

Characterization of Char from the Pyrolysis of Tobacco

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Pyrolysis of tobacco was studied in oxidative and nonoxidative (inert) environments at atmospheric pressure and temperatures ranging from 150 to 750 °C. The objective was to study the effect of pyrolysis conditions on the characteristics of the solid residue, i.e., char. The char was characterized using cross-polarization ¹³C nuclear magnetic resonance (CPMAS NMR), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), the Brunauer–Emmett–Teller (BET) surface area, and the elemental composition. The char yield from pyrolysis (i.e., nonoxidative) decreased sharply with an increase in temperature to ca. 22% (dry, ash-free basis) at high temperatures. In oxidative pyrolysis, i.e., in 5% oxygen, the char was completely oxidized above 600 °C. The gaseous product from pyrolysis at high temperatures contained a significant concentration of hydrogen. The surface area of the char was low, with a maximum of 8 m²/g at 400 °C. SEM analysis indicated that pyrolysis of the tobacco led to a gradual accumulation of inorganic crystals on the exposed surfaces, and some constituents also melted, resulting in the formation of vesicles by evolving gas. NMR analysis showed significant changes in pectin and sugar constituents of the tobacco and breaking of glycosidic bonds of cellulose at 300–500 °C before the char became predominantly aromatic at high temperatures. FTIR results showed a continuous decrease in the intensity of the OH stretch with temperature and the aromatic character to be at maximum at 550–650 °C. The H/C ratio of the char decreased continuously with temperature, while the O/C ratio became constant above 300 °C due to the presence of oxides and carbonates in the char. The results are consistent with the analysis of the evolved gases.

KEYWORDS: Tobacco; char; characterization; pyrolysis

INTRODUCTION

Tobacco has been a widely used agricultural product at least since American colonial times. Currently, high-speed machines fabricate cigarettes by inserting a blend of tobaccos into a paper rod and attaching a filter tip. A cigarette is typically lit by a smoker with a match or other type of lighter and undergoes self-sustaining combustion. Many thousands of chemical substances are generated by combustion and pyrolysis reactions during the formation of cigarette smoke. The peak temperatures in the combustion region of the cigarette coal during a puff can reach 800–900 °C (1). Such high temperatures can lead to the formation of polycyclic aromatic hydrocarbons (PAHs). PAHs are ubiquitous products that form during the combustion of many forms of biomass. They can also be found, for example, in charred foods. A growing body of evidence suggests that PAHs arise from the high-temperature pyrolysis of the solid char that is formed at lower heating temperatures (2–6). Thus, an understanding of the chemistry of the char may lead to a better understanding of the mechanism of the formation of PAHs.

The pyrolysis of tobacco has much in common with the pyrolysis of other forms of biomass. Pyrolysis of biomass is complex and leads to the formation of many volatile and semivolatile products and a solid residue, i.e., char (7–11). The relative distribution of the products is usually dependent on the pyrolysis conditions as well as on the type of biomass. Much of the literature on pyrolysis of biomass is focused on the analysis of the volatile components and the pyrolysis kinetics (12–15). Under severe pyrolysis conditions, it is the volatile products that are believed to undergo secondary reactions, resulting in the formation of PAHs (6, 16, 17). The extent of such reactions in the product char is not known but could be important under smoldering conditions (4, 5, 18–20). The extent of secondary reactions may be dependent on the characteristics of the char.

There is a limited amount of information on the characterization of chars from the pyrolysis of different biomasses. Sekiguchi and Shafizadeh (19) and Mok et al. (21) found that chars from cellulose, formed at temperatures below 400 °C, had higher concentrations of aliphatic carbons and were more reactive compared to chars formed at higher temperatures. Boon et al. (2) also studied cellulose pyrolysis and suggested that the

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cellulose changed first into a furan/phenol polymer at ca. 270 °C. This was followed by disproportionation of the furan-dominated intermediate, which resulted in a completely aromatized product. Bonammy (3) studied the effect of pyrolysis conditions such as temperature and heating rate on transformations in petroleum pitches and other materials at temperatures up to 1000 °C. It was found that temperature or heating rates increase the production of volatiles (governed by chemical reactions) and also favor their retention (controlled by diffusion). Two distinct stages in the carbonization of organic materials were suggested. The first stage, solidification, is characterized by the completion of tar evolution, resulting in a loss of viscoelasticity. The second stage, carbonization, is the complete loss of gaseous products, leaving behind a brittle residue.

Freitas et al. (22) performed NMR analysis on chars from peat and observed a preferential loss of carbohydrates and carboxylic acids before the chars became aromatic above 500 °C. Recent work with chars from chlorogenic acid and pectin (23) showed that the chars became increasingly aromatic with increasing temperature and showed virtually identical characteristics at high temperatures, even though chlorogenic acid is a phenolic compound and pectin is a carbohydrate. The effect of pyrolysis conditions such as temperature and reaction environment on the composition of char from a biomass such as tobacco has not been studied, and it is not clear how the complex makeup of the substrate would affect the char formation via interactions among its various constituents. An understanding of char formation from tobacco may provide an insight into the role of char in secondary reactions that occur during combustion, e.g., in a burning cigarette, as well as help understand the pyrolysis of other types of biomass.

In this work, the effect of pyrolysis conditions on the composition of char from tobacco was studied. The char represents the solid residue that remains after pyrolysis. The pyrolysis experiments were done at atmospheric pressure and temperatures ranging from 150 to 750 °C. Both oxidative and nonoxidative atmospheres were used. The characterization was done using cross-polarization ¹³C nuclear magnetic resonance (CPMAS NMR), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), the Brunauer–Emmett–Teller (BET) surface area, and the elemental composition. The volatile products from pyrolysis were analyzed by on-line mass spectrometry and by gas chromatography/mass spectrometry (GC/MS). The results of characterization are discussed in relation to the evolved gas analysis.

MATERIALS AND METHODS

The tobacco sample was a mixture of Bright, Burley, and Oriental tobaccos in a 0.3/0.3/0.3 ratio. The sample was used in ground form (<400 mesh) to minimize any intraparticle transport effects during pyrolysis. The moisture and ash contents of the sample were 12.1% and 12.9%, respectively, and it contained 50.6% carbon, 6.5% hydrogen, 3.7% nitrogen, 0.6% sulfur, and 38.6% oxygen (by difference), on a dry, ash-free (daf) basis. The ash represented oxides of calcium (28%), potassium (22%), silicon (16%), magnesium (6%), sulfur (6%), and phosphorus (5%), in addition to small concentrations of sodium, aluminum, iron, and titanium.

Pyrolysis Procedure. The tobacco samples were pyrolyzed in a tubular reactor. The experimental details are given elsewhere (23). Briefly, the reactor consisted of a 0.5 in. diameter quartz tube heated by a sliding 6 in. long stainless steel block furnace. The furnace provided a 4 in. long section of uniform temperature profile, with the temperature generally within ±5 °C. A chromel/alumel thermocouple was embedded in the sample to measure its temperature. The carrier gas was helium for pyrolysis and a mixture of 5% oxygen in helium for oxidative pyrolysis. The concentration of oxygen in oxidative pyrolysis was kept

low to prevent the complete oxidation of the tobacco. The volatile products were passed through a Cambridge pad to remove the condensable product before the gases were analyzed and vented into a hood.

A porcelain boat containing up to 300 mg of tobacco sample, spread as a thin layer, was placed about 3 in. from the downstream end of the tube. The tube led directly to the Cambridge pad, which was 1 in. away from the furnace. In other words, a 2 in. section of the tube was in the furnace at the downstream end, 1 in. of which was in the hot zone at the set temperature, while in the other 1 in. the temperature dropped by 20–100 °C depending on the set temperature. The exit line was maintained at ~200 °C. The pyrolyzing gas was introduced at a flow rate of 220 cm³/min, which corresponded to residence times of 550 ms at 200 °C and 250 ms at 750 °C. The furnace initially rested over an empty portion of the tube and was equilibrated at the desired temperature. After the temperature was reached the furnace was moved over the sample to initiate pyrolysis. The runs were made at atmospheric pressure and temperatures ranging from 150 to 750 °C under approximately isothermal conditions (i.e., except for the initial heating time). The sample reached within 5 °C of the desired temperature in 3 min. A sample of the uncondensed gases was analyzed on-line by a Balzers QMG 511 quadrupole mass spectrometer. The spectrometer was operated at a 24 eV energy to minimize molecular fragmentation. The run duration was based on the total ion current in the mass spectrometer and was mostly 10 min. Since the analysis conditions in different runs were kept the same, the ion intensity of a species was taken to represent its concentration in the gas phase. At the end of the run the condensable product on the Cambridge pad was extracted with methanol and analyzed by GC/MS. The product char was allowed to cool to ambient temperature before being recovered. It was stored over dry silica gel under vacuum until it was analyzed. The char yield was calculated on the basis of the initial mass of the unpyrolyzed sample on a daf basis. The experimental error in the yield measurements from replicate runs was less than ±1%.

