Catalysis of carbon dioxide gasification of cellulose char studied by electron paramagnetic [i.e. paramagnetic] resonance

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Catalysis of Carbon Dioxide Gasification
OF Cellulose Char Studied by Electron
Paramagnetic Resonance

by

Marcus Obeng

B.S., University of Science and Technology, Ghana, 1980
Presented in Partial Fulfillment of the Requirements for the Degree of
Master of Science

UNIVERSITY OF MONTANA
1985

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Catalysis of Carbon Dioxide Gasification of Cellulose Char

Studied by Electron Spin Resonance

Director: Richard J. Field

Cellulose, and potassium and sodium carbonate treated cellulose were pyrolyzed under nitrogen flow from 400°C to 700°C for 1.5 to 60.0 minutes. Electron spin resonance was used to study the dependence of the unpaired spin concentrations and line widths on temperature and time.

At 400°C and 500°C the unpaired spin concentration recorded for chars 5K and chars 5N were higher than those of chars R whereas at 600°C and 700°C the unpaired spin concentration in the chars R was higher than those of chars 5K and char 5N.

At 400°C and 500°C the line widths recorded for the untreated cellulose were larger than those of chars 5K and chars 5N whereas at 600°C and 700°C the line widths were smaller than those of the chars 5K and chars 5N.

Variations in the unpaired spin concentrations were associated with the competition of unpaired spin formation and decay processes during pyrolysis. Variations in the line widths were related to dipolar and exchange interactions.

The reactions of chars 5K, chars 5N, and chars 5R prepared at 700°C for 10 minutes with CO₂ were carried out in a thermogravimetric analyzer. Chars R did not show any significant gasification. K₂CO₃ exhibited better catalytic effect than Na₂CO₃. The kinetic equation fit the experimental data for the treated cellulose. The rate of reaction went to zero before complete gasification was achieved. The fraction of carbon gasified before the rate of reaction went to zero was identical for both samples. Chars 7.5K and chars 7.5N showed a higher increase in reaction rates than did chars 5K and chars 5N. The reaction rates for the chars 7.5K and chars 7.5N went to zero earlier than those of chars 5K and chars 5N.
NOMENCLATURE

Char $R = \text{Char prepared from untreated cellulose.}$

Char $5K = \text{Char prepared from cellulose treated with 5\% K}_2\text{CO}_3 \text{ solution.}$

Char $5N = \text{Char prepared from cellulose treated with 5\% Na}_2\text{CO}_3 \text{ solution.}$

Char $7.5K = \text{Char prepared from cellulose treated with 7.5\% K}_2\text{CO}_3 \text{ solution.}$

Char $7.5N = \text{Char prepared from cellulose treated with 7.5\% Na}_2\text{CO}_3 \text{ solution.}$
ACKNOWLEDGMENT

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INTRODUCTION

A. ENERGY FROM BIOMASS

The use of biomass as a source of energy has the potential to replace a substantial amount of fossil fuel. Many of the most favorable uses of biomass result from its direct substitution for liquid and gaseous fuels, where the need is greatest.

Biomass can be burned directly or converted into other forms of fuel through thermal processes such as pyrolysis, gasification, and liquefaction, and biological processes such as fermentation to produce ethanol and methane. Gaseous fuel produced from pyrolysis and gasification can be used in oil and gas combusters. Liquid fuels can be obtained through direct liquefaction of biomass or biomass char. Anaerobic methanation involves anaerobic bacterial digestion of biomass into methane. The conversion of biomass to ethanol involves hydrolysis of the biomass polysaccharide into simple sugars by either enzymes or acid followed by fermentation of the resulting sugars to give ethanol.

Biomass consists of different types of dead and living plant materials. The structure and composition of biomass vary for different parts of the plant and different plant species. The cell wall and the woody tissues of higher plants are made up of approximately 50% cellulose, 30% lignin, and 20% hemicellulose. In this work chemically pure cellulose will be used as an example of biomass, since it is the most abundant plant material and it is the only component which can be
obtained in relatively pure form.

B. CHEMISTRY OF CELLULOSE

Cellulose \((\text{C}_6\text{H}_{10}\text{O}_5)_x\) is a homopolysaccharide composed of linearly linked \(\beta-(1-4)-\text{D}-\text{glucopyranose}\) units (Figure 1). The glucose residues in cellulose are not equivalent, the actual repeating unit is the anhydrocellobiose (1). One anhydrocellobiose residue is 1.03nm in length.

![Figure 1. Structure of cellulose](image)
Atalla et al. (1) using cross-polarization magic-angle spinning techniques, recorded C$^{13}$-nmr spectra of highly crystalline samples of cellulose I (native cellulose) and cellulose II (regerated cellulose). From these spectra, together with vibrational spectra and unit cell dimension, they reported that adjacent anhydroglucose units were not equivalent and that anhydrocellobiose is required as a basic repeating unit in modelling cellulose structure. They observed that the C-1 resonance of both polymorphs (cellulose I and II) and the C-4 resonance of cellulose II were split into two lines of approximately equal intensity. Earl and VanderHart (2) also, using magic angle spinning spectroscopy observed similar C$^{13}$-nmr spectrum for Valonia cellulose.

The unit cell of native cellulose consists of four glucose residues. The length of each glucose unit is of the order of 0.515 nm. Every glucose unit is displaced 180 degrees with respect to its neighbors. The chains of native cellulose microfibrils are oriented in the same direction; that is, they are parallel.

Cellulose molecule is a linear polymer and has a strong tendency to form intra- and intermolecular hydrogen bonds. In cellulose intramolecular hydrogen bonding between OH(3) and O(5) of the next anhydroglucose unit and intermolecular hydrogen bonding between OH(6) and O(1) of the adjacent molecule provides a rigid structure which accounts for its fiber strength. Hydrogen bonds and short range van der Waals forces between chains cause cellulose polymer to be packed into bundles. These bundles are twisted together into rope-like structures.
called microfibrils. The width of the microfibrils has been estimated to be from 30 to 3.5 nm or even less according to the model used (3). Due to the fibrous structure and the strong hydrogen bonding, cellulose has a high tensile strength and is insoluble in most solvents. The number of units, that is, how often the building unit repeats itself in the chain is termed the degree of polymerization. The degree of polymerization in the native cellulose has been estimated to be within the range of 10,000 to 15,000.

