The Reactivity of Free Radicals in Biomass Char Studied by EPR Spectroscopy

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Abstract: In this review, the features of electron paramagnetic resonance (EPR) spectra of biomass chars prepared from single biopolymers (cellulose, pectin, lignin, etc.) to complex plant materials (tobacco) are summarized, and the interaction of biomass chars with air, O_2 and/or H_2O as detected by EPR is critically examined. The effects of inorganic components are emphasized for understanding the creation and annihilation of free radicals in biomass chars in the presence of O_2 or air. While the EPR spectra can be difficult to interpret, the interactions observed reflect fundamental processes occurring in biomass chars during pyrolysis and combustion that may affect the chemical composition of biomass conversion products as well as cigarette emission.

Keywords: EPR, Biomass Char, Tobacco.

INTRODUCTION

A substantial literature has been devoted to the formation and characterization of biomass chars [1-9]. The formation and decomposition of surface oxidation products are two important processes during the combustion and gasification of carbonaceous materials and biomass. The formation of surface oxidation products on carbonized materials is presumably a significant factor in controlling the rate of gasification and combustion of a solid and it is believed to be the initial step leading to formation of the final gaseous products [5]. Many investigations of chemisorption using direct or indirect methods have been made about the surface structures on carbonaceous solids [10, 11]. The main surface functional groups are believed to be carboxyl groups, phenolic groups, lactone moieties, and quinone-like carbonyls. However, the precise mechanisms for surface oxidation reactions are not clear. Various experimental methods, such as titration reactions, infrared (IR), nuclear magnetic resonance (NMR), and electron paramagnetic resonance spectroscopy (EPR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron microscopy, etc., have been used to study the structures of surface oxidation products or surface intermediates on carbonaceous materials [12-23].

It is generally recognized that free radical chemistry is involved in the formation, oxidation, and gasification of chars [24, 25]. Free radical centers on the char surface may be active chemically and they are candidates for involvement in a variety of chemical processes, including oxidation and gasification. Depending on concentrations and lifetimes of the free radicals, in principle EPR can be used to study free-radical intermediates directly during the oxidation or gasification reactions of solid carbonaceous materials. There have been several investigations relating EPR parameters to the oxidation of carbonaceous materials at low temperature [26], but only a few EPR studies on oxidation or gasification of biomass comparing chars with and without inorganic components have been reported [3-6, 27-31].

In this paper, interactions of free radicals in biomass and tobacco chars with oxygen as detected by EPR spectroscopy are examined with an emphasis on the influence of inorganic ions and water on pyrolysis and char-air interactions. Unless otherwise noted, the chars were prepared by heating each material under an inert atmosphere (He) for the indicated heating temperature and time, then transferred in a closed EPR tube before exposing to air during the EPR measurements at room temperature. A "low-temperature" char is a char produced by heating a starting material at T < ~ 400 ℃, while a "high-temperature" char is a char produced by heating at T > ~ 400 ℃.

GENERAL EPR FEATURES OF BIOMASS CHAR

Many EPR-based studies on biomass chars have focused on cellulose char, in part because of its abundance in wood, a major source of renewable biomass. The EPR spectral features of biomass chars (free radical concentration, linewidth, lineshape, power saturation, and g-values) never exposed to oxygen strongly depend on the pyrolysis temperature and pyrolysis time. Surprisingly, all biomass chars, irrespective of chemical composition of their starting materials, show similar overall spectral features and variation behavior with different heating temperatures. A typical EPR spectrum of biomass chars consists of a single symmetric resonance line for pyrolysis temperatures < 700 °C. For example, the EPR spectra of cellulose heated at either 300 or 550 ℃ consist of a single featureless resonance (Fig. **1**). Unlike the case of liquid sample EPR spectra in which sharp resonances often display hyperfine coupling [30], the absence of spectral fine structure in general exacerbates the difficulty of making detailed structural interpretations from the spectra of char. Nevertheless, EPR results can be useful in conjunction with data extracted from other types of experiments to help establish mechanistic insight into these complicated systems. The general features of the EPR spectra of biomass chars have commonly been explained in terms of stable aromatic free radicals, as described below [1-6, 8, 9, 27, 29, 32, 33].

FREE RADICAL CONCENTRATION AND G-VALUE

Generally, the free radical concentration increases rapidly during the initial heating period in the absence of oxygen, followed by a slow, small increase. For pure cellulose, however, the free radical concentration increases over a period of 20-60 min; while for cured tobacco such increase appears in a few minutes, indicating that tobacco is more easily pyrolyzed than pure cellulose [28, 29]. DeGroot and Shafizadeh found that the free radical concentration in cellulose char increases monotonically with temperature when charring time is very short (1.5 s) [5]. In the case of long-time pyrolysis (ca. one hour), as the charring temperature increases, the free radical concentration first increases and then decreases. A maximum spin concentration of the magnitude of 10^{19}-10^{20} spins/g can be found in the temperature range from 500 to 600 °C for all biomass chars [2-9, 27, 29, 32, 33]. The g-value of the char decreases from 200 to 500 °C and stays nearly constant above 500 °C. The g-value of low-temperature char (250-300 °C) ranges from 2.0030 to 2.0047, depending on the starting biomass and pyrolysis time, but for high-temperature char (T > 500 °C) g = 2.0027, independent of the biomass species. The latter value is only slightly larger than the free electron g-value, 2.0023.

LINESHAPE AND LINEWIDTH

The EPR lineshapes and linewidths of typical biomass chars vary with charring temperature and time. EPR spectra of chars pre-

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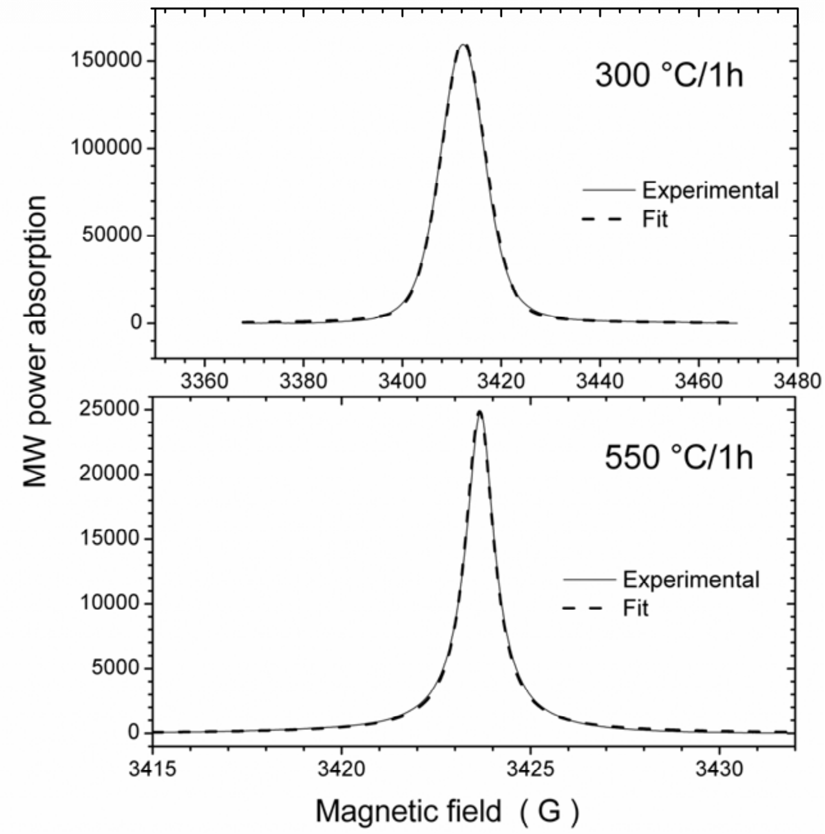