Char Characterization. The elemental analysis of char was performed at Galbraith Laboratories, Inc. The surface area was measured in an automated volumetric gas adsorption apparatus (Autosorb 1 from Quantachrome Co.) using nitrogen as an adsorbate at 77 K. Prior to adsorption measurements, the sample was outgassed at 120 °C for 2 h. Typically, 400 mg of char was used in each measurement of surface area.

The char samples were prepared for SEM evaluation by placing a representative sample on an aluminum stub. A coating of 8 nm Au/Pd film was applied to the sample using a Cressington 208 HR sputter coater. The coated samples were then examined and imaged with the use of a JEOL 840 scanning electron microscope. The elemental content of surface crystals was determined with the use of a Kevex energy-dispersive X-ray spectrometer.

Solid-state ¹³C CPMAS NMR spectra of the chars were obtained on a Varian Unity 200 spectrometer at a carbon resonance frequency of 50.3 MHz. The NMR probe was a Doty Scientific (Columbia, SC) high-speed magic-angle-spinning probe. A cross-polarization contact time of 750 μs and a 1 s pulse repetition rate were employed. The MAS spinning speed was ~8100 Hz, fast enough to move the spinning sidebands away from the region of interest. The short contact time was chosen to obtain the maximum signal for most of the carbons since the objective was to study the trends with the pyrolysis conditions in the intensities of resonances due to the various carbons.

FTIR spectra of the samples were recorded on a Spectra-Tech IR-Plan microscope interfaced to a Nicolet Magna 560 FTIR spectrometer. The samples were held between two KBr salt plates in a microcompression cell. In some cases, preflattening in a diamond cell was necessary prior to mounting. A spectral resolution of 4 cm⁻¹ was used, and the apodization function was of the Happ–Genzel type.

RESULTS AND DISCUSSION

Char Yield. Figure 1 shows the effect of temperature on char yield. As already mentioned, the char represents the solid residue that remains after pyrolysis and consists of organic material with a composition varying from barely pyrolyzed

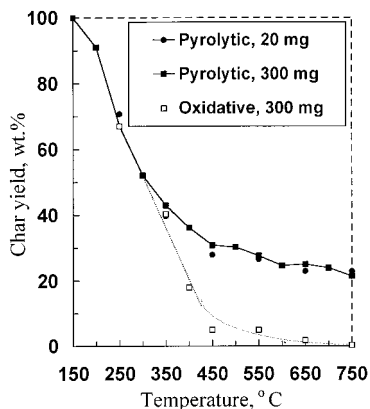


Figure 1. Effect of temperature on char yield from pyrolysis of tobacco.

tobacco at low temperatures to a highly carbonized material at high temperatures. The char also includes any coke that formed by reactions among the volatile components. The yield of char in pyrolysis (i.e., nonoxidative) decreased sharply with an increase in temperature to ca. 30% (daf basis) at 450 °C, before leveling off at ca. 22% at higher temperatures. The char yields from oxidative pyrolysis were identical to those from the pyrolysis up to 350 °C, but lower at higher temperatures. Above 550 °C, the char yield was virtually negligible due to the rapid oxidation of tobacco or char in the presence of oxygen. The chars from oxidative pyrolysis were not characterized in detail since they contained mainly inorganic components at high heating temperatures. The char at 150 °C was also not analyzed due to the small extent of pyrolysis.

It is interesting to note that the char yield was independent of the mass pyrolyzed, indicating that any condensation reactions among the volatile products, leading to the formation of secondary char or coke, were absent under the pyrolysis conditions used. Such reactions, which occur mainly due to the inability of the volatile products to escape rapidly from the thick substrate sample, are generally expected to increase the char yield (9). There is no evidence of coke formation in the literature under the pyrolysis conditions used in this study. Preliminary calculations, based on volatile product formation or weight loss in the temperature range 250–750 °C, showed that the apparent activation energy for char formation was relatively low at 52 kJ/mol. However, the calculated value encompasses various physical and chemical processes that occur during the pyrolysis. The low value suggests that the pyrolysis might be transport-limited. These limitations could be due to the formation of a melt by pyrolysis of some of the tobacco components as seen later in the SEM analysis. Further, the calculated activation energy includes the effect of devolatilization reactions as some of the tobacco components, such as nicotine, volatilize before decomposing.

Evolved Volatile Products. Since the objective of this work was char characterization, the analysis of the volatile products was not studied in detail. Only the major components were identified, and the effect of pyrolysis conditions on the formation of these components was studied. The product assignments are based on matching the mass spectral data with a spectral library (Wiley275) as well as on the previous work (4, 5, 12). The mass spectrometer was not calibrated, and the ion intensities were taken to represent the corresponding concentrations. The volatile products consisted of condensed-phase products as well as gaseous products. The composition of condensed-phase products was complex and changed with the pyrolysis temperature. The major components at 350 °C were nicotine (1-methyl-2-(3-pyridyl)pyrrolidine), myosmine (2-(3-pyridyl)-1-pyrroline),

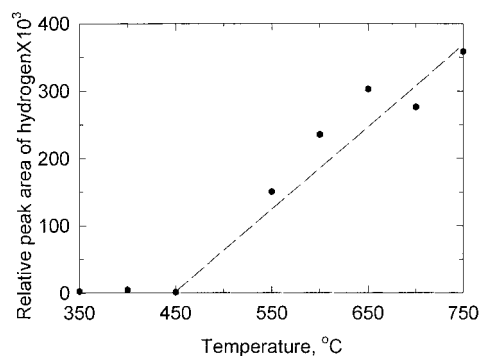


Figure 2. Relative peak area of hydrogen evolved in pyrolysis.

neophytadiene (2,6,10-trimethyl-14-ethylene-14-pentadecene), stigmasteryl (stigmasta-5,22-dien-3-ol), nicotine (1-methyl-2-(3-pyridyl)pyrrole), myristic acid (1-tridecanecarboxylic acid), stearic acid (*n*-octadecanoic acid), *n*-hexadecanoic acid, 1*H*-indole (2,3-benzopyrrole), catechol, phenol, and two- and three-ring aromatic hydrocarbons. Nicotine, which had the highest concentration at 350 °C, decreased rapidly at higher temperatures. The concentrations of *n*-hexadecanoic acid, catechol, and neophytadiene decreased above 550 °C. The concentrations of most other components increased with temperature. At 750 °C, the condensed product consisted mainly of cyclobuteno[*c*]pyridine, 8-aminoquinoline, cresols, myosmine, indole, phenol, and various PAHs. It should be added that some of the product components at high temperatures could have been formed via secondary gas-phase reactions among the initial products instead of from the tobacco or its char.

The uncondensed gaseous product contained mainly water, carbon monoxide, carbon dioxide, and hydrogen, along with small concentrations of organic components. The concentrations of water and carbon oxides increased as the temperature was increased, suggesting that the major pyrolysis reactions were dehydration, decarboxylation, and decarbonylation. The amount of hydrogen also increased with temperature, as shown in Figure 2. This result shows that there was some direct dehydrogenation of the char at high temperatures. The analysis showed that the concentration of carbon dioxide was higher than that of carbon monoxide at low temperatures (<550 °C) and at the onset of pyrolysis. However, at higher temperatures and after the bulk of the products had been evolved, the carbon monoxide concentration was higher than that of carbon dioxide.

Of particular interest were the relative concentrations of organic components in the gaseous product from pyrolysis. Among these, the main components might correspond to acetic acid ($m/z = 60$), furan/isoprene ($m/z = 68$), methylfuran ($m/z = 82$), toluene ($m/z = 92$), phenol ($m/z = 94$), and catechol ($m/z = 110$). The highest concentration was that of mass 60 followed by masses 68, 94, 110, 82, and 92. The relative areas appeared to decrease gradually with increasing temperature. Other components with $m/z = 16, 32, 56, 78, 96, 122,$ and 136 were also observed in small concentrations. These could represent methane ($m/z = 16$), methanol ($m/z = 32$), butene/acrolein ($m/z = 56$), benzene ($m/z = 78$), furfural/dimethylfuran ($m/z = 96$), benzoic acid ($m/z = 122$), and vinyl catechol/dipentene ($m/z = 136$). These assignments are based on our work with other materials (5, 23) and are consistent with the results from other studies on the pyrolysis of high molecular weight tobacco leaf constituents, such as cellulose, pectin, lignin, and pigments (12–13). The latter studies also reported the presence of acetaldehyde, acetic acid, methane, hydrogen cyanide, formic acid, methanol, and formaldehyde.

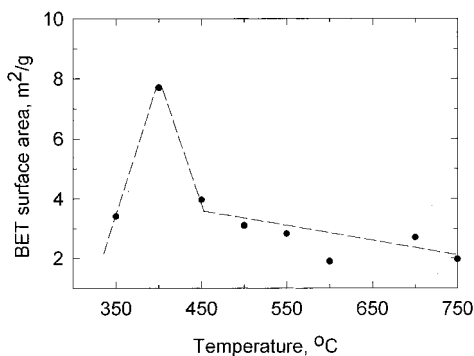


Figure 3. Effect of temperature on the surface area of pyrolysis chars.

