9, 2.9, and 5.7 mmol/g char·min.²⁰ These differences can account for the enhancement and suppression of the smoldering combustion by NaCl and (NH₄)₂HPO₄, respectively. It is also interesting to note that NaCl or other sodium salts are used as catalysts for gasification and combustion of carbon black and coal that contains aromatic structures.^{23,24}

For better definition of the rate of oxidation of the chars prepared at 500°C and the effect of inorganic additives, the dynamic TG curves shown in Figure 15 were analyzed by the method of Freeman and Carroll,²⁵ assuming that the reactions follow pseudo-first-order kinetics. It is known that this treatment is subject to complexities of heterogeneous kinetics,²⁶ which include oxygen chemisorption on reactive sites of the char forming surface oxides that can be detected as C=O and OH by IR spectroscopy.⁹ This process results in a slight weight increase before the weight loss due to gasification of the surface oxides.⁸⁻¹⁰ Another problem in this case is the weight of the additives, which are not subject to oxidation. Despite such complexities the kinetic data obtained on a major part of the TG curves are still useful for evaluating the relative effects of the additives.

Figure 16 shows the Arrhenius plot for oxidation of chars with and without additives. It reveals that the oxidation reactions apparently proceed in two steps, which roughly relate to the two exotherms observed in the DSC curves. Therefore, it is reasonable to assign the first step to oxidation of nonaromatic structures and the second step to oxidation of aromatic structures. The kinetic parameters determined are summarized in Table III. The first-step oxidation starts at ~380°C and the resulting weight loss is in the range of 10–30%. Furthermore, the activation energies and maximum rates calculated for different

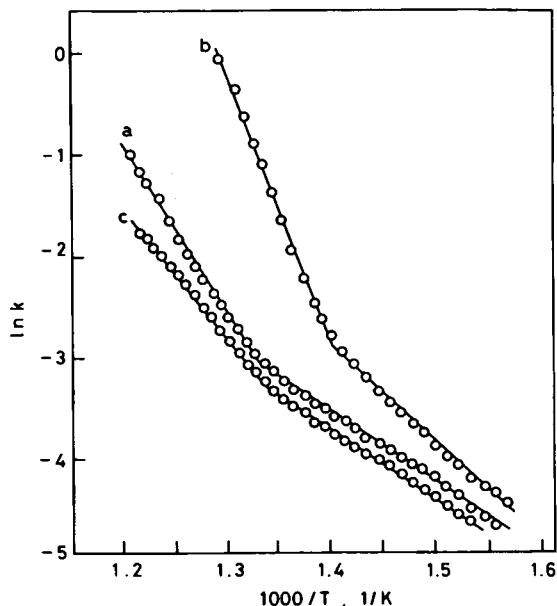


Fig. 16. Arrhenius plots for oxidation of chars prepared at 500°C: (a) untreated; (b) with NaCl; (c) with $(\text{NH}_4)_2\text{HPO}_4$.

samples in this range are similar. The second stage, where aromatic structures are oxidized, is considerably affected by the inorganics. Addition of $(\text{NH}_4)_2\text{HPO}_4$ lowers the activation energy and both the maximum rate and the rate at 485°C. Only 34% of the char was gasified in the 480–540°C temperature range, indicating that $(\text{NH}_4)_2\text{HPO}_4$ acts as a strong antioxidant. On the other hand, NaCl increased the rate of oxidation by more than threefold and lowered the reaction temperature. NaCl also increased the activation energy which is rather unexpected but may be partially attributed to physical effects such as changes in entropy.

SUMMARY AND CONCLUSIONS

Combustion of cellulosic materials proceeds through pyrolysis of the substrate by two alternative pathways. These pathways involve decomposition of the glycosyl units to form a char and depolymerization of these units to form tarry volatiles containing anhydrosugar derivatives. Oxidation of the volatiles in the gas phase gives flaming combustion and oxidation of the char in the solid phase produces smoldering or glowing combustion.