Fig. (1). EPR lineshape for two typical cellulose chars (low and high charring temperatures). High-temperature char exhibits pure Lorentzian lineshape (bottom); low-temperature char shows a linear combination of Lorentzian (0.35) and Gaussian (0.65) components (top), from reference [27].

pared at temperatures above ca. 400 °C usually exhibit an approximately Lorentzian lineshape (Fig. **1**), while the spectra of chars prepared below ~400 °C cannot be characterized by either a single Lorentzian or Gaussian component but a linear combination of the two components. The Gaussian part is the major component of the spectra of the low-temperature chars, while the Lorentzian component increases steadily with increasing charring temperature. The Gaussian lineshape has been attributed to isolated, non-interacting free radicals, while the narrow Lorentzian lineshape is a result of electron to electron spin-exchange processes [2, 7, 9, 28]. Coulombic spin-exchange interactions arise as a result of overlapping electronic wave functions when the concentration of radicals is high and the unpaired electrons are delocalized over networks of π bonds in large polycyclic aromatic rings. The expected broadening that typically is observed due to the electron-proton hyperfine and electron dipolar interactions is reduced by the rapid exchange of the electron spins, yielding the average frequency that is observed for all the EPR transitions [34].

The EPR resonance of chars of pure cellulose heated above 500 °C are extremely sensitive to the presence of oxygen or air in the samples. The linewidths can increase by as much as a factor of 100 or more by the paramagnetic effect of oxygen. This phenomenon results from the physisorption of oxygen molecules on internal surfaces of sample and was noted many years ago in carbonized organic materials. The linewidth has been shown to be proportional to the partial pressure of oxygen over the sample [2, 9, 35-37]. The difference between the linewidths in the presence and absence of air appears to reflect the change in surface area and thus the extent of oxygen penetration into internal pores. The minimum in the peak-to-peak linewidth (~1 G) appears at charring temperatures between 500-600 °C (Fig. **2**). For pure cellulose char, the oxygen-induced broadening of the EPR resonance is reversible and the narrow signals can be restored by rigorous evacuation of the sample. The sensitivity of the EPR resonance to oxygen or air gradually decreases above ca. 750 °C but the signal remains very broad and weak even in the absence of oxygen. This is due to the onset of electrical conductivity and the skin-depth effect on microwave penetration [25].

MICROWAVE POWER SATURATION

The intensity of EPR resonance can be affected by the electron spin-lattice relaxation time, T_{1e}. A large T_{1e} value corresponds to an easily saturated resonance that results from applying too high microwave irradiation power. The low-temperature biomass chars (for example, a pectin char heated at 300 °C for 1 h) show EPR saturation behavior at a low microwave power (less than 1 mW), which is typical of lower concentration, isolated radicals. Therefore, to quantify the concentration of radicals in the low-temperature chars, a sufficiently low microwave power must be chosen to avoid the saturation effect. For high-temperature chars, e.g., a 500 °C char of pure cellulose, complete microwave power saturation does not occur even at a very high microwave power of 100 mW.

EFFECTS OF INORGANIC ADDITIVES

Biomass usually contains various endogenous inorganic compounds. Chars prepared from cellulose mixing with different inorganic additives have often been used to model other biomass chars and the effect of the additives. These inorganic additives have included Na_2CO_3, $NaHCO_3$, Li_2CO_3, K_2CO_3, NaCl, $Na_2B_4O_7$, H_3BO_3, metallic nickel, iron oxides, and others. The EPR spectra of these chars all exhibit similar spectral characteristics that are qualitatively similar to the pure cellulose chars; the inorganic additives only cause quantitative variations to the spin concentrations, linewidths and power saturation, etc. DeGroot and Shafizadeh found that radical concentrations do not differ significantly between the chars prepared by heating pure cellulose and cellulose mixtures with in-

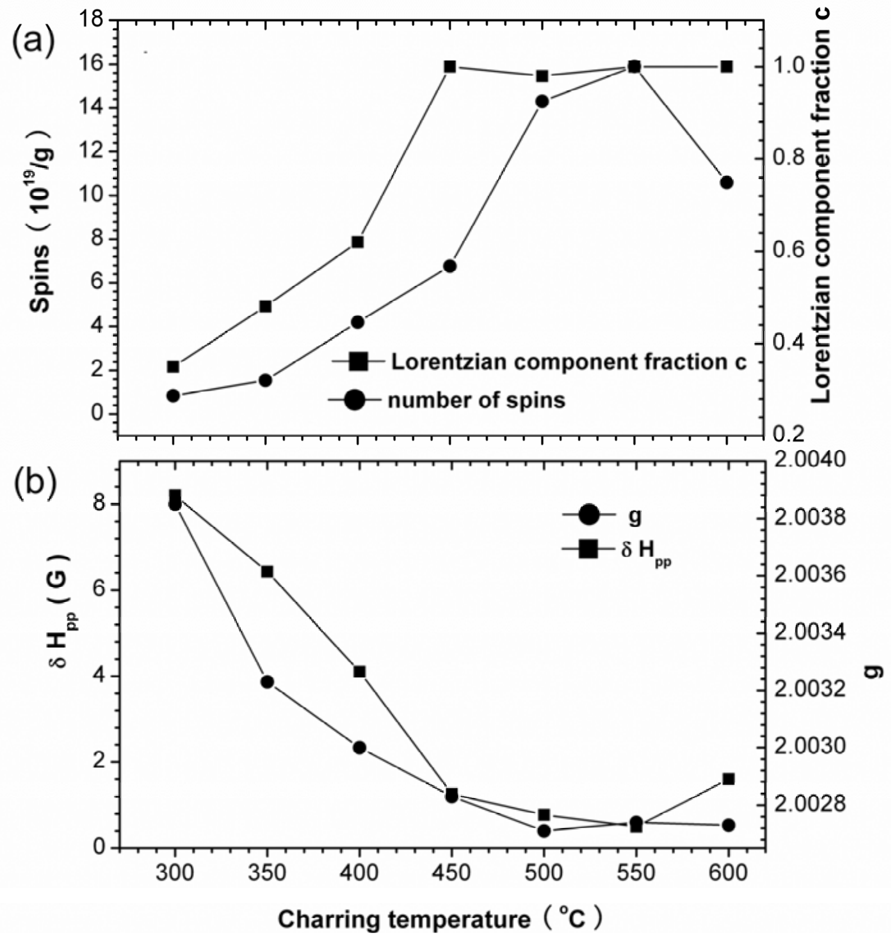

Fig. (2). Variations of EPR g-values and spin concentrations with charring temperature for cellulose/Na_2CO_3 char (no air exposure), from reference [27].