Char Characterization. Surface Area. The surface area of the char may determine its reactivity and combustion behavior. The surface areas of various chars from pyrolysis, presented in Figure 3, were measured by the BET method. The surface area increased with temperature to a maximum of 8 m²/g at 400 °C before decreasing at higher temperatures. This result shows that there was an optimum temperature for the maximum surface area and that the use of high temperatures was detrimental to the pore structure of the char. Since the SEM results (presented later) indicated the presence of fine particles and pores in chars even at high temperatures, the low surface area values suggest

that these pores might be partially closed, preventing any access to the adsorbing gas. It should also be realized that SEM reveals only large macropores that contribute only little to the surface area. The relatively low values of the surface area also suggest that the chars may undergo an incomplete combustion at high temperatures.

SEM Analysis. Only the chars from pyrolysis (i.e., nonoxidative) were analyzed by SEM. The tobacco sample consisted of lamina and stem fragments 10–150 μm in diameter (Figure 4A). The cell parts and components that were recognizable within the sample included the cuticle layer, wax deposits on the cuticle layer, epidermal cells including stoma cells, and xylem elements from stem fragments. The interior palisade and spongy mesophyll cells were not identified. The cuticle layer is found on all exposed cell surfaces and consists of polymerized fatty acids embedded in wax (24). The cell wall contains carbohydrates such as cellulose, hemicellulose, and pectin. Pectin is also found between cells in the middle lamella and between the cuticle and cell wall. The pectin acts as a binder for cellulose fibers and holds the cuticle to the cell wall. Xylem cells found in the stem and vascular bundles of the lamina contain lignin, a phenolic compound.

Crystals of inorganic salts, such as calcium oxalate, were found throughout the lamina and stems in this study, either as individual crystals or druses (spherical aggregates of prism- or

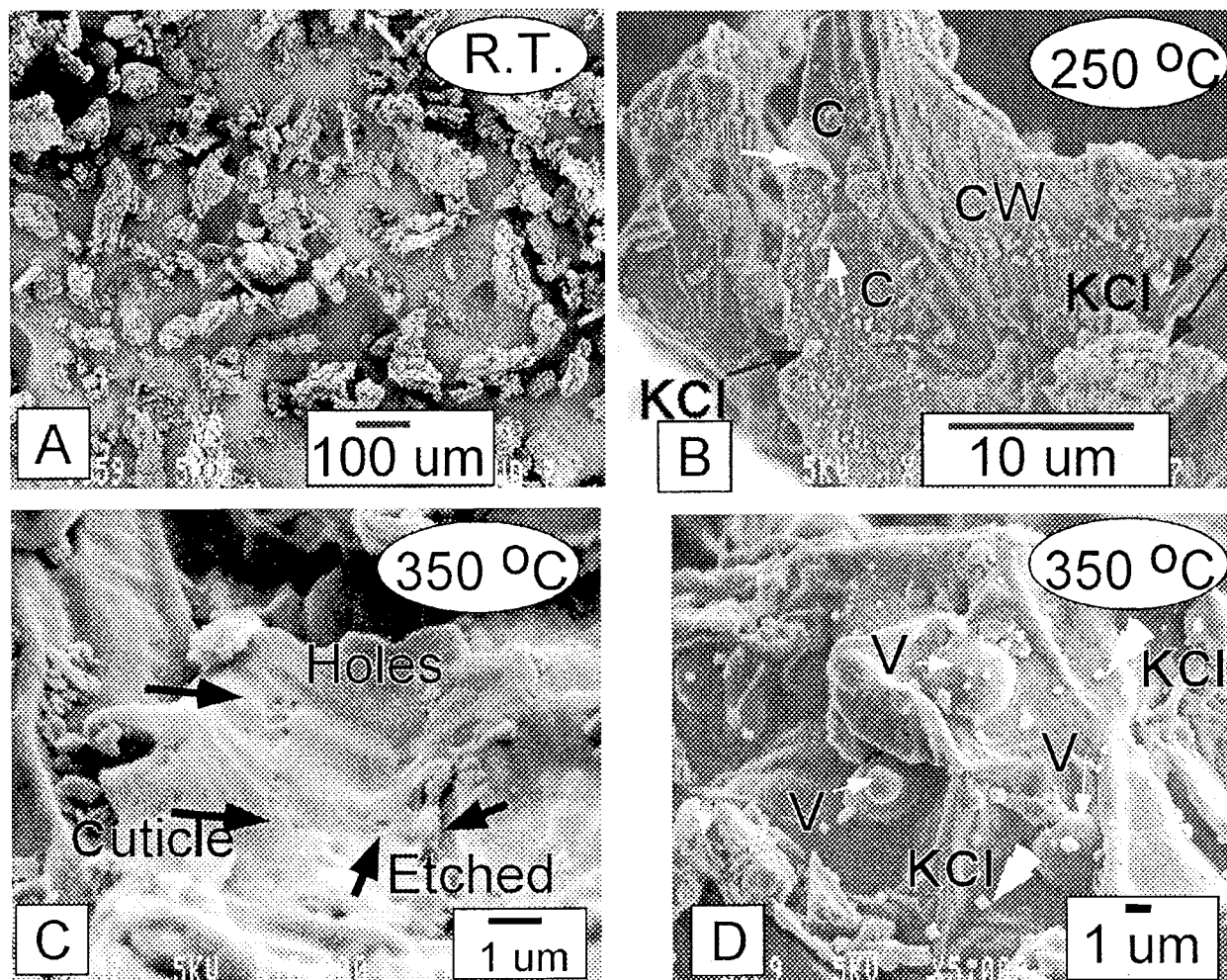


Figure 4. SEM micrographs of (A) tobacco, (B) pyrolysis char at 250 °C, an epidermal cell fragment showing separation and folding of the cuticle layer (single arrow) from the cell wall (CW), KCl crystals (double arrow) plus other inorganic crystals, the wrinkled cell wall, and (C, D) pyrolysis char at 350 °C, (C) a cuticle fragment showing loss of material through etching and volatile gas release (arrows), and (D) a cell fragment showing expanded vesicles (V, single arrow) and cuticle KCl crystals (double arrow) plus other inorganic crystals (pyrolysis temperature as indicated).

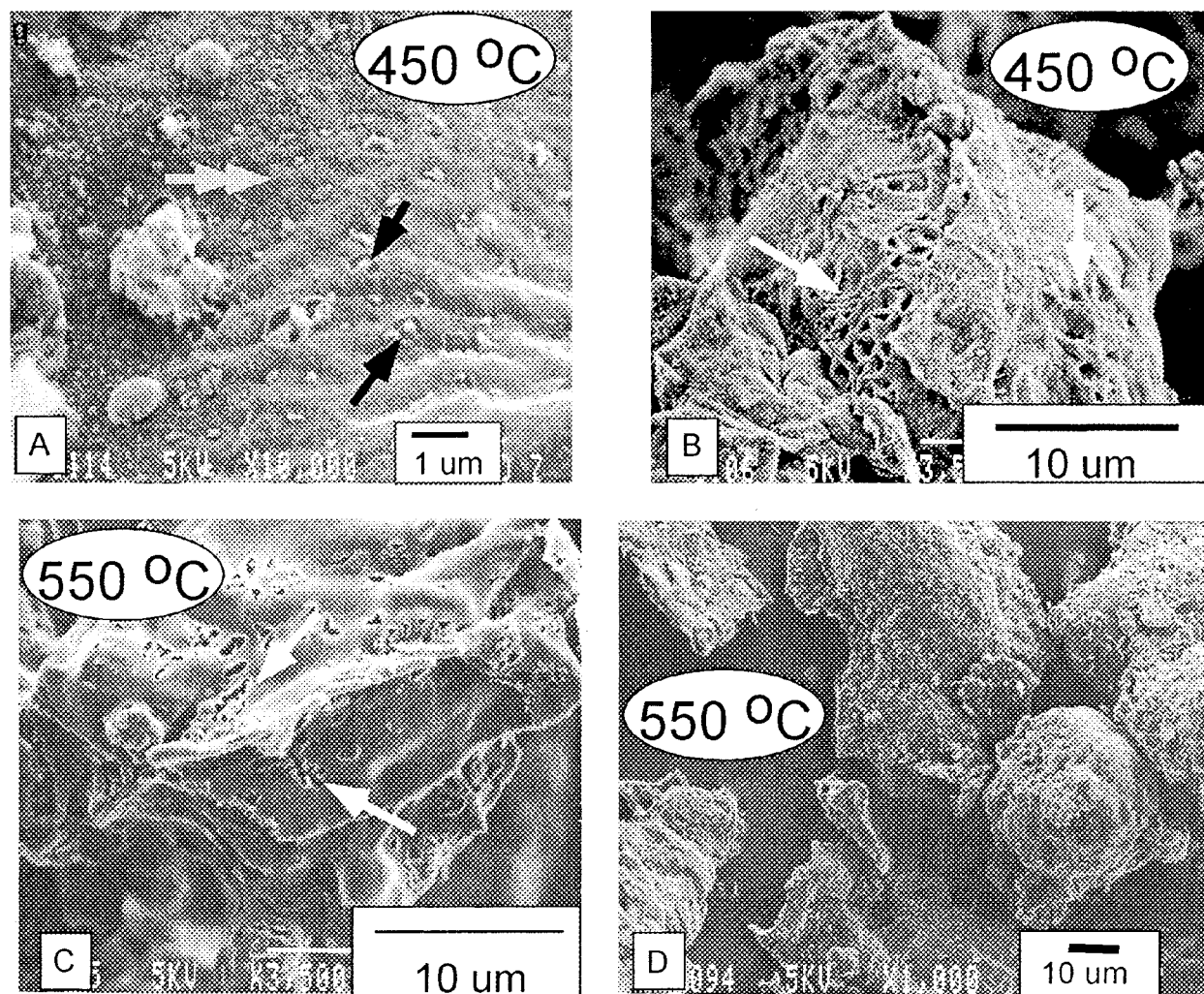


Figure 5. SEM micrographs of pyrolysis char at 450 °C, showing (A) loss of material through etching from the organic matrix (double arrow) and from inorganic crystals (single arrow) and (B) the altered cell wall with triangular patterns, and pyrolysis char at 550 °C, showing (C) vesicles and dendrite-shaped patterns etched in the smooth surface (arrows) and (D) expanded cell forms, rough in texture and covered with inorganic crystals (pyrolysis temperature as indicated).

pyramid-shaped crystals with angular points projecting from all surfaces). Calcium oxalate is known to occur in tobacco in the monohydrate form (25, 26) and has been observed directly in the intact leaf by ^{13}C CPMAS NMR (27).