The crystalline structure impedes any attack on cellulose chain by enzymes or chemical reagents. However, aqueous solutions such as alkaline metal salts can swell the cellulose crystalline structure. The fibers shrink and their cross-sectional area increase when cellulose is soaked in an alkaline solution. Due to the hydroxyl functional groups in cellulose, it has the characteristic chemical reactivity of an aliphatic alcohol. Cellulose can undergo esterification and etherification, and scission of the glycosidic ether linkage resulting in a shortening of the polymer chain.

Cellulose can be analytically isolated from wood. Lignin is first removed by treating the wood with chlorous acid. This leaves a combination of cellulose and hemicellulose known as holocellulose. The hemicellulose is then removed by exhaustive extraction with a 24% aqueous NaOH solution containing 4% boric acid.
C. **PYROLYSIS OF CELLULOSE**

Pyrolysis can be simply defined as the thermal degradation of a molecule into lower molecular weight degradation products. In general the pyrolysis products are CO\(_2\), H\(_2\)O and various low molecular weight hydrocarbons, tar and char (4). Tar consists of compounds containing six or more carbons. Char is a highly cross-linked polymer formed from non-volatile degradation products (5).

Pyrolysis of cellulose can take place under different conditions. Some of the operational conditions include pyrolysis under inert atmosphere, pyrolysis in the presence of a catalyst, oxidative pyrolysis, high pressure reductive pyrolysis, and high pressure caustic fusion. However, only pyrolysis of cellulose under vacuum or an inert atmosphere and in the presence of a catalyst will be reviewed here.

Thermal decomposition of cellulose proceeds by two alternative pathways (5). The first pathway, which occurs below 300°C, involves reduction in molecular weight or degree of polymerization (DP) by bond scission. This results in elimination of water, appearance of free radicals, and formation of carbonyl, carboxyl groups and carbonaceous char. The free radicals are associated with the carbonaceous char.
The other pathway occur above 300°C and its rapid. Above this temperature the macromolecules are depolymerized by an alternative path which provides a tarry pyrolyzate containing levoglucosan, other anhydro-sugars, oligogluccosides and other furanoid and pyranoid dehydration products, and non-volatile char. At still higher temperatures other processes such as disproportionation, decarboxylation and decarbonylation occur.

The chemical composition of the lower molecular weight volatile compounds has been extensively investigated (6,7,8,9,10) However, little is known about the chemical structure of the cellulosic char and the reactions involved in its formation. In view of the important roles played by chars in gasification, combustion, liquefaction and other processes, it is necessary to get information about the chemical composition and functionality of the char. This will improve our understanding of the chemistry of gasification of cellulosic char and other carbonaceous materials.

Pictet and Sarasin (11) reported that when cotton cellulose is pyrolyzed under vacuum a yellow paste is formed. From the paste they identified levoglucosan along with carbonaceous char. Since then there have been extensive investigations of the pyrolysis of cellulose. In recent years it has been reported that there are about sixty other organic products which can be identified as a result of cellulose pyrolysis (12). Halpern and Patai (13) using X-ray diffraction reported that the non-crystalline regions of cellulose were the first to be
affected.

Another study of thermal degradation of cellulose showed that the char residue was formed simultaneously with dehydration. X-ray examination of the char residue indicated that the basic cellulosic skeletal structure is retained up to temperatures of 275°C-300°C (14). At temperatures higher than 300°C the lattice reverts gradually to a three-dimensional structure containing a condensed polynuclear aromatic structure. Some investigators (15,16) considered pyrolysis to involve cleavage of the 1,4-b-glycosidic bond, continuously unzipping levoglucosan from the scissed end. This is followed by ring rupture to generate furan derivatives and low molecular weight products, and inter-molecular reactions to form a char residue.

Shafizadeh and Sekiguchi (17) studied the formation and structure of cellulose chars formed by isothermal pyrolysis in the temperature range of 300°C to 500°C. They reported that the chars contained different proportions of carbonyl, paraffinic and aromatic carbon depending on the heat treatment temperature (HTT) and the presence of inorganic materials. They observed that there was rapid weight loss and development of aromatic structures between 350°C and 400°C. The H/C ratio gradually decreases from 1.5 to 0.7. Above 400°C, they reported that the rate of weight loss decreases as 'stable' chars are formed and the yield of aromatic carbon remains constant. The aromatization process continues with rapid reduction in H/C ratio through condensation and the growth of individual aromatic clusters to form a polycondensed

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The overall carbonization process is complex. Lewis (18) reported that aromatics are the key building block for char formation. He considered carbonization to proceed through C-C and C-H bond scission to form reactive free radicals followed by molecular rearrangement, thermal polymerization and aromatic condensation.

Pyrolysis of cellulose with inorganic additives under an inert atmosphere also has been studied. However, the majority of investigations in this area are mainly related to flame retardants (6, 19, 20).

Madorsky et al. (19) studied pyrolysis of cotton cellulose treated with Na₂CO₃ in vacuum. They reported that the reaction occurs at temperatures between 200°C and 230°C which is relatively low as compared with 340°C to 370°C for the pyrolysis of raw cotton cellulose.

Shafizadeh et al. (6) tested a series of Lewis acids and other chloride-containing compounds such as antimony chloride (SbCl₃). They reported that the yield of levoglucosan decreased drastically, whereas char formation increased. Wodley (20) suggested that the char formation was due simply to the effect of the Lewis acid on levo-glucosan rather than on cellulose itself.
D. SURVEY OF GASIFICATION

Gasification is the thermal reaction of coal, wood or other carbonaceous materials with a controlled amount of either an oxidizing atmosphere (e.g. $O_2$, $CO_2$) or a reducing atmosphere (e.g. $H_2$). In either case a combustible gas is produced. The following equations show different types of gasification.

\[
C + 2H_2 = CH_4 \quad (1)
\]
\[
C + H_2O = CO + H_2 \quad (2)
\]
\[
C + \frac{1}{2}O_2 = CO \quad (3)
\]
\[
C + CO_2 = 2CO \quad (4)
\]

Reaction (1) is hydrogasification, reaction (2) is steam gasification, reaction (3) is oxygen gasification and reaction (4) is Boudouard gasification or $CO_2$ reaction. Some or all of these reactions can take place at the same time. For instance during steam gasification (reaction 2) the following reactions also can occur. The water-gas shift reaction

\[
CO + H_2O = CO_2 + H_2, \quad (5)
\]

the Boudouard reaction

\[
C + CO_2 = 2CO, \quad (6)
\]

and the hydrogasification reaction

\[
C + 2H_2 = CH_4 \quad (7)
\]
The rate of C-CO$_2$ reaction is slow compared to either C-H$_2$O or C-O$_2$ reactions but faster than C-H$_2$ reaction (21). The C-CO$_2$ reaction requires a catalyst.