organic additives (NaCl, $Na_2B_4O_7$, and H_3BO_3) at high heating temperatures (600-700 °C) for a very short heating period (1.5 min), but the radical concentrations in a cellulose/NaCl char heated at 400-550 °C is markedly higher than that in the corresponding pure cellulose char [3]. This difference was ascribed to the accelerated pyrolysis of cellulose promoted by the addition of NaCl. Feng *et al.* compared EPR behaviors of the pure cellulose char, cellulose/NaCl (6.9 wt %) and cellulose/Na_2CO_3 (6.9 wt %) chars by heating under He at 350 °C for one hour [28]. The free radical concentration, linewidth and g-value from pure cellulose char and cellulose/NaCl char were found not to be significantly different, while the free radical concentration in 350 °C/1h cellulose/Na_2CO_3 char is about 20-30% lower than that of the corresponding pure cellulose char. They also compared the ^{13}C NMR spectra of the above cellulose chars and found that the aromatic-to-aliphatic carbon ratio in the pure cellulose and cellulose/NaCl chars is very close, but remarkably higher than that of the corresponding cellulose/Na_2CO_3 char. Therefore, the *free radical concentration appears to be correlated with the concentrations of polycyclic aromatic clusters* [28, 38].

EPR BEHAVIOR AND BIOMASS CHAR STRUCTURE

In general, low-temperature biomass chars observed before any exposure to O_2 exhibit low spin concentrations, broad non-Lorentzian lineshapes, large *g*-values, and low saturation powers; on the contrary, high-temperature chars show high spin concentrations, narrow Lorentzian lineshapes, small *g*-values, and high saturation powers. It is generally recognized that free radicals in chars primarily reside in stable aromatic systems [10, 25]. A low concentration of aromatic structures is assumed to limit the concentration of stable organic free radicals. The small size of the aromatic clusters in the low temperature chars and the presence of oxygen in their structure are regarded as the main reasons for a large *g*-value, since oxygen has a spin-orbit coupling constant that is much larger than that of carbon [25, 39, 40]. The broad Gaussian lineshape observed in the low-temperature biomass chars is attributed to inhomogeneous spin interactions (i.e., unresolved hyperfine interactions between unpaired electrons and protons) and the inhomogeneity of the related *g*-tensors that results from variations of structure and orientation of aromatic moieties in the chars.

Reversible changes of the EPR parameters (i.e., restoration of the EPR intensity, linewidths and g-values by vacuum evacuation or N_2 displacement) caused by O_2 or air exposure of chars at room temperature have been widely reported for other carbonaceous materials [2, 4, 5, 25, 25]. Evacuation of the sample or displacement of the O_2 by an inert gas eliminates the spin-spin interactions between the unpaired electrons of physisorbed oxygen on the surface with the unpaired electrons in the char as well as the formation of weak charge-transfer complexes of aromatic molecules with O_2 (chemisorption) [10, 11, 18, 25, 40, 41]. However, exposure to O_2 or air at higher temperatures (230 °C) for high-temperature chars results in a reduction of the free radical concentration that is *not* reversible in vacuum at room temperature, but *is* reversible at higher temperatures (~ 400 °C). This result indicates that the char radicals react directly with oxygen to form the surface oxides. DeGroot and Shafizadeh compared the number of the char radicals removed by O_2 with the amount of chemisorption O_2, and found that the former is only on the order of one percent of the latter [5]. They concluded

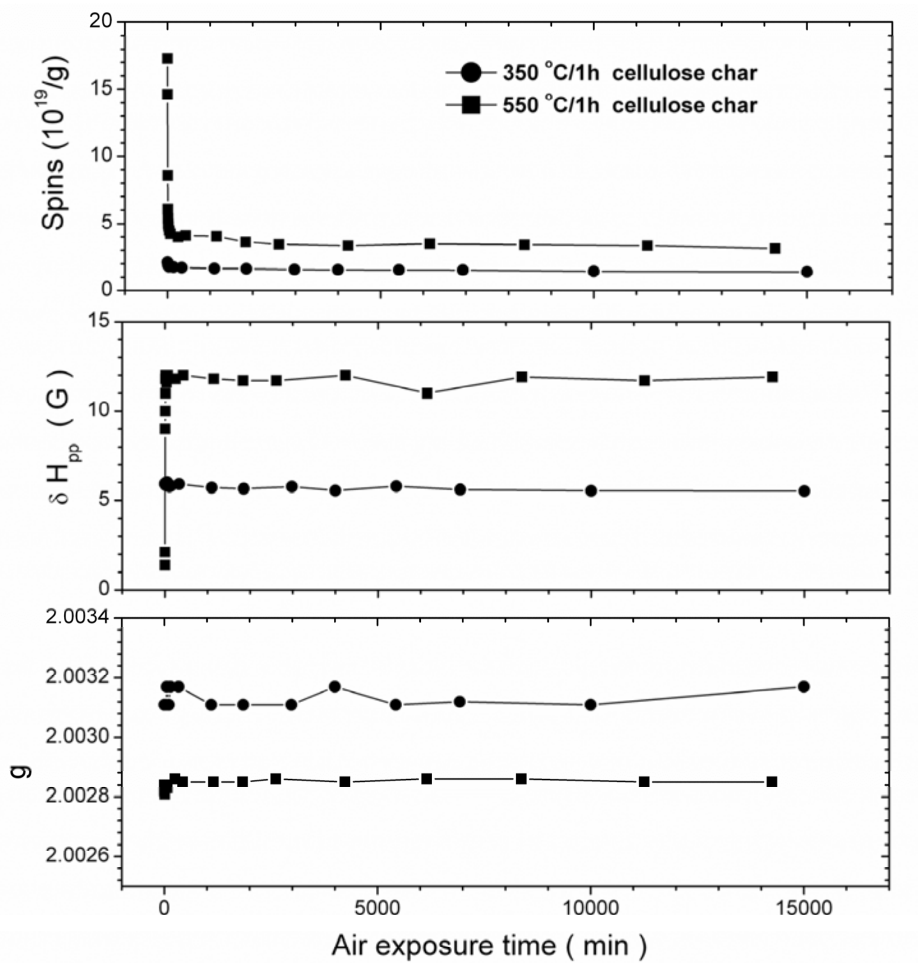

Fig. (3). Variations of EPR parameters for pure cellulose chars at room temperature with air exposure time for heating time/duration: 350 °C/1h (•) and 550 °C/1h (■), from reference [42].

that *surface functional groups other than free radicals could be major reactive sites*. Harker *et al.* investigated the role of free radicals in oxidation of cellulose char and concluded that the free radicals are in fact *not* highly reactive to oxygen due to the stabilization of the unpaired electrons over large aromatic ring systems [35].