At 250 °C, a separation between the cuticle layer and the epidermal cell wall was noted (Figure 4B). The separated cuticle layer had folded back upon itself. In our previous study (23), pectin showed signs of initial melting at 150 °C and was liquefied by 250 °C. The pectin in that study contained nearly 35% glucose. The melting of pectin could result in a loss of the binding capacity of pectin between the cuticle and the cell wall. In the current study, the cuticle layer also showed signs of softening and etching on the surface. The major inorganic crystalline components on the lamina and stem fragments at 250 and 350 °C were potassium- and chlorine-containing components, probably as potassium chloride, as identified by energy-dispersive spectrometry (EDS). These components were also found at higher temperatures throughout the pyrolysis series but not as the dominant crystal type. KCl melts at 770 °C, higher than the temperatures employed in this study. Calcium oxalate crystals were also present on most surfaces as individual particles and as druses. No noticeable change in the morphology of calcium oxalate was observed at 250 °C. Calcium oxalate undergoes dehydration at 200 °C, followed by a loss of CO

and CO₂ and the formation of CaCO₃ at 473 °C and CaO at 743 °C (25). The NMR results, presented later, showed that calcium oxalate was absent from chars above ca. 450 °C.

Closed vesicles were found within the lamina matrix at 350 °C, indicating the formation of volatile products. The cuticle surface had smooth areas and round holes, suggesting melt formation and evolution of volatile products (Figure 4C). Surface etching was also observed. Crystals of potassium chloride and calcium oxalate were present on the lamina and stem fragment surfaces (Figure 4D). The cell walls of the lamina showed a wrinkled pattern.

Both open and closed vesicles were observed in the char at 450 °C and appeared to develop from beneath the cellulose layer. The organic and inorganic matrixes showed signs of mass loss through surface etching (Figure 5A). Brittle components, possibly cellulose, fractured and split as the vesicles expanded. Cell wall components showed signs of change by the formation of open triangular forms (Figure 5B). The basic shape of the xylem elements did not change. Crystals of many shapes, such as platelet, acicular, and equant shapes, were found covering much of the exterior surfaces as well as the interior of the vesicles. Equant-shaped aggregates of platelet-shaped crystals were also beginning to appear. Vesicle formation suggested the loss of volatile components. Since the rate of volatile formation

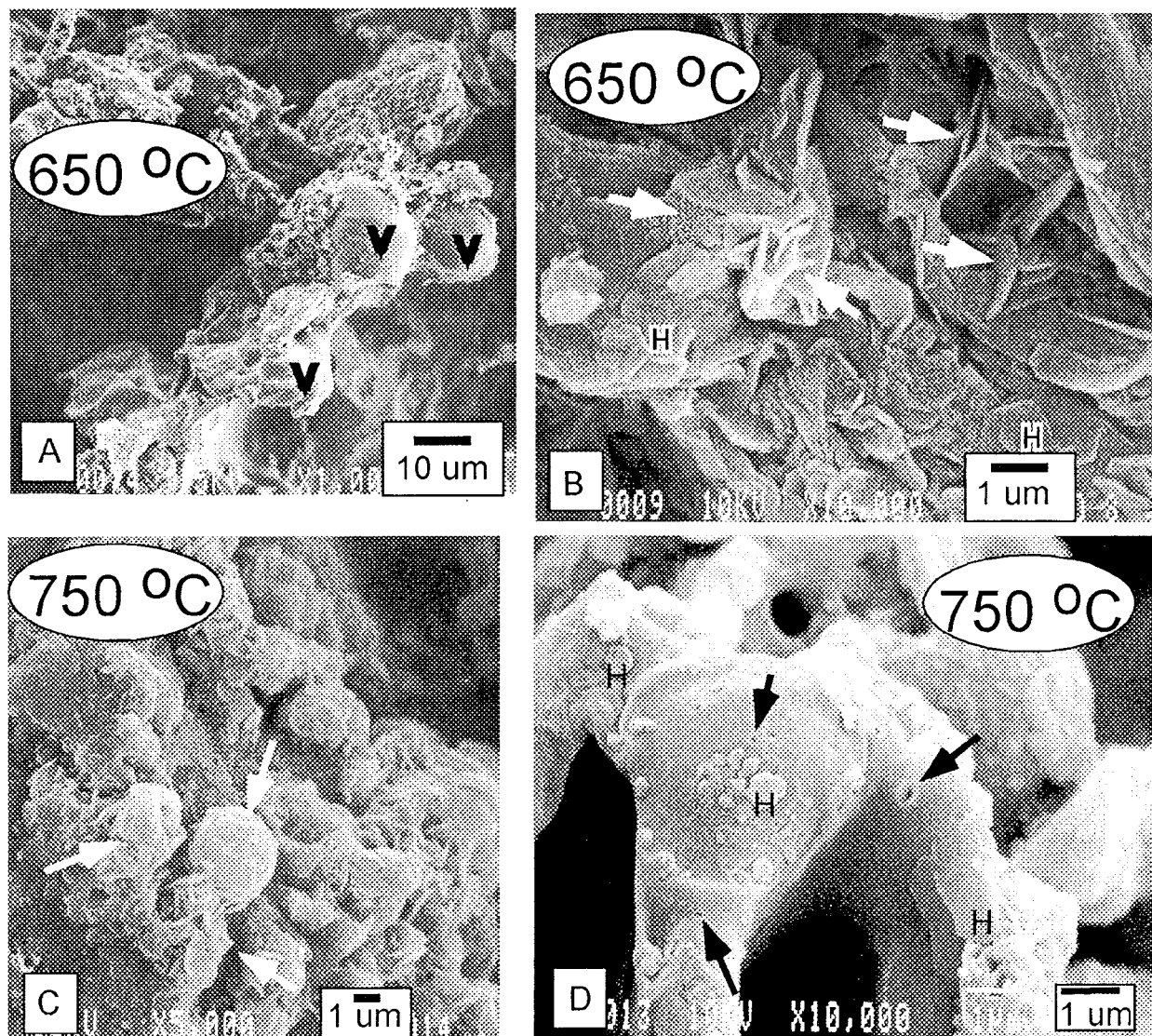


Figure 6. SEM micrographs of pyrolysis char at 650 °C, (A) smooth vesicles (V) and brittle material and (B) platelet-shaped crystals as hexagons (H) and rosettes (arrows) and equant-shaped particles, and pyrolysis char at 750 °C, (C) rosettes of platelets (arrows) composed of inorganic material and (D) the xylem element with hexagonal platelet-shaped crystals (H) and holes due to gas release (arrows) (pyrolysis temperature as indicated).

from chars of cellulose and pectin is expected to be small at 450 °C (10), the evolved product probably originated from the melting and devolatilization of char from lignin, a constituent of xylem cells. It should be added that the volatility of most biomaterials is low and the volatile products arise from the decomposition of the biomaterials. The textural change in the tobacco cell wall from a wrinkled sheet to a triangular pattern may be a result of the degradation of cellulose and hemicellulose. The degradation of cellulose occurs between 225 and 400 °C (10). This could influence the fracture and splitting of the cell wall components around the expansion of the vesicles. Hemicellulose degradation is known to occur over a relatively broad range of temperatures, and it forms more char than cellulose (14). Thus, the evolutions of volatile products from cellulose and hemicellulose are different. This may lead to the triangular-shaped patterns that developed in some of the cell wall areas in this study.

Vesicles were still forming at 550 °C, which suggested continued melting. Some vesicles exhibited a rough texture, often with holes through the vesicle shell. Surface etching was widespread, and the presence of dendritic-shaped etched patterns in some locations (Figure 5C) suggested that these regions were

crystalline (28). The “puffed” cell forms of tobacco fragments were covered with inorganic crystals, mainly platelets containing potassium along with either sulfur or phosphorus (Figure 5D).