The catalytic effect of inorganic additives on the rate of gasification of carbonaceous materials has been known for a long time, and excellent reviews are available (21,22,23). The information that is available on the gasification of wood or cellulose (24,25) generally includes the reactivity towards specific oxidizing gas or concerns the application of specific catalyst. Alkali, alkaline earth, and some transition metal (eg. Vanadium) carbonates are used to promote the gasification reactions of carbonaceous materials using carbon dioxide, steam, oxygen and hydrogen.

In recent years the catalytic effect of inorganic salts on the gasification rates of not only coal or coal-derived chars but also of biomass and even urban solid waste has received a great deal of attention.

There have been investigations of catalysis of CO$_2$, H$_2$O, O$_2$ and H$_2$ gasification of carbonaceous materials by inorganic salts using GC-mass spectrometry, NMR, FT-IR and ESR spectroscopies. The catalyst is considered to participate in the gasification process by undergoing chemical and/or electronic interaction with the carbonaceous materials. However, the mechanisms of these gasification reactions remain controversial. Most gasification work has been done on coal and coal-derived chars. Hence what is known of the kinetics and mechanisms
of catalysis of gasification is associated with coal and coal-derived chars. Notwithstanding the fact that cellulosic char and coal char differ in pore structure and ash content, the gasification process appears to be similar. The rate of gasification depends on pyrolysis temperature and time, the partial pressure of reacting gas, the surface area and porosity of the char, and dispersion of the catalyst in the carbon network (21).

In this study the discussions are limited to either potassium- or sodium-catalyzed C-CO$_2$ reaction. This reaction is the best understood of the four gasification reactions. The mechanism proposed herein can be used to explain the catalysis of C-H$_2$O, C-O$_2$ and C-H$_2$ reactions. The mechanisms proposed by various investigators will be reviewed here. However, criticisms and suggestions will be given in the mechanistic proposal section.

Kroger et al. (26) proposed a mechanism based on oxygen atom transfer from the gas phase to the carbon surface. Generally, in this mechanism the catalysts undergo an oxidation-reduction cycle on the carbon surface during gasification. The metal forms an intermediate metallic oxide in the presence of the oxidizing gaseous atmosphere. The oxide is reduced on contact with the carbon substrate and the cycle repeated. Amariglio et al. (27) supporting the oxygen atom transfer mechanism proposed that only metals which undergo a cycle between two oxidation states could exhibit catalytic activity during gasification.
Fox and White (28) suggested that catalysis of C-CO$_2$ reaction by Na$_2$CO$_3$ results from transfer of CO$_2$ between the gas phase and the carbon surface by sodium. Thus the Na$_2$CO$_3$ is reduced at the surface of the carbon. Due to its high vapor pressure, the sodium metal formed evaporates into the gas phase. There sodium reacts with CO$_2$ and the Na$_2$CO$_3$ formed is redeposited onto the surface of the chars.

$$2\text{Na} + 2\text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{CO} \quad (8)$$
$$\text{Na}_2\text{CO}_3 + 2\text{C} = 2\text{Na} + 3\text{CO} \quad (9)$$
$$\text{C} + \text{CO}_2 = 2\text{CO}$$

Long and Sykes (29) explained catalysis of the C-CO$_2$ reaction in terms of electron transfer reactions. This electron transfer mechanism is based on the observation that many of the known gasification catalysts have unfilled energy bands that are capable of accepting electrons from the carbon. Alternatively the additives may possess labile electrons that can be donated to the carbon. This electron transfer results in the weakening of the carbon-carbon bonds at edge sites of the carbon and an increase in carbon-oxygen bond strength during the catalyzed oxidation reaction.

Franke and Maraikib (30) suggested that during C-CO$_2$ reaction catalyzed by Na$_2$CO$_3$, the sodium metal intercalates into the graphite lattice and introduces extra electrons into the carbon lattice. This will promote chemisorption and dissociation steps, thereby increasing the reaction rate.
\[
\begin{align*}
\text{CO}_2 + e^- &= \text{CO} + \text{O}_{\text{ads}} \quad (10) \\
\text{O}_{\text{ads}} + \text{C} &= \text{CO} + e^- \quad (11) \\
\text{C} + \text{CO}_2 &= 2\text{CO} \\
\end{align*}
\]

McKee et al. (31) proposed that the mechanism of catalysis of CO\(_2\) gasification consists of three elementary reactions.

\[
\begin{align*}
\text{K}_2\text{CO}_3 + 2\text{C} &= 2\text{K} + 3\text{CO} \quad (12) \\
2\text{K} + \text{CO}_2 &= \text{K}_2\text{O} + \text{CO} \quad (13) \\
\text{K}_2\text{O} + \text{CO}_2 &= \text{K}_2\text{CO}_3 \quad (14) \\
\end{align*}
\]

Which give an overall reaction

\[
\text{C} + \text{CO}_2 = 2\text{CO}
\]

Mims and Pabst (32) proposed that surface complexes of potassium such as K-O-C are the active species during gasification. They observed that K\(_2\)CO\(_3\) decomposed at temperatures as low as 500°C in the presence of carbon. They demonstrated the presence of K-O-C by titylation with methyl iodide (33), and the NMR spectra of an alkylated K\(_2\)CO\(_3\)-C sample after steam gasification at 700°C showed that there was a correlation between the methyl content and K\(_2\)CO\(_3\) content which agreed with a plot of rate vs. K/C ratio.

Kapteijn et al. (34) formulated catalytic elementary steps responsible for C-CO\(_2\) reaction by the cycle

\[
\text{K}_x\text{O}_y + \text{CO}_2 = \text{K}_x\text{O}_{y+1} + \text{CO} \quad (15)
\]

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\[ K_{xOy+1} + C = K_{xOy} + CO \quad (16) \]
\[ C + CO_2 = 2CO \]

Spiro et al. (35) suggested that in char gasification a hydride-hydroxide cycle is operative in addition to the McKee mechanism, due to the high hydrogen content of the char.

\[ KH + CO_2 = KOH + CO \quad (17) \]
\[ KOH + C = KH + CO \quad (18) \]
\[ C + CO_2 = 2CO \]

Wood et al. (36) suggested that the formation of a M-C bond may cause weakening of an adjacent C-C bond in the carbon network with a rupture of aromatic rings leading to formation of highly reactive aliphatic fragments.