INTERACTION OF CELLULOSE CHARS WITH O_2 OR AIR

Various inorganic compounds not only modify the pyrolysis properties of biomass but also dramatically affect the oxidation behaviors of the biomass char. To study the role of certain inorganic additives, chars prepared by heating cellulose mixed with a variety of inorganic additives including NaCl, $Na_2B_4O_7$, H_3BO_3, Na_2CO_3, $NaHCO_3$, K_2CO_3, Li_2CO_3, and calcium acetate have been investigated. These effects are described below.

OXIDATION OF PURE CELLULOSE CHAR

The EPR behavior of pure cellulose chars (free of any inorganic contaminants) during exposure to air (or O_2 and/or H_2O) at room temperature strongly depends on the charring temperature. DeGroot and Shafizadeh showed that EPR signals for pure cellulose chars prepared at temperatures less than 500 °C are slightly enhanced on room-temperature exposure to air; this signal enhancement ascribed to the saturation effect [4, 5]. For the low-temperature cellulose chars ($T < 400$ °C), Feng *et al.* found that the EPR signal is totally insensitive to room-temperature O_2 exposure and largely insensitive to room-temperature air (or O_2/H_2O) exposure [27, 29, 42]. In the latter case, only a small decrease in free radical concentration was observed as a result of air exposure, and the linewidth and *g*-value remained almost constant (Fig. **3**). The EPR signal of low-temperature cellulose char that was air-exposed does not change very much after evacuation at room temperature, while the full EPR signal of the unexposed char was restored by vacuum evacuation at higher temperature (for example at 140 °C).

In contrast, the EPR of the high-temperature cellulose chars ($T \geq 400$ °C) is very sensitive to O_2 or air exposure at room temperature [4, 5, 27, 42]. As seen in Fig. (**3**), the intensity of EPR signal decreases rapidly during the initial air exposure. Correspondingly, the linewidth of the single EPR peak also increases rapidly with increasing exposure time for about 10 minutes, from 1.4 to 12 G, then leveling off to a near constant value. The *g*-value stays nearly constant throughout the entire air-exposure period. The EPR signal can be restored by evacuating the air-exposed samples at room temperature or by simply purging the air-exposed samples with N_2 at room temperature.

EFFECTS OF INORGANIC ADDITIVES ON CELLULOSE CHAR OXIDATION

Oxidation behaviors of cellulose mixture chars prepared by heating cellulose mixtures with various inorganic additives have been investigated by EPR. The EPR behavior of pure cellulose and cellulose mixtures with inorganic salts (NaCl, $Na_2B_4O_7$, and H_3BO_3) with oxygen exposure does not differ significantly between these two types of chars [4, 5]. Feng *et al.* found that the EPR spec-

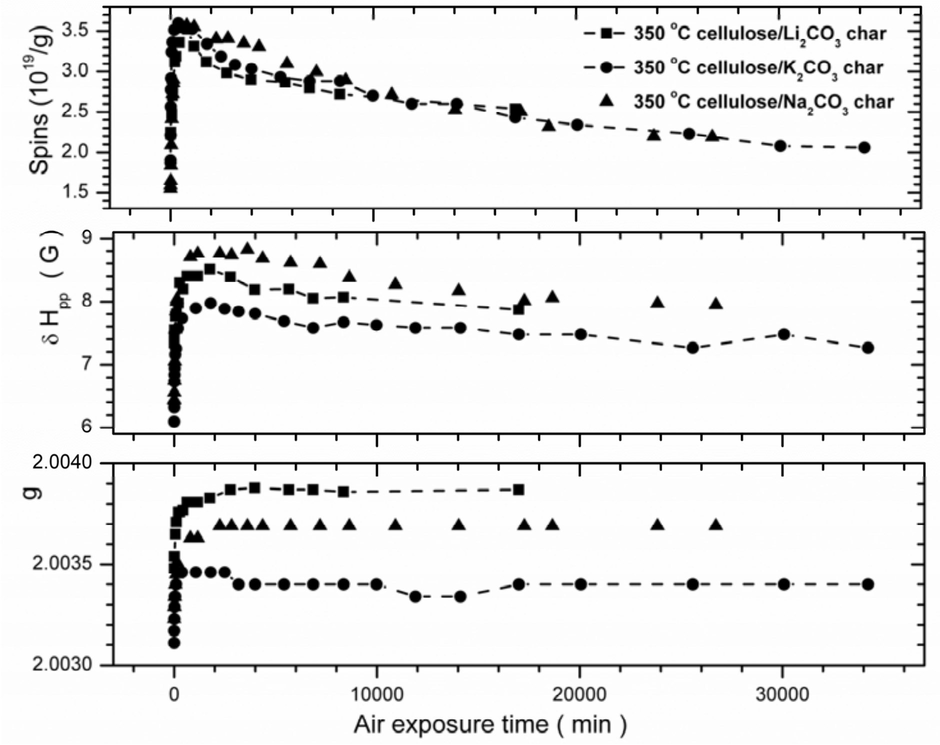

Fig. (4). Effects of air exposure on EPR characteristics of 350 °C/1h cellulose chars with different additives (Li_2CO_3, Na_2CO_3, K_2CO_3), from reference [27].

trum of a 350 °C/1h cellulose/NaCl char is largely insensitive to air exposure at room temperature, like the corresponding pure cellulose char. Thus, it appears that the addition of NaCl, $Na_2B_4O_7$ or H_3BO_3 does not change the EPR-detected oxidation behavior of the low-temperature chars. In contrast, the presence of other inorganic additives in cellulose chars, such as alkali carbonates, alkali bicarbonates and calcium acetate (Li_2CO_3, K_2CO_3, Na_2CO_3, $NaHCO_3$ or calcium acetate), dramatically changes the room-temperature oxidation behavior of cellulose chars. EPR behaviors of the chars of these cellulose mixtures during exposure to air at room temperature also strongly depend on the charring temperature. The following patterns summarize the EPR results.