The coarse texture found on the surfaces suggested solidification of some of the organic material. As mentioned before, Bonnamy (3) suggested two distinct stages in the carbonization of organic materials. The first stage, solidification, is the completion of tar evolution, and the second stage, carbonization, is the complete loss of gaseous products, leaving behind a brittle residue. The temperature for the first stage usually ranges from 450 to 550 °C depending on the material. In this study, the formation of new vesicles that still exhibited elastic behavior suggested that not all of the tobacco components reached the solidification stage by 550 °C.

At 650 °C, puffed char fragments were still present, many of which contained holes in the shell. Both rough- and smooth-textured vesicles were observed. The material near the smooth vesicles had split to allow the vesicles to expand (Figure 6A) and suggested a brittle fracture of the split component. Etching and round holes were found in smooth-surfaced regions that indicated a melt formation and volatile gas release. The surface was covered with crystalline particles in multiple shapes, varying

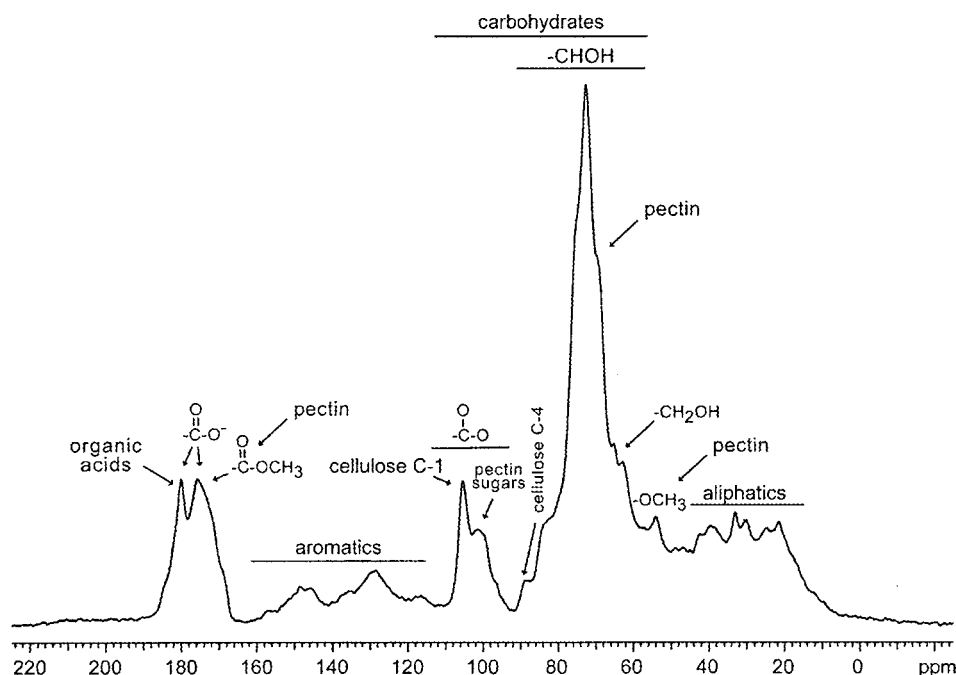


Figure 7. ^{13}C CPMAS NMR spectrum of a mixture of cured Bright, Burley, and Oriental tobaccos, representative of a cigarette blend.

from hexagonal platelets, equant particles, and rosettes of platelets to rectangular tablets (Figure 6B). The crystals contained various elements such as potassium, calcium, magnesium, phosphorus, sulfur, chlorine, oxygen, and carbon. Many of the vascular xylem elements with their lignified secondary cell wall thickenings were still present.

The surface details of the char at 750 °C were similar to those at 650 °C. Clusters of crystalline platelets containing calcium and potassium formed a coating over most char particles (Figure 6C). Hexagonal-shaped platelets, both individually and in rosette form, were common crystal shapes on the surface of the xylem elements (Figure 6D). Small equant-shaped particles were associated with some of these crystals. Holes due to the volatile release and etching of the xylem surface were also evident. Some of the fractured cell walls exhibited conchoidal fractures. The expanded char fragments remained as individual particles without melting. Most particles appeared as solidified shells covered with an inorganic crust. However, some particles still contained vesicles exhibiting a smooth appearance. This suggests that some melting, possibly of a lignin component, was still taking place. Lignin tends to be less volatile than cellulose or hemicellulose and yields a relatively large amount of char over a greater temperature range (14). The xylem elements with the lignified cell wall thickenings were still a recognizable part of the char.

NMR Analysis. As mentioned earlier, only the char product from pyrolysis was analyzed by NMR. Also as mentioned before, a short contact time was chosen to obtain the maximum signal for most of the carbons since the objective was to study the trends with the pyrolysis conditions in the intensities of resonances due to the various carbons. The ^{13}C CPMAS NMR of tobacco (Figure 7) shows several resonance peaks indicative of the presence of carbohydrates and aliphatic, aromatic, and carboxylic acid molecular groups. These groups are representative of the constituents of biomass materials such as cellulose, pectin, and lignin. The assignment of the ^{13}C resonances to the various constituents is based on our previous investigations and those of others on a variety of biomaterials including pectin (23), cellulose (19, 29), and tobacco (27).

The spectra of the chars are presented in Figure 8, along with the spectrum for the unpyrolyzed tobacco. A char prepared at 750 °C could not be analyzed due to its high electrical conductivity. The spectra changed progressively as the temperature increased above 200 °C, and the overall changes were similar to those occurring in the pyrolysis of most organic materials (29). The spectra can be approximately grouped into three regimes. For chars prepared at 200 and 250 °C, significant changes (relative to unpyrolyzed tobacco) were observed in the resonances corresponding to the pectin and sugar components, while the resonances due to the cellulose component were not appreciably affected, as discussed below. The spectral intensities in the aliphatic, aromatic, and carboxyl carbon regions increased relative to the intensities of the cellulose resonances. For 300–500 °C chars, the glycosidic bonds of cellulose were clearly broken and the chars became progressively more aromatic and less aliphatic in nature. At temperatures of 550 °C and higher, the chars were predominately aromatic, with only ca. 12% being carboxyl- or carbonate-type carbons.

In the lowest heating temperature regime, a careful comparison of the spectrum of the char prepared at 250 °C relative to the char at 200 °C revealed that the shoulder on the carbohydrate peak at 72 ppm (assigned to pectin) had disappeared at 250 °C. The broad resonance at 100 ppm corresponding to the pectin and other polysaccharide and sugar anomeric carbons was also reduced in intensity. These small changes can be visualized more clearly by subtracting the spectrum of the 200 °C char from the 250 °C spectrum. The difference is shown in Figure 9. The relative intensities of the two spectra were adjusted so that the cellulose resonances at 89 and 105 ppm canceled upon subtraction. Thus, the difference spectrum reveals changes relative to the amount of cellulose in the sample. The results showed that pectin and neutral sugars decreased in the 250 °C char but the aliphatic, aromatic, and carboxyl groups increased. Since free sugars are known to combine with protein and free amino acids to form pyridines, pyrazines, Amadori compounds, melanoidin polymers, and other materials, some of the changes can be attributed to reactions involving sugars. The results of our earlier

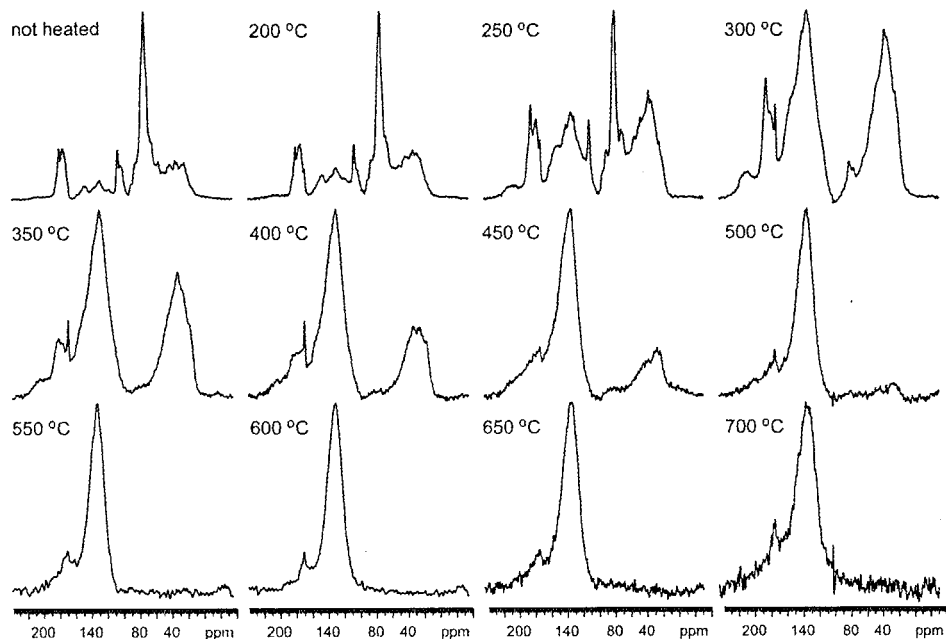


Figure 8. ^{13}C CPMAS NMR spectra of chars from tobacco pyrolysis (pyrolysis temperature as indicated).