Rand and Marsh (37) explained that a catalyst promotes gasification of carbon by channelling through the solid leading to the formation of large pores. They observed that when the catalyst becomes inactive gasification proceeds by the uncatalyzed route only and micropores are formed predominantly. Ross and Fong (39) reported that when jack pine bark is treated with \( K_2CO_3 \) the gasification temperature is lowered, the rate of gasification and the gas yield are increased, while the heat content of the fuel gas is raised. They explained the catalytic effect of \( K_2CO_3 \) using the oxidation-reduction cycle.
Shafizadeh and DeGroot (39) observed that catalysis of gasification appeared to involve ion exchange of added salts for the natural mineral fraction at specific sites with a resulting increase in the reactivity of the sites.

Hawley et al. (40) observed that when K$_2$CO$_3$ and Na$_2$CO$_3$ are added to wood (Poplar spp) prior to pyrolysis there was degradation of the regular cellular structure and an increase in the rate of gasification.

E. ELECTRON SPIN RESONANCE

The bond scission during pyrolysis of cellulose results in the formation of a high concentration of free radicals in the char (5). The free radicals play an important role in gasification, liquefaction, coalification and other chemical mechanisms. The unpaired electrons can be detected by electron spin resonance (esr) spectroscopy. This method concerns the study of re-orientation of the magnetic dipoles of electrons by applying electromagnetic radiation of a fixed frequency in the presence of a suitable magnetic field (41).

Many investigators have used esr to study the chemistry of coal (42,43,44,45) and carbonization of organic compounds (46,47,48,49) since the discovery of free radicals in coal by Uebersfeld (50) and Ingram (51). Also, a powerful approach to the problem of electronic structure
of carbons is provided by the technique of esr.

In esr the common parameters measured are the concentration of unpaired electrons, peak-to-peak line width of the first derivative curve, the spectroscopic splitting constant (g-value) and the line shape (42,52,53,54).

1. **Unpaired spin concentration**

The unpaired spin concentration is the number of free spins or unpaired electrons in a given amount of a sample. In carbonaceous materials the number of unpaired electrons depend on pyrolysis temperature and time, and the origin of the material.

Hyde (55) suggested two methods of determining the spin concentration in a given amount of carbonaceous material. The first method, known as absolute measurement, involves the calculation of the unpaired spin concentration directly from the spectroscopic parameters and from the relationship between spin concentration and the magnetic susceptibility. The magnetic susceptibility is given by

\[ X_0 = \frac{4y}{\mu \times W \times H_1} \int P_a H_0 \]

Thus, if a paramagnetic substance is examined in esr the static spin...
susceptibility, \( X_0 \), is proportional to the area under the esr curve of power \( P_g \). The power is a function of the static magnetic field \( H_0 \). The variable \( \omega \) is the angular frequency and \( H_1 \) is the amplitude of oscillatory magnetic field. The variable \( \gamma \) is related to the g-value by

\[
\gamma = \frac{\beta}{h} g \tag{19}
\]

where \( \beta \) is the Bohr magneton and \( h \) is Planck's constant. The unpaired spin concentration is then calculated from a relationship between \( X_0 \) and \( N \) (spin concentration). However, this relationship depends on the nature of the spin species and how the energy levels of the spins in the magnetic field are populated. At thermal equilibrium, the relationship between \( X_0 \) and \( N \) of doublet state unpaired spins is given by Curie's law

\[
X_0 = \frac{N g^2 \beta^2 S(S+1)}{3kT} \tag{20}
\]

where \( S \) is the spin quantum number and \( k \) is the Boltzmann constant.

In the second method, known as the comparison method, the unknown spin concentration is measured relative to a standard such as 1,1-dipheny-2-picrylhydrazyl (DPPH) which possesses one unpaired electron per molecule and has a long-term stable unpaired spin. At fixed electrical and magnetic parameters, the unknown spin concentration can be calculated from the ratio of the areas under the esr curves recorded for the reference and the unknown sample. In the absence of
any saturation by the radio frequency the relationship between the unpaired spin concentration and the areas of the esr curves is given by Curie's Law

\[
\frac{N_{\text{unk}}}{N_{\text{std}}} = \frac{A_{\text{unk}} \cdot M_{\text{std}}}{A_{\text{std}} \cdot M_{\text{unk}}} \quad (21)
\]

where \( A_{\text{unk}} \) and \( A_{\text{std}} \) are the areas under the esr curves of the unknown and the standard respectively. \( M_{\text{unk}} \) is the mass of the unknown sample and \( M_{\text{std}} \) is the mass of the standard. In this work the comparison method will be used, since it is easier, fast and reliable.

Singer (41) suggested that the measurement of the integrated absorption \( X_0 \), requires that the following conditions be met. The spin system must be in thermal equilibrium with its surroundings. Thus, there should be no saturation. The line width must be small compared to \( H_1 \) at resonance. Skin depth effects must be absent. Skin depth is the depth through which an electromagnetic wave will penetrate before falling to 1/e of its original amplitude. The magnitude of the skin depth \( d \) is given by

\[
d = \left( \frac{\mu_0 m}{\sigma_{\text{w}}} \right)^{1/2} \quad (22)
\]
where $\mu$ is the permeability of the material, $\sigma$ is the conductivity in mho/meter, and $\omega$ is the angular frequency. The integrated absorption also can be affected by the line shape.

2. g-VALUE

The spectroscopic splitting constant, g-value, can be obtained from the energy equation

$$hv = g^*B^*H_0$$  \hspace{1cm} (23)

the variable $v$ is the frequency, $g$, $B$ and $H_0$ are defined earlier. The g-value also can be measured by comparison method. At fixed frequency then from equation (22)

$$g_{\text{unk}}^*B^*H_{\text{unk}} = g_{\text{std}}^*B^*H_{\text{std}}$$ \hspace{1cm} (24)

$$\frac{(g_{\text{unk}}-g_{\text{std}})}{g_{\text{unk}}} = \frac{(H_{\text{std}}-H_{\text{unk}})}{H_{\text{std}}}$$ \hspace{1cm} (25)

The g-value of DPPH is 2.0036. $H_{\text{unk}}$ and $H_{\text{std}}$ are the magnetic fields obtained by a double modulation method for the unknown and the standard, which is usually DPPH, respectively. The g-value of an unpaired electron is quite sensitive to its chemical environment, and particularly, to the presence of oxygen, nitrogen and sulfur which have spin-orbit coupling constants much higher than that of carbon (41).
3. Line width

There are two common ways to express the line width in ESR as shown in figure 2. First is the half width at half height of the absorption curve. The second is to measure the distance between the two inflection points of the first derivative curve.