FORMATION OF “NEW” RADICALS BY CHAR OXIDATION

The low-temperature chars prepared from cellulose/inorganic mixtures (Li_2CO_3, K_2CO_3, Na_2CO_3, $NaHCO_3$ and calcium acetate) at temperatures 250-400 °C all display very similar EPR spectra during air exposure (Fig. **4**). The free radical concentration in these chars increases rapidly during the initial air-exposure period. Correspondingly, the peak-to-peak EPR linewidth and *g*-value also increase rapidly. Upon prolonged air exposure (more than a week), the free radical concentration decreases slowly accompanied by a slow and small decrease in linewidth, but the *g*-value does not change during this slow process. Similar EPR variations were observed in an atmosphere of pure O_2. This pattern indicates that air or O_2 exposure of these chars involves at least two different types of chemical processes, the *production* and *annihilation* of free radicals. The “new” radicals formed in chars (250-400 °C) during air (O_2) exposure have *g*-values from 2.0030 to 2.0048, which are larger than those of “old” free radicals in the corresponding chars generated directly by pyrolysis. The concentration of new radicals is comparable with, or in some cases higher than, that of the “old” free radicals. These “new” free radicals *presumably form at non-radical sites* of the char surface, *not* primarily through a direct reaction of O_2 with “old” free radical centers, since the latter process only transforms carbon-centered radicals into ephemeral peroxy free radicals and do not increase the total concentration of free radicals. The *g*-values of the “new” free radicals are similar to the *g*-values of various oxygen-containing polycyclic aromatic hydrocarbons [41, 43, 44].

Evacuation of the air-exposed low-temperature cellulose/Na_2CO_3 chars indicates that there are *two different types of desorption processes* with different thermal activation characteristics, i.e., simply evacuating the sample at room temperature does not restore the EPR signal. Vacuum evacuation at temperatures of 140 to 210 °C *enhances* the EPR intensity; however, subsequent evacuation at 310 °C *decreases* the EPR intensity and the EPR signal of the original, unexposed char appears to be recovered. The cellulose/alkali carbonate (or bicarbonate) chars obtained at *higher* pyrolysis temperatures (450, 500, 550, and 600 °C/1h), show *completely different* EPR behavior on exposure to air from that described above for the low-temperature chars (charring temperature ≤ 400 °C) (Fig. **5**). The EPR intensity of the high-temperature chars decreases rapidly with increasing air exposure time, apparently showing no short-term intensity increase. During air exposure period, a *narrow* EPR component and a *broad* EPR component can be observed. The narrow EPR peak has the same linewidth and the same *g*-value as that of the unexposed chars. This is a *different* case from the high-temperature pure cellulose chars, where only one EPR peak was observed during the air exposure period and its linewidth increased with increasing air-exposure time. Moreover, the EPR measurements show that the interaction of air with high-temperature pure cellulose chars occurs more rapidly upon air exposure than with the corresponding cellulose/Na_2CO_3 chars. For this kind of high-temperature chars, the EPR signal reduction induced by air exposure can be reversed by evacuating the air-exposed samples at room temperature or by simply purging the air-exposed samples with nitrogen.

The coexistence of narrow and broad EPR components has also been observed during the air or O_2 exposure of Yallurn brown coal [45], wood char, and sucrose/$ZnCl_2$ char [37, 46]. A priori, possible interpretation of the two-resonance observation is that the narrow

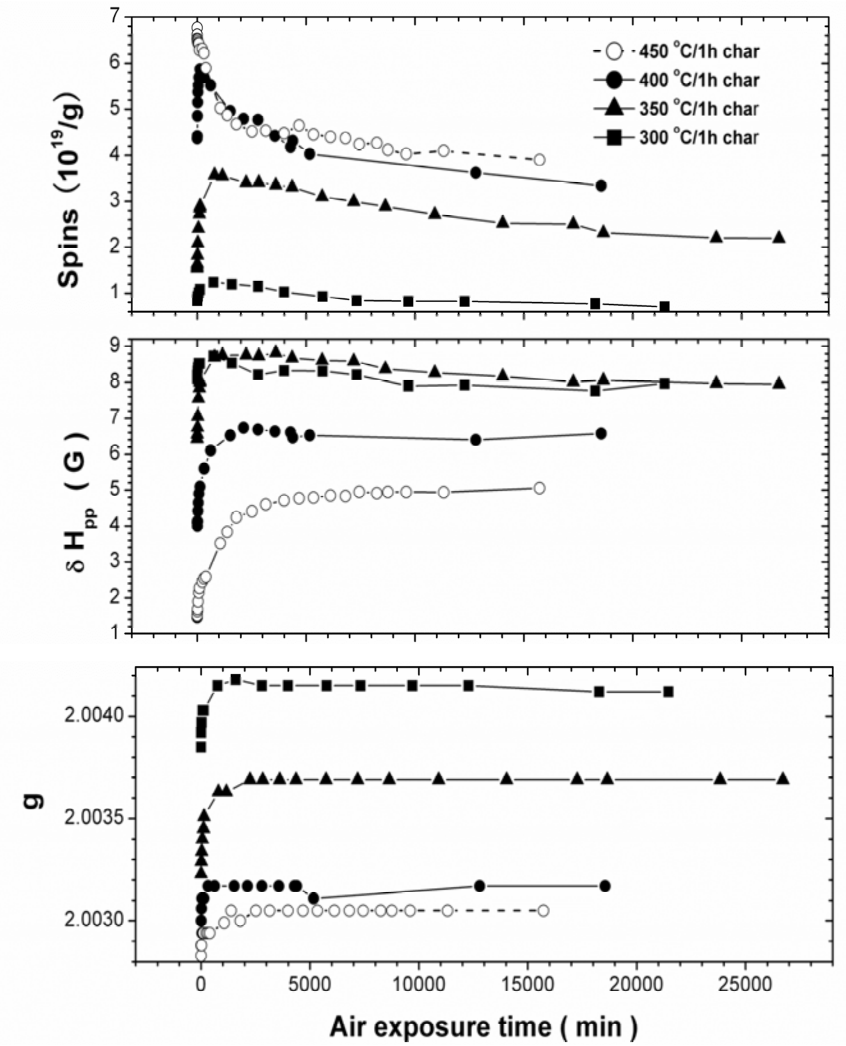

Fig. (5). Room-temperature EPR variation with air-exposure time for cellulose/Na_2CO_3 chars obtained at various heating temperatures, reproduced from data in reference [27].

EPR signal is generated by aromatic free radicals in the core of the char, which are not accessed by O_2 and/or H_2O, and have the same *g*-value and the same peak-to-peak linewidth as those of the unexposed char; *the broad EPR signal represents surface free radicals that interact with* O_2. According to this interpretation, the fact that no narrow EPR component (from interior radicals) is present in pure-cellulose chars during air exposure implies that high-temperature chars of pure cellulose have a very high surface-to-volume ratio, so most of the radicals are at or near the char surface.