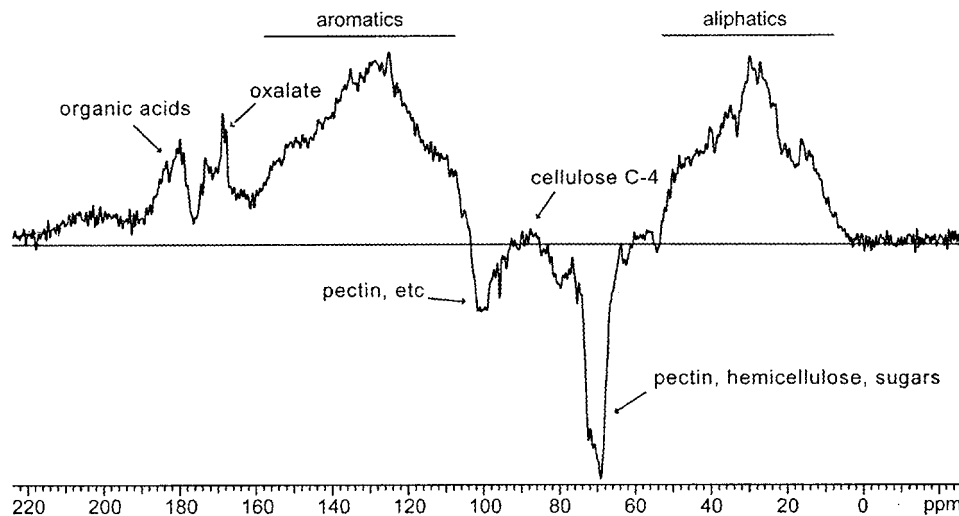


Figure 9. ^{13}C CPMAS NMR difference spectrum obtained by subtracting the spectrum of the 200 °C char from that of the 250 °C char. The relative intensities of the spectra were adjusted so that the cellulose resonances at 105 and 89 ppm exactly cancel.

work (23) also showed that the decomposition of pectin occurs at a lower temperature than for cellulose.

In the pyrolysis regime between 300 and 500 °C, cellulose and all other remaining polysaccharides were completely decomposed. Only very weak residual carbohydrate peaks (60–110 ppm) appeared in the spectrum of the char prepared at 300 °C. Under these conditions, the char was composed of approximately equal amounts of aromatic and aliphatic carbons. There was also a noticeable amount of ketone carbons as indicated by the peak at 200 ppm, as also observed in pectin (23) and cellulose (29) chars. The aliphatic and ketone carbons declined to zero as the temperature exceeded 500 °C.

A dipolar dephasing experiment was performed on the char prepared at 300 °C to deconvolute the broad aromatic and aliphatic resonances into some of their contributing components. This NMR experiment selectively detects nonprotonated and methyl carbons (30). The results are shown in Figure 10. The difference in the normal ^{13}C CPMAS and the dipolar dephased spectra was used to estimate the relative amounts of protonated and nonprotonated aromatic carbons from the aromatic region,

and the amounts of methyl and paraffinic carbons from the aliphatic region. Approximately 23% of the total aromatic carbons were protonated, with the remainder being substituted with various alkyl, oxygenated, or other aromatic molecular groups. Approximately 36% of the aliphatic carbons were found to be methyl carbons. An absorbance at 2889–2829 cm^{-1} corresponding to a CH_3 group bonded to an aromatic ring was also observed in the IR spectrum (see below).

The chars from pyrolysis above 550 °C were almost completely aromatic. The spectra of these chars differed from the spectra of cellulose chars prepared at comparable temperatures by the presence of a persistent broad resonance centered at ca. 170 ppm (Figure 8). This resonance represents carboxyl-type carbons and was likely to be due to the presence of a mixed carbonate/bicarbonate mineral phase in these chars. As mentioned already, the elemental composition of tobacco showed a high concentration of calcium and potassium salts. Under conditions of complete pyrolysis, this mineral phase was all that remained of the tobacco in the form of ash. The increase in the noise level in the 650 and 700 °C spectra was indicative of a

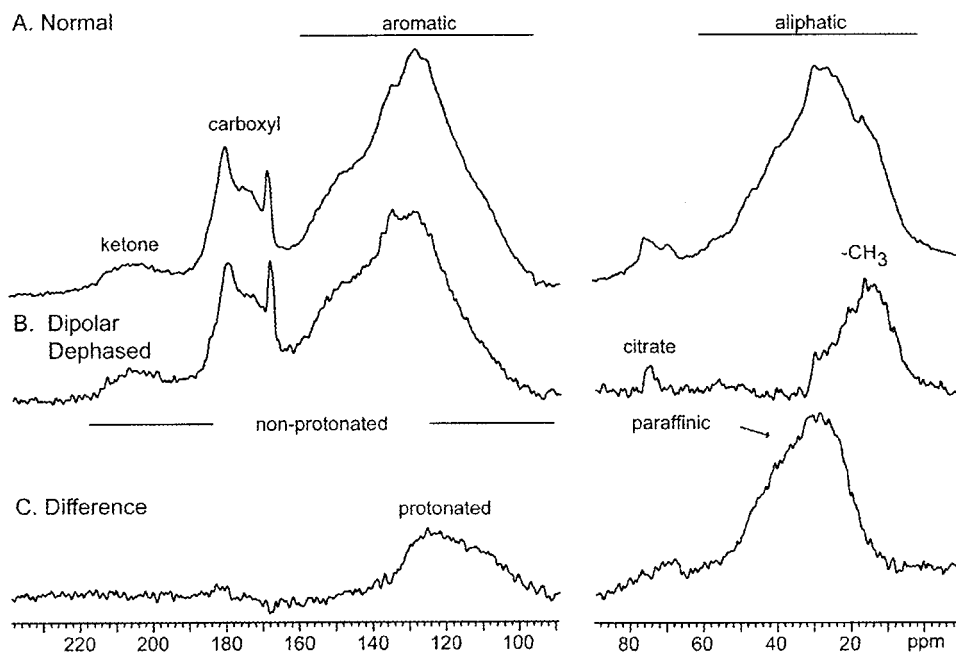


Figure 10. Dipolar dephasing experiment for the 300 °C char: (A) normal ^{13}C CPMAS spectrum; (B) ^{13}C CPMAS spectrum obtained with a 40 μs interruption of the high-power proton decoupling revealing the nonprotonated and methyl carbons; (C) difference spectrum revealing protonated aromatic carbons and paraffinic aliphatic carbons. The aromatic and aliphatic regions were subtracted separately because of the difference in the rate of spin dephasing for the different molecular groups.

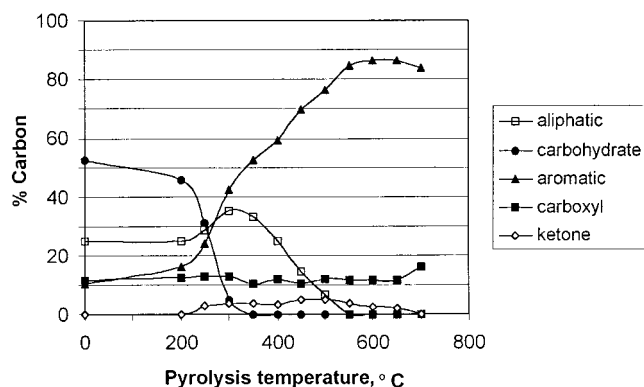


Figure 11. Relative composition of chars determined by ^{13}C CPMAS NMR analysis. The results are expressed as percentages of total carbon. Corrections for differences in cross-polarization transfer times were not made, but such corrections are expected to be only on the order of 10–15% between the aromatic and aliphatic groups and not greater than the uncertainties in the peak area measurements.

large increase in the amount of unpaired electrons in these samples. The strong dipolar fields of the electron spins severely broaden the resonances of nearby carbons, thereby reducing the total amount of carbon that can be observed by NMR (29).

The spectra in **Figure 8** were used to estimate the relative proportions of carbons bonded to different molecular groups as a function of pyrolysis temperature. The results are presented in **Figure 11** and are given in terms of the percentage of carbon in each group based on the total carbon in the char. No corrections were made for the small differences in cross-polarization transfer rates for the different molecular groups (31). In the absence of such corrections, the relative resonance peak intensities are subject to some uncertainty, but the trend of each molecular group as a function of heating temperature is more accurate. The two major molecular groups in the unheated tobacco were carbohydrate and aliphatic moieties, constituting ca. 50% and 25%, respectively, of the total carbon. The

concentration of carbohydrate carbons decreased sharply above 200 °C, becoming negligible above 300 °C. The concentration of aliphatic and ketone carbons decreased gradually and was negligible above 550 °C.

The variations in the aromatic and carboxyl carbons were particularly interesting. The concentration of aromatic carbons, which accounted for only ca. 10% in tobacco, increased monotonically with temperature to over 80% above 500 °C. These results indicate that tobacco heated at 250 °C forms a char composed predominately of aromatic, aliphatic, and carboxyl groups that becomes increasingly aromatic and carbonaceous in nature with increasing temperature. However, not all the oxygenated groups are lost on pyrolysis. The concentration of carboxyl or carbonate carbons, after volatilization of all other components, remains in approximately the same relative proportion (ca. 12%) as in the unheated tobacco over the entire temperature range.