The magnitude of an ESR line width is usually affected by mechanisms that can contribute to the broadening or narrowing of the ESR curve. In addition to the external magnetic field \( H_0 \), each electron spin also is subjected to another magnetic effect, known as local magnetic field \( H_{1\text{oc}} \), produced by the neighboring spins. Thus, each electron spin experiences a resultant magnetic field consisting of the external and the local magnetic fields and as a result the resonance frequency will be displaced. Hence, equation (22) becomes

\[
\hbar \nu = g^* \Theta^*(H_0 + H_{1\text{oc}})
\]  

(26)

This effect, known as electron spin-electron spin dipolar interaction, can lead to broadening of the ESR line. The electron spin-electron spin dipolar interactions depend on the separation between the spins and their relative orientation. Electron spin-nuclear spin interactions also lead to broadening of the ESR curve. This effect is similar to the electron spin-electron spin dipolar interactions except that the local magnetic fields are produced by nuclei in the vicinity of the electron spins (53). For solids the electron spin-electron spin interaction contributes to line broadening more than the electron spin-nuclear spin interaction.

20
Figure 2. A graph of the first derivative (a), the absorption (b) and the second derivative (c) curves of esr.
Other sources of line broadening include an inhomogeneous magnetic field and anisotropic interactions of randomly oriented system in the solid sample. In the latter case the disturbances of local magnetic field resulting from the anisotropic g and hyperfine interactions give rise to the inhomogeneity (53,54).

Spin-lattice interactions, the interactions between the spin system and its lattice, can affect the line width. The time required for an initial excess of energy given to the spins to fall to 1/e of its value is known as the spin-lattice relaxation time. This is determined by the rate of sharing of spin energy with the thermal vibration of the lattice. A strong spin-lattice interaction leads to a short spin-lattice relaxation time. If the relaxation time $T_1$ is very short, the line width is governed by $T_1$, and the esr line can become extremely broadened. A long relaxation time also can lead to saturation. Saturation occurs when the input power is sufficiently intense to raise molecules from a lower to a higher energy level at a rate faster than the relaxation processes can restore thermal equilibrium. This causes reduction in peak intensity and the line width increases.

An important mechanism which contributes to narrowing of the esr absorption is the exchange interaction or exchange narrowing effect (52,53,56). The exchange narrowing effect results when the unpaired electrons of two free radicals exchange their spin states. This effect is to reduce the electron spin-electron spin dipolar broadening. This effect is observed in samples which have high concentration of free
4. **Line shape**

The esr line shape for the majority of carbonaceous materials falls somewhere between the extremes of Gaussian or Lorentzian (57). An esr line which possesses a Gaussian property approaches the baseline quickly and is narrow, whereas, an esr line which possesses Lorentzian property approaches the baseline slowly. The factors that affect line width also can affect the line shape.

There are several methods of analyzing the shape of an esr line. However, the most common is that a plot of \( \log (x/y) \) against \( x^2 \) will be linear for a Gaussian curve whereas a plot of \( (x/y)^{1/2} \) against \( x^2 \) will be linear for a Lorentzian curve. The quantity \( y \) is the height of the first derivative curve and \( x \) is the distance from the cross-over point to a particular value of \( y \).

Ingram et al. (58) proposed that the free radicals observed in esr were formed by the cleavage of bonds at the edges of condensed carbon rings, and the liberated electrons become resonance stabilized in the ring.

Retcofsky et al. (44) obtained a correlation between esr line widths and \( H \) content of vitrains (coal). They reported that variation of the line widths with coal rank is a direct result of spin-spin interactions between the free radicals and electron and proton interactions. Kwan and Yen (43) explained the changes in the line
widths with coal rankings by the Wiess and Anderson theory (59) of exchange narrowing in paramagnetic substance.

Nanassy and Fung (60) used esr to examine pyrolyzed wood (Douglas fir) under vacuum at temperatures between 300°C and 600°C and pyrolysis times from 5 minutes to 60 minutes. They attributed the variation in the line widths, line shape and exchange integral to changes in dipolar and exchange interactions.

Mrozowski (61) suggested that carbons prepared within the temperature range of 500°C-800°C can be treated as intrinsic semi-conductors possessing an energy band completely filled with electrons at absolute zero and separated from an empty conduction band by an energy gap \( e \). During carbonization, when a peripheral hydrogen atom is removed a \( \sigma \)-electron is left unpaired. A \( 1\) electron from the \( 1\)-band then forms a spin-pair with the \( \sigma \)-electron thereby creating a hole or positive charge carrier in the filled band.

Changes in esr spectral parameters of catalyzed chars also have been studied. Hinojoso et al. (62) reported that the esr spectral intensity for chars from treated cellulose was greater than that of untreated cellulose when both samples were pyrolyzed under the same conditions. Nanassy and Fung (49) examined Douglas fir char treated with \( \text{NH}_4\text{H}_2\text{PO}_4 \) under vacuum at temperatures from 250°C to 600°C and pyrolysis times of 5 minutes to 240 minutes. They observed that the mass loss, line width and the g-factor were smaller whereas the unpaired spin concentrations were larger than those of untreated chars prepared
under the same conditions. In this work only the unpaired spin concentration and line width were measured. By studying the changes in line widths it is possible to obtain information about the exchange effect, and thus the size and compactness of the char.
RESULTS AND DISCUSSION

A. ELECTRON SPIN RESONANCE

1. Results

a. Unpaired spin concentration

The esr lines for both treated and untreated cellulose showed single symmetrical lines without any hyperfine structure.

Figure (3) shows a plot of unpaired spin concentration vs. pyrolysis time at various temperatures for chars R. At HTT of 400°C and 500°C there is a steady increase in the unpaired spin concentration as the pyrolysis time increases. The unpaired spin concentration does not peak within the pyrolysis time range. The unpaired spin concentrations at HTT of 600°C increase to a maximum at a pyrolysis time of 10 minutes and then decreases steadily. The maximum unpaired spin concentration for a HTT of 700°C occurred at the identical pyrolysis time as the maximum unpaired spin concentration for a HTT of 600°C.