EFFECT OF WATER VAPOR ON RADICAL FORMATION

The spectral features at room-temperature upon exposure to O_2 of the cellulose/alkali carbonate (or bicarbonate) chars prepared at high heating temperatures are substantially different from those upon exposure to air [27, 29]. A rapid initial increase in free radical concentration with unchanged linewidth and *g*-value can be observed on room-temperature exposure to pure O_2 for high-temperature cellulose/Na_2CO_3 char, but an initial *decrease* in radical concentration seen with air exposure is absent with O_2 exposure. This behavior is apparently related to the free radical decreases when H_2O vapor is introduced into the He/O_2 gas stream. The annihilation of radicals on the char surface by water may be related to the annihilation of radicals in cigarette smoke particulate matter [47]. The above O_2 and H_2O exposure patterns indicate that any interpretation of the air-exposure results just in terms of oxidation by O_2 is oversimplified. The rapid radical concentration decrease seen in the air exposure of high-temperature cellulose chars does not necessarily mean that no “new” free radicals are formed in these high-temperature chars during air exposure, since the annihilation rate of free radicals induced by H_2O can be larger than the rate of radical generation by O_2, giving rise to a net decrease in EPR intensity. However, it should be noted that the “new” free radicals generated by O_2 have the same *g*-value as that of the “original” free radicals, about 2.0027. Thus, for the cellulose/Na_2CO_3 550 °C/1 h char, any *simple interpretation in terms of* O_2 *oxidation to form O-centered radicals is not readily supported by the data.*

IN-SITU HIGH-TEMPERATURE EPR MEASUREMENTS

Feng *et al.* performed *in-situ* EPR measurements during O_2 exposure of pure cellulose chars and chars of cellulose/inorganic mixtures at temperatures from 315 °C to 485 °C. Pure cellulose was isothermally pyrolyzed under flowing He atmosphere for a relatively long period (~2h) and subsequently pyrolyzed under flowing O_2/He mixture at the same temperature, and finally charred under flowing He gas. During the three different periods, EPR signal as function of pyrolysis time was *in-situ* recorded. O_2 exposure at 315 °C leads to a small increase in free radicals, but O_2 exposure at 485 °C results in substantial decrease in free radicals. These two process are irreversible because the O_2-induced variation in the second period (O_2/He) cannot be recovered by subsequent He purging. This

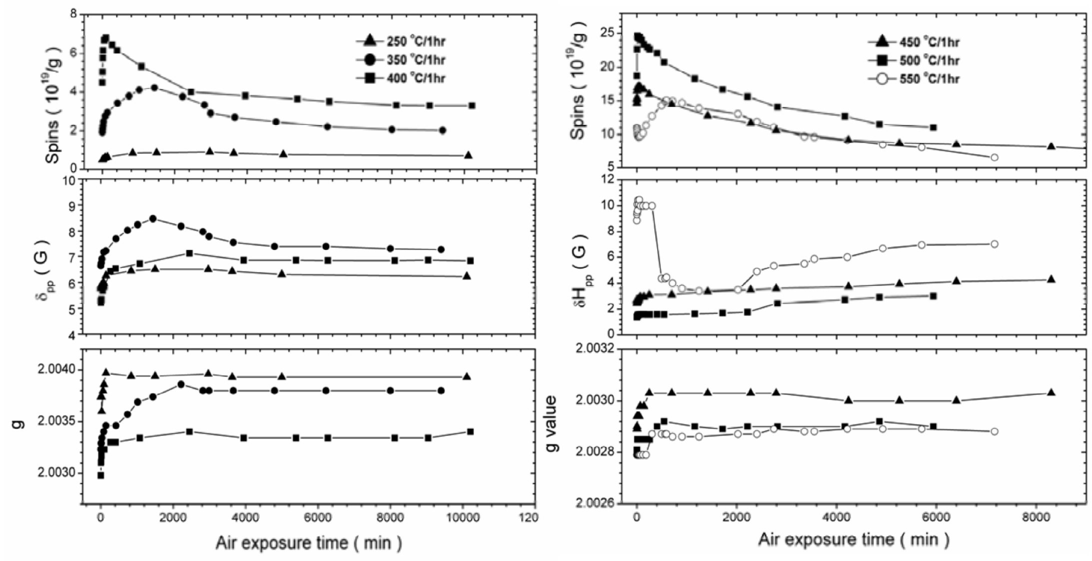

Fig. (6). Effects of air exposure time (room temperature) on EPR characteristics pectin chars prepared at by heating in the absence of air for 1 hour at the indicated temperatures [42].

indicates that *O_2 reacts with surface functional groups at 315 °C but with free radicals at 485 °C.*

The oxidation behaviors of cellulose/Na_2CO_3 chars were also investigated by *in-situ* high-temperature EPR and compared with results of the pure cellulose char. Cellulose/Na_2CO_3 mixture was first charred under He at 315 or 485 ℃ for a relatively long period and then exposed to O_2/He mixture gas at the same temperature with simultaneous EPR measurement. Compared with the pure cellulose chars, the EPR signals for the cellulose/Na_2CO_3 chars are much more sensitive to O_2 exposure. O_2 exposure at both low- and high-temperatures results in initially rapid increase in free radicals. This indicates a rapid reaction of O_2 with surface functional groups or non-radical sites on the char surface to form additional *new* radicals during the initial O_2 exposure at 315 °C ~ 485 °C. However, these new radicals disappear upon further O_2-exposure, possibly via decomposition or gasification of radical-related groups [29].

INTERACTION OF OXYGEN WITH PECTIN CHAR CONTAINING NA

Pectin (methyl esters polygalacturonic acid) is an abundant polysaccharide in herbaceous plants. The cured tobacco leaf, for example, contain ca. 10-14 % pectin by dry weight [48]. The formation of pectin char with added sodium has been studied by DSC, DTA, SEM, and ^{13}C CPMAS NMR. A commercial citrus pectin (Hercules) containing 2 wt % Na was charred in an inert atmosphere at temperatures from 250 to 600 °C [49]. Fig. (**6**) summarizes the variation of the EPR spectral parameters with charring temperature for the pectin chars during air exposure. The pectin chars produced at 250 °C to 500 °C show a pronounced initial increase in free radical concentration when exposed to air at room temperature, indicating that additional free radicals are formed as intermediates during air exposure. Correspondingly, the peak-to-peak EPR linewidth and *g*-value also increase rapidly. However, with prolonged exposure the free radical concentration decreases slowly accompanied by a slow and small decrease in linewidth, but the *g*-value does not change during this slow process. The above air exposure pattern of pectin chars is *similar* to that of the low-temperature cellulose/Na_2CO_3 chars (300-400 °C), in contrast to the pure cellulose chars.

When the charring temperature is increased to 550 °C or to 600 °C, the increase in free radical concentration upon air exposure becomes slow accompanied by an abnormal variation in linewidth. The air-exposure pattern of high-temperature pectin chars is *different* from that of the high-temperature cellulose/Na_2CO_3 chars (450-600 °C). For the latter, there is an initial rapid *decrease* in free radical concentration upon air exposure and *no increase* in free radical concentration can be seen during the whole air-exposure period. This phenomenon may be related to the observations of Waymack *et al.* [49] who showed that the uronic acid groups initially bound to sodium or potassium salts in pectin decompose during pyrolysis between 200 and 400 °C to produce a metal complex in the char that apparently inhibits/shields the carbonaceous char from oxidation at the oxidation temperatures less than ca. 550 °C. Temperatures in excess of 600 °C are needed in either oxygen or inert gas to decompose the metal–char complex and allow oxidation of surrounding carbon.