An interesting feature that appears in the spectra of the chars formed between 250 and 400 °C is a sharp resonance peak at 169 ppm (**Figure 8**). This resonance was previously assigned to calcium oxalate by comparison of a tobacco spectrum to a spectrum of pure calcium oxalate monohydrate (27). A close inspection of the 169 ppm peak reveals it to be a doublet, whereas pure calcium oxalate monohydrate exhibits a triplet structure. The triplet structure is actually a pair of overlapping doublets, corresponding to a pair of nonequivalent molecules of oxalate in the crystal lattice. As noted earlier, calcium oxalate crystals were detected in these chars by scanning electron microscopy, and calcium oxalate undergoes dehydration at ca. 200 °C. The conversion of the oxalate resonance from a triplet to a doublet after pyrolysis at 300 °C indicated a change in the oxalate crystal structure, probably due to dehydration. The oxalate resonance became more prominent in the spectra of chars prepared at 350–400 °C. This result suggests that some calcium oxalate was formed as a result of pyrolysis reactions, but the change in resonance intensity may also be due to more efficient cross-polarization resulting from physical changes in the crystal

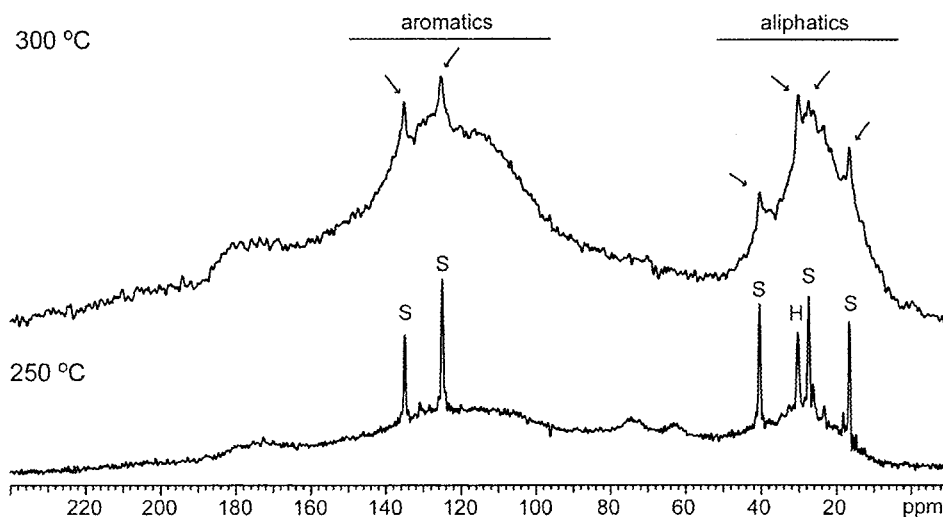


Figure 12. ^{13}C CPMAS NMR spectra of the 250 and 300 °C chars obtained with single-pulse excitation (without cross-polarization) showing solanesol (S) and hydrocarbon (H) wax.

lattice. At temperatures of 450 °C and above, the oxalate peak disappeared, indicating that the oxalate had decomposed to give CaCO_3 by decarbonylation. It should be mentioned that the oxalate does not contribute to the ketonic resonances.

Another thermal transition is illustrated in **Figure 12**. If the ^{13}C spectrum is obtained with single-pulse excitation rather than cross-polarization, resonance signals can be observed for mobile molecular groups that do not typically give cross-polarization spectra. As shown in **Figure 12**, the char heated at 250 °C exhibits a set of sharp resonances more characteristic of liquid NMR than solids. These resonances were previously assigned to solanesol (S) and hydrocarbon waxes (H) (32). Similar, but broader, resonances were observed for the char heated at 300 °C. These resonances were not detectable in chars heated at higher temperatures. Thermogravimetric analysis has shown that pure solanesol mainly decomposes to isoprene and other products at 347 °C although a small fraction may distill or remain as char (33). Thus, at least some solanesol persists in chars even after the decomposition of pectin and cellulose.

FTIR Analysis. The infrared spectra of tobacco and selected char samples are presented in **Figure 13**. Each spectrum is an average of many spectra collected for each sample. To improve the spectral quality, bands due to the atmospheric contributions of water and CO_2 have been subtracted from the spectra. The spectra show an increasing drift in baseline with wavenumber as the pyrolysis temperature increases. Kroo et al. (34), in their work on the FTIR spectroscopy of coal ash, attributed the drift in the baseline to an interaction between the ash particles and the KBr before the sample was prepared for the IR analysis. However, in our previous work (23), a similar drift in the IR baseline was observed although the chars in that work contained no ash. Thus, the baseline drift in this study was most likely due to the scatter that was produced by the more carbonized component of the char. The increase in the drift may be an indication of the increase in the amount of this component, i.e., the char being relatively more aromatic and refractory at higher heating temperatures.

Various bands in the spectra were identified corresponding to stretches for free OH (at a wavenumber of 3631–3650 cm^{-1}), hydrogen-bonded OH (3093–3577 cm^{-1} , br), aromatic CH (3023–3093 cm^{-1}), aliphatic CH_3 (2946–2987 cm^{-1}), aliphatic CH_2 (2888–2946 cm^{-1}), aromatic CH_3 , i.e., CH_3 on an aromatic ring (2829–2888 cm^{-1}), $\text{C}=\text{C}$ (1525–1731 cm^{-1}), and an aromatic CH wag, i.e., an aromatic ring (various bands between

700 and 900 cm^{-1}). Most bands covered a range of wavenumbers since the bands showed a shift in the wavenumbers with sample heating temperature. The $\text{C}=\text{O}$ stretch was seen only as shoulders on the broad $\text{C}=\text{C}$ stretching region (1731–1525 cm^{-1}) at 1695–1699 cm^{-1} for heating temperatures between 200 and 250 °C that shifted to 1738–1740 cm^{-1} between 300 and 400 °C. The $\text{C}=\text{C}$ stretch occurred at ca. 1618 cm^{-1} in tobacco and low-temperature chars but shifted gradually with heating temperature to 1579 cm^{-1} above 600 °C. There are many spectral bands in the region between 1440 and 900 cm^{-1} . Possible vibrational modes in this region include CH_2 bends, skeletal vibrations of $\text{C}-\text{C}$ and $\text{C}-\text{O}$, and OH bending, to name a few. The region between 1495 and 1348 cm^{-1} represents mostly aromatic bands. The region between 1242 and 1294 cm^{-1} contains a band near 1318 cm^{-1} , which by analogy to phenols and alcohols appears to be an in-plane OH bend. The region between 1188 and 958 cm^{-1} is the COOH region.

The IR spectrum of the unpyrolyzed tobacco was complex and showed broad bands for resonances corresponding to multiple molecular components including cellulose, pectin, hemicellulose, sugars, amino acids, alkaloids, and other plant components. As the pyrolysis temperature increased, the complexity of the spectrum decreased. At a heating temperature of 300 °C, most of the bands due to these molecular components had disappeared. This result is consistent with the NMR results that showed that the native plant structures in tobacco heated at 300 °C had disappeared, leaving a char composed primarily of aliphatic, aromatic, carboxyl, and some ketone groups. The absorbances due to the aliphatic CH_2 and aromatic CH_3 groups first increased with temperature up to 300–400 °C and then declined. These absorbances were absent above 450 °C as the char became more aromatic, consistent with the NMR.

The OH stretching region also changed its appearance with temperature. Initially at the lowest heating temperatures, the stretch was centered at 3343 cm^{-1} , corresponding to hydrogen-bonded structures, but as the temperature increased, another maximum at lower wavenumbers became apparent. The presence of this second maximum indicates multiple types of OH groups. The bands due to the OH stretches decreased rapidly and broadened above 450 °C and were totally absent in the 700–750 °C chars, indicating a disappearance of hydroxyl groups at high temperatures, a result that was also observed in pectin chars (23). The shift in the OH stretching frequency to lower wavenumbers with increasing temperatures can be attributed