Figure (4) shows the unpaired spin concentrations as a function of pyrolysis time at various pyrolysis temperatures for chars 5K. At 400°C and 500°C the unpaired spin concentration increases steadily and never reaches a maximum within the pyrolysis time range. At 600°C the unpaired spin concentration increases to a maximum at a pyrolysis
Figure 3. A plot of unpaired spin concentration vs. pyrolysis time at various temperatures for chars R.
Figure 4. A plot of unpaired spin concentration vs. pyrolysis time at various temperatures for chars 5K
Figure 5. A plot of unpaired spin concentration vs. pyrolysis time at various temperatures for char 5N
5 minutes and then decreases. The unpaired spin concentration quickly reaches a low maximum at a pyrolysis time of less than 2 minutes at HTT of 700°C and then decreases rapidly to a very small value. Thus, it is likely that the maximum occurred prior to the first measurement in this sample.

Figure (5) shows unpaired spin concentration vs. pyrolysis time at various HTT for chars 5N. At 400°C and 500°C the unpaired spin concentration increases steadily. At the HTT of 600°C the unpaired spin concentration increases to a maximum at about 5 minutes and then decreases steadily. At 700°C the unpaired spin concentration decreases steadily from a maximum attained before the first measurement at a pyrolysis time of 1.5 minutes.

The unpaired spin concentration in chars 5K and chars 5N were found to be higher than the chars R at HTTs of 400°C and 500°C. However, at 600°C and 700°C the unpaired spin concentrations were higher in the untreated cellulose than the treated cellulose. At HTTs of 400°C and 500°C the unpaired spin concentration of chars 5K were higher than those of chars 5N. The unpaired spin concentration of chars 5K at 600°C and 700°C were lower than those of chars 5N. The observed maximum suggests the competition of spin formation and decay processes during pyrolysis. The former process increases unpaired spin concentration while the latter process decreases unpaired spin concentration.
b. Line width

Figure (6) shows variation of the peak-to-peak line widths of the first derivative curves with pyrolysis time at various temperatures for chars R. The line widths show a steady decrease at a HTT of 400°C, 500°C, and 600°C. At a HTT of 700°C the line width decreases to a minimum at a pyrolysis time of 5 minutes and then increases.

Figure (7) shows the variation of line width with pyrolysis time at various temperatures for chars 5K. At HTT of 400°C and 500°C the line width decreases constantly within the pyrolysis time range. However, at HTT of 600°C and 700°C the line width increases constantly.

Figure (8) shows variation of line width as a function of pyrolysis time for chars 5N at various temperatures. At 400°C and 500°C the line widths decrease constantly. At a HTT of 600°C the line widths decrease to a minimum at a pyrolysis time of about 10 minutes and then increase. The line widths at a HTT of 700°C show a constant increase in magnitude within the pyrolysis time range.

At 400°C and 500°C the line widths of chars 5K were found to be lower than the uncatalysed chars while at 600°C and 700°C the line widths were higher than those of chars 5N.
Figure 6. A plot of line width vs. pyrolysis time at various temperatures for char R
Figure 7. A plot of line width vs. pyrolysis time at various temperatures for char 5K.
Figure 8. A plot of line width vs. pyrolysis time at various temperatures for char 5N.
The results obtained from the esr indicate that the generation of unpaired-electrons and variation of line width depend on the pyrolysis time, HTT, and catalyst type.

2. Factors that may affect unpaired spin concentration and line width.

a. Unpaired spin concentration

Dehydration is the process which occurs first during pyrolysis (14). Although this reaction results in dehydration of the glucose unit, there are large number of glucose rings that remain unattached. These remaining glucose units are then degraded into different intermediates. The unpaired electrons start to appear during the initial reduction of DP by bond scission and dehydration reaction. As the pyrolysis time increases more unpaired electrons are produced as a result of decomposition and depolymerization.

A mechanism that could contribute to the decrease in unpaired spin concentration is pairing up of the unpaired electrons in the char. Aromatization occurs concurrently with decomposition and depolymerization at HTTs above 400°C. The individual small aromatic rings condense and cross-link to form the polycondensed aromatic system (63).
Addition of inorganic salts to cellulose could enhance pairing up of the unpaired electrons and production of conduction carriers. The inorganic salts could also alter the decomposition and depolymerization processes.

b. Line width

The line widths for the chars R at a HTT of 400°C where the unpaired spin concentration is less could be affected by static electron spin-electron spin dipolar interaction mechanism which depends upon the average distance between the electron spins and their relative orientation. Also the electron-proton hyperfine interaction could lead to a broader esr line. This could be due to considerable amount of hydrogen atoms present at 400°C (15).

A strong spin-lattice interaction could play a significant role in broadening the esr line. If strong spin-lattice interactions exist in the char, the spin-lattice relaxation time will be very short and there could be uncertainty broadening in the esr curve (42,47).

Through aromatization, which occurs concurrently with decomposition and depolymerization, the unpaired electrons associated with the aromatic sheets become closer together, and free electron transfer from one aromatic site to another is possible. This would result in an exchange narrowing effect, which makes the esr lines narrower if the free electrons involved in the exchange have similar spins, for instance
either both unpaired electrons are associated with aliphatic or aromatic carbon (53). However, if the environments are different, then exchange broadening can occur. The breakdown of the exchange interaction also could be due to strong bond strains. Bond strain resulting from extensive cross-linking destroys the similarity of the spins necessary for exchange of electron spins to occur (64). This argument helps to rationalize the increasing line width with decreasing unpaired spin concentration and decreasing similarity of spin centers.

A high concentration of conduction carriers also could result in esr line broadening due to the interaction between the unpaired spin and the conduction carriers.

2. DISCUSSION

A. Unpaired spin concentration

At 400°C chars 5K and char 5N have higher unpaired spin concentration than those of chars R. This observation could be attributed to rapid dehydration, decomposition and depolymerization of the treated cellulose. This is in line with the suggestion by Mrozowski and Westcott that the catalyst lowers the pyrolysis temperature and shortens the pyrolysis process.
At 400ºC the unpaired spin concentrations of chars 5K were relatively higher than those of chars 5N. This observation suggests that K$_2$CO$_3$ probably has the ability to lower the pyrolysis temperature and thereby shorten the pyrolysis process more than does Na$_2$CO$_3$.