Although the EPR signal of low-temperature pectin chars (350 °C) cannot be restored by evacuating or purging the sample with N_2 at room temperature, subsequent evacuation at higher temperatures (> 210 °C) enhances the EPR signal dramatically. With further evacuation at 310 °C of this maximum-intensity sample, the EPR intensity decreases and the EPR intensity, linewidth, and *g*-value, nearly returns to the values of the original, unexposed char. However, for the 550 °C/1 h pectin char, N_2-purging at room-temperature restores the maximum free radical concentration that appeared during the preceding air exposure period, but this restored EPR signal has a smaller peak-to-peak linewidth and the EPR lineshape of the original, unexposed char cannot be restored. Obviously, such a desorption pattern of the pectin char generated in 1 h at 550 °C is *different* either from that of the 350 °C/1 h pectin char or from that of the 550 °C/1 h pure-cellulose char and cellulose/Na_2CO_3 char.

INTERACTION OF TOBACCO CHAR WITH OXYGEN

Tobacco is a complex material that consists of 6-15% cellulose, 10-15% pectin, roughly 2% lignin, and a variety of other organic components. The most abundant metal ions are K, Ca, and Mg, respectively [51]. In one study [28, 42], tobacco was washed with acid and water to remove the content of inorganic components. The untreated tobacco and water-washed tobacco were then pyrolyzed at temperature from 300 to 600 °C for one hour; the effect of air-exposure on their EPR spectra was compared. The variations of EPR parameters of the unwashed tobacco chars during air exposure are similar to those of the corresponding Na-containing pectin

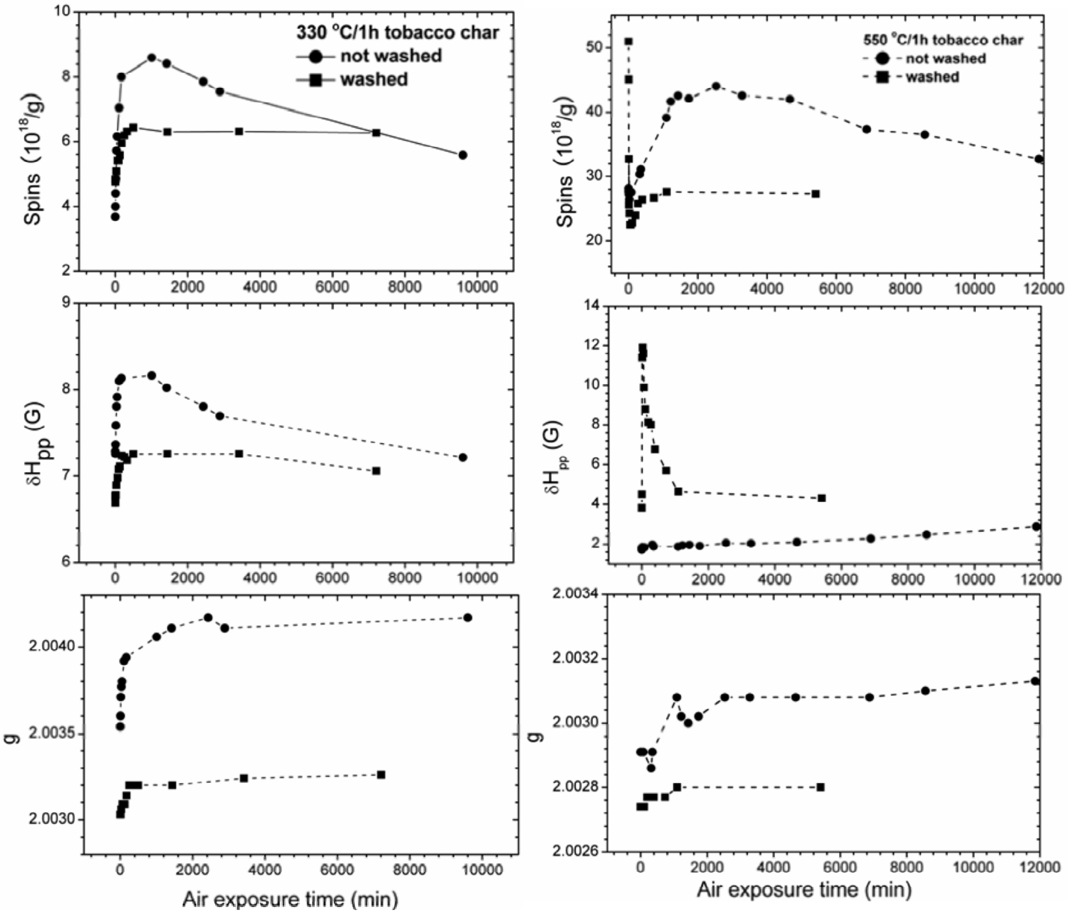

Fig. (7). Variations of EPR intensity, peak-to-peak linewidth and g-value on air exposure to air at room temperature for untreated and treated Burley tobacco chars, 330 ^{o}C/1h (left) and 550 ^{o}C (right).

chars, except for different linewidth of the 550 °C/1 h tobacco and 550 °C/1 h pectin chars [28, 42]. Two typical air-exposure behaviors, one representing the low-temperature 330 °C/1h char and the other representing the high-temperature 550 °C/1h char, are shown in Fig. (**7**). The low-temperature char of treated tobacco (charring at 330 °C for 1 h) still exhibits the characteristic initial increase in free radical concentration, which is ascribed to the effect of inorganic components, but the increase is significantly reduced relative to that of the corresponding char of unwashed tobacco. This shows that the inorganic components was not completely removed by washing.

For a high-temperature char of water washed tobacco (charring at 550 °C for 1 h), the EPR intensity decreases dramatically and then increases significantly at the early stage of air exposure, in contrast to the initial increase in EPR intensity observed in the untreated tobacco char. The process associated with increase in EPR intensity becomes less obvious in the treated tobacco chars due to the reduced inorganic content. This result suggests a complicated chemical interaction involving the *creation* and *destruction* of carbon-centered and oxygen-centered radicals. These results also confirm that the presence of certain alkaline and alkaline earth metals promote the formation of new free radicals during tobacco pyrolysis, which may have implication for radical formation in the oxygen-deficient “pyrolysis zone” inside the hot coal of a burning cigarette [50].

MECHANISMS OF FREE RADICAL FORMATION IN BIOMASS CHARS

Free radicals are important to explain oxidation or gasification of carbonaceous materials [4, 11, 27, 29, 41, 42]. However, it is not clear whether free radical reactions have dominant importance in the charring or char oxidation of these materials. The various changes observed in the EPR spectra are entirely due to free radicals and free radical processes. A variety of mechanisms have been suggested for generation of free radicals during charring or char oxidation. Schemes 1-7 shown in Fig. (**8**) summarize much of the known, hypothesized, or *a prioi* anticipated radical processes; these include radical formation processes (Schemes 1, 5a, and 6c), radical propagation processes (Schemes 2, 3, 4, 6a, and 6b), and radical termination processes (Schemes 7 and the reverse of 6c). A detailed discussion of the suggested mechanisms has been given [27].