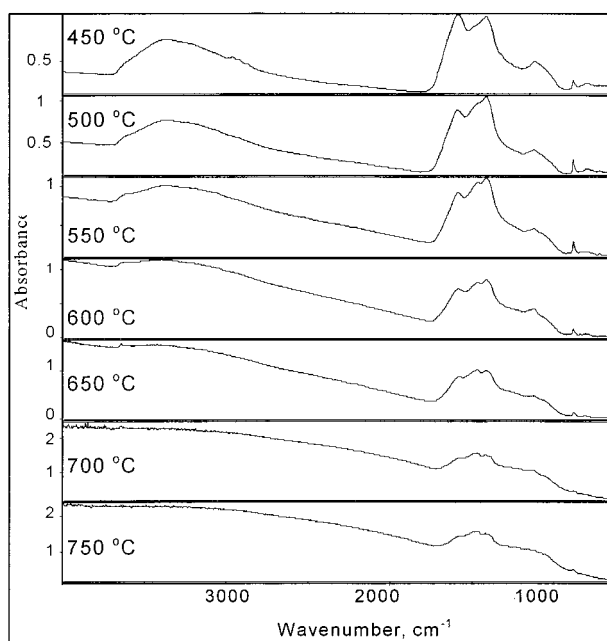
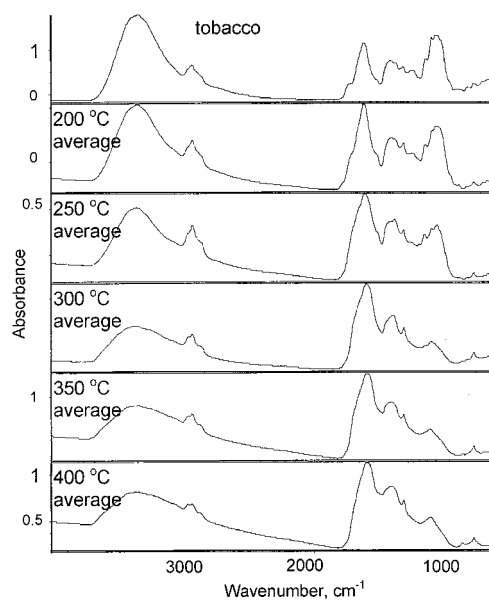


Figure 13. FTIR spectra of tobacco and its chars from pyrolysis: (A, top) tobacco and chars from 200 to 400 °C; (B, bottom) chars from 450 to 750 °C.

to the loss of hydrogen-bonded structures, while the broadening indicates a loss of structural order. These changes accompany the loss of hydrogen-bonded groups in the tobacco polysaccharides, which is essentially complete at 300 °C, and the formation of phenolic hydroxyl groups. The broadness of the OH stretch band for the 650 °C sample suggests that some strong intramolecular hydrogen bonds persist up to very high heating temperatures before the loss of these groups occurs. On the other hand, the intensity in the region between 3651 and 3631 cm^{-1} corresponds to the free OH stretching regions, which indicates the presence of some isolated phenolic hydroxyl groups in the highly carbonaceous char.

Several bands might in principle be used to monitor the aromatic character of the char. From **Figure 13A**, it can be seen that the aromatic CH stretching bands (3023–3093 cm^{-1}) are too weak for this purpose. Morterra and Low (35) also observed very weak aromatic CH absorbances for charred cellulose,

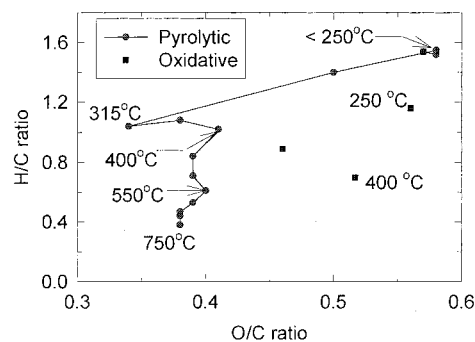


Figure 14. Relationship between the H/C and O/C ratios of chars (pyrolysis temperature as indicated).

choosing instead the aromatic CH wagging modes to monitor the appearance of the aromatic network. The aromatic CH wag modes in the 900–650 cm^{-1} region for the charred tobacco are also weak but more distinct. A band at 871–874 cm^{-1} becomes prominent in the 450 °C char and persists up to the highest heating temperatures. A shoulder on this band at 860 cm^{-1} first appears in the 450 °C char and is also likely due to an aromatic CH wag. The number of CH wag absorbance bands in the region first decreases with increasing temperature up to 300–400 °C and then increases again at higher temperatures. This indicates the decomposition of native plant components such as amino acids and alkaloids at the lower heating temperatures followed by a rise in the number of single and fused aromatic ring structures of progressively greater complexity as the char becomes more carbonaceous. A C=C stretching mode is present in the unheated tobacco spectrum at 1618 cm^{-1} . As the heating temperature increases and aromatic structures form in the char, the C=C band shifts to 1579 cm^{-1} . This absorbance band is also one of the few bands that persist up to the highest heating temperatures.

Since the chars at high temperatures consisted mainly of condensed ring aromatics, the decrease in the intensity of the aromatic bands above 550 °C could be due to a loss of the peripheral hydrogen of the chars. This is consistent with the increased evolution of hydrogen at high temperatures, observed earlier. The spectrum for the 750 °C char showed the absence of most bands and indicated a complete aromatization of the char. The results are consistent with the NMR results. Boon et al. (2) observed an increase in the aromatic character and a loss of oxygen functionalities of cellulose chars at high temperatures. Mok et al. (21) made similar observations from the IR analysis of chars prepared from cellulose at temperatures of up to 450 °C. It was hypothesized that the formation of aromatic units in the char followed the dehydration and elimination of carbonyl and aliphatic groups from cellulose. Similar types of transformations may be occurring in this study during the formation of char from tobacco.

Elemental Composition. **Figure 14** shows the relationship between the hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratios of the chars. The corresponding temperatures for some of the chars are also shown in the figure. The point labeled “<250 °C” represents the ratios for tobacco as well as for chars prepared below 250 °C. The H/C ratio decreased continuously with increasing temperature, from ca. 1.5 for unpyrolyzed tobacco to 0.4 for char at 750 °C. However, the O/C ratio decreased initially as the temperature increased to 300 °C but became constant at higher temperatures. These results are consistent with the composition of the volatile product that showed a monotonic increase in the evolution of hydrogen with temperature.

The elemental analysis of chars is also consistent with the results of the NMR and IR analyses indicating an increase in the aromatic nature of the chars with an increase in temperature. The aromatization occurred probably via condensation and growth of individual clusters, leading to lower H/C ratios at high temperatures. The increased aromaticity at high temperatures was accompanied by a decrease in the char yield. The decrease in yield indicates elimination of the aliphatic substituents, accompanied by some dehydrogenation and condensation/fusion of the products. The process may take place through homolytic cleavage and condensation of the resulting free radicals. Since the O/C ratio remained unchanged at high temperatures, the loss of hydrogen might result mainly from the direct dehydrogenation of the char. It should be reiterated that the volatile product was comprised mainly of CO, CO₂, and H₂O; the concentration of the organic components was relatively low. The invariability of the O/C ratio with temperature for various chars does not exclude the possibility of oxygen loss by decarbonylation as the amount of carbon monoxide was observed to increase with temperature. The bulk of the oxygen in the char at high temperatures was most likely in the inorganic salts in addition to the oxygen contained in the phenolic compounds. Interestingly, the oxidative pyrolysis led to a similar decrease in the H/C ratio of the char with temperature although the O/C ratio was not significantly affected. This behavior is different from those for chars obtained from chlorogenic acid or pectin (23), where the two ratios were not affected by the change in the reaction environment. In addition, an almost linear relationship between the decreases in the H/C and O/C ratios was observed for those substrates, at least until 550 °C. The content of inorganics in both chlorogenic acid and pectin was negligible as compared to that of tobacco.

Comparison of the Characterization Results. The results in this study showed that both the yield and characteristics of chars were dependent on the pyrolysis conditions. The yield decreased sharply at low temperatures before leveling off at ca. 22% above 450 °C under an inert atmosphere. The physical and chemical characteristics of chars showed a similar behavior. The char surface area decreased above 400 °C. The maximum surface area appeared to be associated with the completion of the solidification stage within the char, as described by Bonnamy (3). The ensuing carbonization step at high temperatures was detrimental to the development of a porous structure in the char. Of particular interest was the low surface area of the chars. First, such chars are unlikely to undergo a complete combustion. Second, the low surface area values appear contrary to the SEM results. The SEM analysis showed the presence of fine particles and pores in chars even at high temperatures. With such fine particles the surface area should be higher. However, the pores in the chars might be partially blocked as a result of the softening, melting, and carbonization of some of the tobacco constituents. This would prevent the access of the adsorbing gas to the pores and lead to a low surface area. It should also be realized that SEM reveals only large macropores that contribute little to the surface area.

The chemical characteristics of the chars also showed major changes with the pyrolysis conditions. The O/C ratio of the char first decreased with an increase in temperature before becoming constant above 400 °C. According to SEM analysis, above 600 °C, the char surface was mostly covered with inorganic crystals. The invariance of the O/C ratio suggested that the chars contained mostly inorganic oxygen at high temperatures, the bulk of the organic oxygen probably being lost to the volatile products below 500 °C. The volatile product contained phenols,

carboxylic acids, and pyridines, in addition to water, carbon dioxide, carbon monoxide, and hydrogen. Both the FTIR and NMR analyses indicated a near complete loss of the hydroxyl groups and a loss of carbohydrate carbon, with pectin, cellulose, and sugar moieties, below 500 °C. However, the chars contained carboxyl carbons even at 750 °C, as indicated by the NMR analysis. The H/C ratio of the char also decreased continuously, and the ratio at 750 °C was less than 50% of its value at 450 °C. The decrease is consistent with the rapid evolution of hydrogen at high temperatures (Figure 2). Both FTIR and NMR analyses also indicated a rapid loss of aliphatic groups and an increase in the aromatic character of the char above 450 °C. Even though the char did not show a significant change in its yield, the characteristics of the char continued changing even at high temperatures.

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