At 600ºC and 700ºC chars R have higher unpaired spin concentrations than those of chars 5K and chars 5N. This could be ascribed to rapid pairing up of the unpaired electrons due to the presence of catalysts in chars 5K and chars 5N. At a higher HTT the production of unpaired electrons is masked by the rapid spin decay, that is, pairing up of the unpaired electrons. Pairing up of free electrons also occurs in the chars R, but the process is not as fast as in chars 5K and chars 5N.

It is known that K$_2$CO$_3$ and Na$_2$CO$_3$ react with carbon well below their melting points (32). At higher HTT some of the free electrons could be lost when K$_2$CO$_3$ or Na$_2$CO$_3$ decomposes to form surface salts like potassium or sodium phenolate and other oxygen containing compounds such as "K-O-C" (33). The structure of "K-O-C" is not yet known. Thus qualitatively, due to the greater stability of Na$_2$CO$_3$, K$_2$CO$_3$ should form surface salts faster than Na$_2$CO$_3$. Thus the unpaired spin concentration in the chars 5K should be lower than those of chars 5N.
b. Line width

At a HTT of 400°C the larger line width of the chars 5R relative to chars 5K and chars 5N may be due to electron spin-proton spin interactions. The dehydration process occurs faster in the treated cellulose than in the untreated cellulose. Thus the hydrogen content of chars 5R is greater than that of chars 5K (17). The interactions between the unpaired electron spins and the hydrogen nuclei could result in esr line broadening. Also, at 400°C, due to the low unpaired spin concentration observed in the chars 5R, the static electron spin-electron spin dipolar interaction would lead to line broadening.

The narrower line widths observed in the spectra of chars 5K and chars 5N at 500°C relative to those of chars R could be due to a strong exchange interaction resulting from a higher concentration of unpaired electrons. At this higher HTT the concentration of unpaired electrons in chars 5K and chars 5N is high so they are closer to one another and may exchange their spins rapidly. This strong exchange interaction is stronger than any mechanism, such as an electron spin-electron spin interactions, that could broaden the esr line (63).

The relatively broader esr lines in the chars 5K and chars 5N compared to chars R at 600°C and 700°C could be due to a number of factors. An increased concentration of the conduction carriers could interact with the spins of the unpaired electrons. This would lead to a broader esr line. Also, a spin-lattice interaction could play an important role in broadening the lines. The interaction between the...
catalyst and the carbon could lead to changes in the electronic environment of the carbon. The spin-lattice relaxation time would then decrease, which could lead to broadening of the esr lines.

At higher HTTS, 600°C and 700°C, the exchange narrowing effect should be strong and increase with growth of aromatic clusters. However, at 600°C and 700°C the esr lines were broader for chars 5K and chars 5N. In the chars 5K and chars 5N it could be suggested that there was a breakdown in the exchange narrowing effect. The breakdown of the exchange narrowing effect may be associated with the transition between two distinct types of spin centers. The formation of K-O-C could weaken the carbon-carbon bonds in the chars with rupture of the less condensed rings leading to the formation of aliphatic fragments. It is probably the transition between the free spins associated with aromatic rings and aliphatic that leads to the breakdown of the exchange narrowing effect.

Wood et al. (36) observed a broad esr line when K$_2$CO$_3$ was heated with carbon at temperatures above 500°C. They ascribed the broad esr line to an unresolved nuclear hyperfine interactions between the unpaired electrons associated with the carbon and the potassium nuclei. However, it is not likely that a K-C bond can exist above 500°C ()

The broad esr line observed in chars R could be explained in terms of the breakdown of the exchange narrowing effect due to a highly strained structure. The extensive cross-linkage in the chars R could result in severe bond strain. The bond strain destroys the similarities
of the free spin centers necessary for the exchange effect to occur. Also, if strong spin-lattice interactions exist in the untreated cellulose at 700° C then this could lead to esr line broadening.
1. Results

A series of CO₂ gasification experiments were done using chars R, chars 5K and chars 5N prepared at 700°C and a pyrolysis time of 10 minutes. In this study K₂CO₃ and Na₂CO₃ which are known to show catalytic activity during C-CO₂ reaction were used.Chars R did not show any significant gasification.

Figure (9) shows the fraction of carbon gasified as a function of time for chars 5K and chars 5N. The fractional conversion or the fraction of carbon gasified on an ash free basis is given by

\[ X = \frac{W_i - W_t - M_p}{W_i - W_{ash}} \]  

(27)

where

\[ X = \text{fraction of carbon gasified} \]

\[ W_i = \text{initial weight of char} \]

\[ W_t = \text{weight at any time after exposure of the char to CO}_2 \]
\( M_p \) = mass lost due to pyrolysis during gasification

\( W_{ash} \) = weight of the ash

Figure (10) shows the experimental rate of reaction as a function of fraction of carbon gasified for chars 5K and chars 5N at 700°C. In both experiments the reaction rates increase rapidly to a maximum within a very small fractional conversion and then decreases to zero before complete gasification. The rate of \( \text{CO}_2 \)-chars 5K reaction was greater than that of \( \text{CO}_2 \)-chars 5N. The fraction gasified was almost the same for both catalysts. The composition of the residue after gasification is not known.

There have been different observations concerning the variation of rate as a function of fraction of carbon gasified during \( \text{CO}_2 \) catalytic gasification of carbonaceous materials. The reaction rate may initially decrease to a certain percent of carbon gasified and then rise to a maximum before dropping to zero (65,66). The initial rate may increase a maximum and then decreases monotonically to zero (67). In this study it was observed that the rate of gasification initially increases to a maximum and then
Figure 9. A plot of fraction of carbon gasified vs. time for char 5K (►) and char 5N (■)
Figure 10. A plot of experimental rate of gasification of char 5K (I) and char 5N (II) vs. fraction of carbon gasified at 700°C.
decreases constantly to zero

**Kinetic Equation**

For the kinetic analysis of the data the following kinetic equation was used. The equation seems different from others (69) used previously, but it fits the data well.

\[
\frac{dx}{dt} = K_1[(1-e^{-K_4*t})(1-k_2*e^{-k_3*x})(A-x)]
\] (29)

The quantities \(K_1\) and \(K_4\) have units of sec\(^{-1}\) and \(k_2\) and \(k_3\) are dimensionless. The quantity \(A\) is the fraction of carbon gasified before the rate goes to zero. The kinetic equation is formulated to fit about 70% of the carbon gasified.