O_2-based mechanisms have often been suggested for the formation, transformation or annihilation of free radicals in chars [5, 27, 29, 33, 42]. However, Harker et al. have investigated role of free radicals in oxidation of cellulose char and concluded that the free radicals in chars are not highly reactive to oxygen due to the π-character of unpaired electrons [35]. DeGroot *et al.* suggested that functional groups could be major active sites even though free radicals are reactive species in carbon and they further indicated that sodium chloride could catalyze the formation of “active sites” during carbonization and thus enhances char combustion [4, 5]. But EPR-detected oxidation behaviors of pure cellulose char and cellulose/NaCl char observed at room temperature are not significantly different. Free radical intermediates have been observed only rarely during the reaction of O_2 with related carbonaceous solids [45]. The air oxidation or gasification of most carbonaceous materials occurs at temperatures above 200 °C [11].

The presence of alkali carbonates or bicarbonates, the oxidation of both low- and high-temperature chars can occur even at room temperature, whereas the EPR characteristics of *low*-temperature pure-cellulose chars is relatively insensitive to air or O_2 exposure.

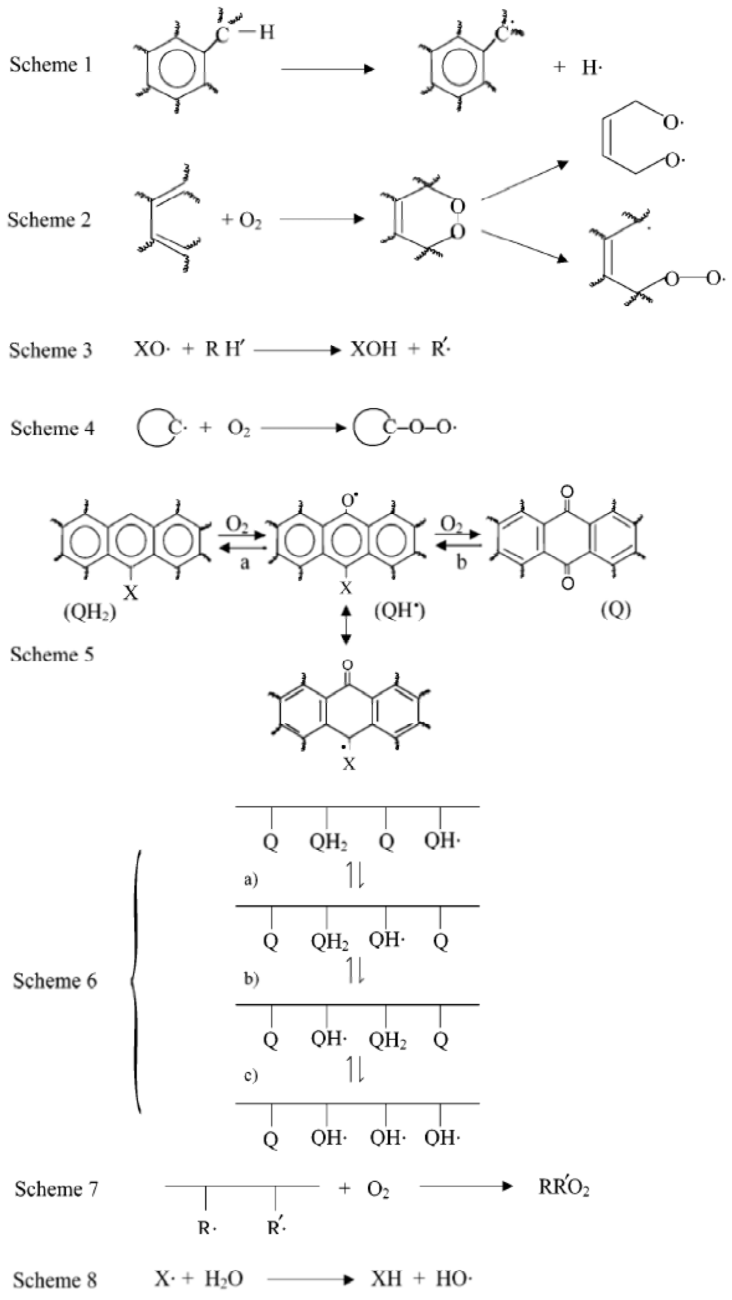

Fig. (8). Schemes 1-8 showing various proposed mechanisms for involvement of radical reactions in biomass char surface chemistry (from reference [27]).

This difference may be anticipated to be due to effects of the inorganic compounds, most specifically the catalytic oxidation of chars by oxygen [33, 40], which leads to a facilitation of oxidation and a lowering of the temperature required for oxidation. As demonstrated by comparing the air-exposure behavior with O_2-exposure and O_2/H_2O-exposure behaviors of cellulose/Na_2CO_3 chars, the overall air-exposure results *can not be ascribed only to the oxidation by* O_2, and *water is a major factor for the rapid attenuation of radical concentration accompanying air exposure.* This latter pattern implies a possible role for processes such as that seen in Scheme 4, assuming the manifestation of efficient $^{\bullet}OH$-initiated propagation/termination mechanisms that quickly quench the free radical concentration. Scheme 5b also involves a decrease in unpaired electron concentration with the formation of diamagnetic species (e.g., Q) and could perhaps contribute to the slow decrease in EPR intensity at long air or O_2 exposure times.

DISCUSSION

The EPR results reviewed so far are important to explain the different char structures from different biomass after pyrolysis and combustion [51]. The knowledge may also be relevant to understand the role played by endogenous inorganic compounds or other additives in altering combustion products, such as smoke constituent formation in cigarettes and biomass conversion products. For example, it has been shown that pyrolysis of a low-temperature (300 °C) pectin char at high temperature (600 °C) yields significantly less benzo[a]pyrene in its pyrolysate than a similarly heated cellulose char (350 °C) [52, 53]. In the case of tobacco, it has been shown that the charring temperature of pectin (which contains endogenous metal ions) in tobacco leaves (ca. 250 °C) is nearly the same as in isolated pectin [15]. Tang *et al.* also showed that most of the pectin in such plants is not intimately associated with cellulose

[54]. Pure cellulose does not contain endogenous metal ions, which decomposes at a higher heating temperature (ca. 300 °C). For cellulose chars prepared at 300 to 450 ℃ in the absence of O_2, it is clear that the addition of alkaline or alkaline earth metal ions to the cellulose significantly alters their EPR behavior, e.g., when they are subsequently exposed to air at room temperature, an overall enhancement the amount of surface oxygen-centered radicals is observed. A similar but opposite effect occurs in chars of water washed tobacco due to the removal of endogenous metal ions.

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