Addition of acidic inorganic compounds, namely, $(\text{NH}_4)_2\text{HPO}_4$ and ZnCl_2 , promote the decomposition reactions and form more char than combustible volatiles, and thus suppress flaming combustion. These materials lower the temperature range of the decomposition reactions, which initially involve dehydration and evolution of CO and CO_2 . The intermediate chars contain glycosyl units and aliphatic and aromatic groups. The aliphatic groups consist of paraffinic, olefinic, carbonyl, and carboxyl functionalities. When decomposition of the glycosyl units is complete, a relatively "stable" char is formed, which

TABLE III
Kinetic Parameters of Char Oxidation in Air

Additives	First step				Second step				
	Temp range (°C)	Wt loss (%)	E (kcal/mol)	Max rate (%/min)	Temp range (°C)	Weight loss (%)	E (kcal/mol)	Max rate (%/min)	Rate at 485°C (%/min)
(NH ₄) ₂ HPO ₄	380-475	21	14	3.2 (475°C)	480-540	34	25	6.4 (530°C)	3.2
None	370-480	26	15	4.0 (480°C)	485-570	64	36	8.8 (540°C)	4.0
NaCl	365-420	11	18	3.2 (420°C)	445-500	68	51	14.4 (485°C)	14.4

undergoes further pyrolysis by decomposition of less stable aliphatic groups, evolution of hydrogen, and conversion of the residue to highly condensed polycyclic aromatic structures. Addition of the acidic inorganics accelerates the decomposition of the glycosyl units rather than the reactions of the already decomposed residue. In this manner they increase the char yield and affect the composition of the intermediate products, but composition of the final products or "stable" char is not materially affected. Rather surprisingly, addition of NaCl slightly increases the stability of the glycosyl units and char yield is increased.

The residual chars are oxidized at two stages. The first stage gives an exotherm centered at about 360°C determined by DSC and corresponds with oxidation of the aliphatic components. The second stage that gives an exotherm centered at about 520°C corresponds with oxidation of the aromatic components. Thus, combustion temperature of the chars and their rate of heat release or reactivity are greatly affected by the time and temperature profile involved in formation of the char and the effect of the additives which alter the amount, composition, and char formation temperature. The aliphatic components of the chars have the greatest reactivity, and their combustion is almost simultaneous with their formation by decomposition of the glycosyl units. Consequently, the threshold temperature for combustion of the aliphatic components of the char is lowered by treatment of cellulose with $(\text{NH}_4)_2\text{HPO}_4$ and raised by treatment with NaCl. Furthermore, pure cellulose forms very little char and makes only a small contribution to the solid phase combustion, mainly at the first stage. On the other hand, the additives that facilitate the formation of stable char containing relatively high proportions of aromatic components show combustion exotherms at both stages. The second stage combustion exotherm of the $(\text{NH}_4)_2\text{HPO}_4$ -treated sample, however, is broader and more prolonged than the corresponding exotherm of the NaCl-treated sample, which is much sharper and takes place at lower temperatures. This indicates that additives also affect the reactivity and the rate of oxidation of the aromatic components of the char.

This conclusion is confirmed by thermal analysis of the chars formed at 350°C and 500°C, and a kinetic analysis of the resulting data. These studies clearly indicate that NaCl lowers the combustion temperature of the aromatic components of the char by $\sim 40^\circ\text{C}$ so that they are oxidized shortly after the more reactive aliphatic components. Furthermore, it more than triples the rate of oxidation and expands the size of the exotherm corresponding with the amount of heat release. Addition of the $(\text{NH}_4)_2\text{HPO}_4$, however, produces an opposite effect by slightly lowering the rate of oxidation and the amount of heat release. The latter effect is produced by changing the nature of the oxidation process or the ratio of CO to CO_2 . This is because the heat of formation of CO_2 is ~ -94.1 kcal/mol as compared to -26.4 kcal/mol for CO. Since the heat release provides the driving force for propagation of smoldering combustion, these additives substantially enhance or inhibit the solid state combustion of carbonaceous materials in general, and smoldering of cellulosic materials in particular. The results indicate that the aliphatic components of the char are highly pyrophoric and can be oxidized as they are formed. Thus, initiation of the smoldering process is controlled by pyrolytic decomposition of the glycosyl units that takes place at relatively low temperatures, but the main driving force is apparently

provided by oxidation of the aromatic components. The chars that are formed at higher temperatures are less readily combustible because of the low content of the more reactive aliphatic groups. This information provides a chemical basis for analysis of various reactions and the interactions which take place as the smoldering front moves through the cellulosic substrate.

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References

1. F. Shafizadeh, *J. Anal. Appl. Pyrol.*, **3**, 283 (1982).
2. F. Shafizadeh and A. G. W. Bradbury, *J. Appl. Polym. Sci.*, **23**, 1431 (1979).
3. F. Shafizadeh, R. H. Furneaux, T. G. Cochran, J. P. Scholl, and Y. Sakai, *J. Appl. Polym. Sci.*, **23**, 3525 (1979).
4. A. G. W. Bradbury, Y. Sakai, and F. Shafizadeh, *J. Appl. Polym. Sci.*, **23**, 3271 (1979).
5. F. Shafizadeh, P. S. Chin, and W. F. DeGroot, *J. Fire Flamm. Fire Retardant Chem.*, **2**, 195 (1975).
6. F. Shafizadeh, *The Chemistry of Solid Wood*, R. M. Rowell, Ed., Academic, New York, to appear.
7. F. Shafizadeh, *Biomass Conversion Processes for Energy and Fuels*, S. S. Sofer and O. R. Zaborsky, Eds., Plenum, New York, 1981, p. 103.
8. F. Shafizadeh and A. G. W. Bradbury, *J. Thermal Insulation*, **2**, 141 (1979).
9. A. G. W. Bradbury and F. Shafizadeh, *Carbon*, **18**, 109 (1980).
10. A. G. W. Bradbury and F. Shafizadeh, *Combust. Flame*, **37**, 85 (1980).
11. F. Shafizadeh and Y. Sekiguchi, *Carbon*, **21**, 511 (1983).
12. Y. Sekiguchi, J. S. Frye, and F. Shafizadeh, *J. Appl. Polym. Sci.*, **28**, 3513 (1983).
13. F. Shafizadeh and Y. Sekiguchi, *Combust. Flame*, to appear.
14. C. W. George and R. A. Susott, USDA Forest Service Research Paper INT-90, 1971.
15. A. Menlibaev, D. Z. Serazetdinov, and A. B. Bekturov, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, **26**, 55 (1976); *Chem. Abstr.*, **86**, 47631x (1977).
16. F. Shafizadeh and P. P. S. Chin, unpublished results.
17. F. Shafizadeh, G. D. McGinnis, R. A. Susott, and M. H. Meshreki, *Carbohydr. Res.*, **33**, 191 (1974).
18. F. Shafizadeh, Y. Z. Lai, and C. R. McIntyre, *J. Appl. Polym. Sci.*, **22**, 1183 (1978).
19. G. N. Richards, F. Shafizadeh, and T. T. Stevenson, *Carbohydr. Res.*, to appear.
20. F. Shafizadeh, A. G. W. Bradbury, W. F. DeGroot, and T. W. Aanerud, *Ind. Eng. Chem., Prod. Res. Dev.*, **21**, 97 (1982).
21. J. P. Neumeyer, P. A. Koenig, and N. B. Knoepfler, in Proceedings of the Twelfth Cotton Utilization Research Conference, Agricultural Research Service, USDA, ARS 72-98, 1972, p. 55, New Orleans, La., May 8-10, 1972.
22. T. J. Ohlemiller and F. E. Rogers, *Combust. Sci. Technol.*, **24**, 139 (1980).
23. S. Patai, E. Hoffman, and L. Rajbenbach, *J. Appl. Chem.*, **2**, 306 (1952).
24. M. J. Veraa and A. T. Bell, *Fuel*, **57**, 194 (1978).
25. E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
26. P. D. Garn, *J. Therm. Anal.*, **7**, 475 (1975).

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