The complete reaction profile is assumed to consist of four regions. The initial rapid adsorption of CO\(_2\), a slow approach to a maximum, the steady state and finally the monotonic decrease in gasification rate to zero. The \([(1-e^{-K_4*t})]\) factor of the kinetic equation fits the initial rapid adsorption of CO\(_2\). The value of \(K_4\) was chosen to reproduce the initial rapid increase in rate. The \([(1-k_2*e^{-k_3*x})]\) factor is associated with both the slow approach to a maximum region and the steady state. The \(K_1*(A-x)\) factor fits the region where the rate decreases monotonically to zero. An approximate value of \(K_1\) was obtained from the DTG curve and refined to a value that gave a
reasonable fit of the kinetic equation to the experimental data.

Figures 11a and 11b show two experimental and simulated graphs for the rate of gasification as a function of fraction of carbon gasified for two chars 5K. Figures 12a and 12b show two experimental and simulated graphs for the rate of gasification as a function of the fraction of carbon gasified for two chars 5N. The values of $k_1$, $k_2$, $k_3$ and $k_4$ are given in table 1.

The experimental curves do not start from zero and this could be due to the initial rapid adsorption of CO$_2$ onto the char surface. It is possible that gasification occurs concurrently. The adsorption of CO$_2$ onto the char is necessary for the gasification reaction to be initiated (21).

The slow approach to a maximum is characterized by an increase in the rate of gasification. In the esr study the broad esr line observed for chars 5K and chars 5N prepared at 700°C were associated with the breakdown of the exchange narrowing effect. This breakdown was ascribed to the exchange of spins between aliphatic carbons and aromatic carbons. The rapid increase in the rate of gasification could be due to the gasification of the aliphatic fragments. During the induction period the chars 5K show a higher rapid increase in gasification rate than to the chars 5N. The reasons why chars 5K show a higher increase in
Figure 11a. A plot of experimental rate of gasification of char 5K vs. fraction of carbon gasified (——) and simulated graph (-----) at 700°C.
Figure 11b. A plot of experimental rate of gasification of char 5K vs. fraction of carbon gasified (---) and simulated graph (-----) at 700°C.
Figure 12a. A plot of experimental rate of gasification of char 5N vs. fraction of carbon gasified (solid line) and simulated graph (dashed line) at 700°C.
Figure 12b. A plot of experimental rate of gasification of char 5N vs. fraction of carbon gasified (---) and simulated graph (-----) at 700°C.
<table>
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</table>

The values of $K_1$, $K_2$, $K_3$ and $K_4$ for chars 5K and chars 5N.
gasification rate than do the chars 5N is not yet understood. However, a suggestion can be made here. In the esr study the line widths observed in the spectra of chars 5K prepared at 700°C and pyrolysis time of 10 minutes, were larger than those of chars 5N. It could be assumed that the chars 5K contain a larger proportion of aliphatic fragments before the gasification process than do the chars 5N.

Wood et al (36) speculated that the formation of K-C bonds alter the electron density in the vicinity of the bonds and weaken adjacent C-C bonds in the carbon network. This will result in rupture of aromatic rings leading to formation of highly reactive aliphatic fragments. They concluded that the increase in gasification rate was due to the presence of aliphatic fragments. As explained earlier it is the formation of potassium or sodium oxygen containing compounds which is responsible for the formation of the aliphatic fragments rather than the K-C bonds. Moreover, it is unlikely that K-C bond can exist within the gasification temperature range (68).

The complex nature of gasification is due to the fact that a considerable number of different reactions occur concurrently. For example, the steady state region may be characterized by the following processes. During the gasification process less condensed aromatic rings can fragment to produce aliphatic fragments and free radicals. The free radicals, particularly the unstable ones, can either react with CO₂ or polymerize to produce very stable structures (69). At the same time the aliphatic fragments could undergo gasification. Thus, during
the steady state period the less active species (aromatic carbon) could be converted to the more active aliphatic fragments with simultaneous consumption of the active species.

The rate of reaction decreases monotonically to zero after the steady state. The reason why the rate goes to zero before complete gasification is not completely clear. One possible explanation is that during the C-CO$_2$ reaction the ratio of the potassium or sodium oxides to carbon increases. The catalyst then blocks the pores thus making CO$_2$ inaccessible to the active sites and slowing down the gasification processes (67). Also, during gasification, stable structure can be formed which could slow down the gasification process. Some of the residue is likely the catalysts themselves.

The results obtained in this work are inconsistent with an observation by Mims and Pabst (32). They suggested that during steam or carbon dioxide gasification of carbonaceous materials, the rate of reaction remained constant between about 20% to 70% of the carbon gasified. Gasification is a complex process. Competing processes occur concurrently during gasification, so it is not likely that the rate would remain constant. During gasification there is constant transformation of the less condensed aromatic rings to aliphatic fragments some of which are gasified and some of which repolymerized to form stable polyaromatic structures which slow down the reaction. Also there is a constant loss of catalyst through various mechanisms, such as evaporation of the catalyst (67).
The kinetic equation was tested for gasification of chars 7.5K and chars 7.5N. Figure 13 shows the fraction of carbon gasified as a function of time. Figure 14 shows the experimental rate of reaction as a function of fraction of carbon gasified for these chars. The graph shows an initial rapid increase in the rate of reaction like those of chars 5K and chars 5N. The initial rapid increase in the rate of reaction is followed by a slow approach to a maximum. The rate then decreases to zero before complete gasification. From the graph it can be seen that the rates of gasification of chars 7.5K and chars 7.5N go to zero at identical values of A. The initial rapid increase in the rate of gasification of chars 7.5K was greater than those of chars 7.5N. Figure 15 shows the experimental rate of reaction as a function of fraction of carbon gasified for chars 7.5 K and chars 5K. Figure 16 shows the experimental rate of reaction as a function of fraction of carbon gasified for chars 7.5N and chars 5N. The rate of reaction goes to zero earlier than in the case of the chars 5K and chars 5N. The initial rapid rate of gasification, greater than those of chars 5K and chars 5N, is possibly due to the fact that chars 7.5K and chars 7.5N contain a higher proportion of reactive aliphatic fragments to begin with. As the gasification proceeds, the rates decrease constantly to zero. This result is due to the blocking of the pores by
Figure 13. A plot of fraction of carbon gasified vs. time for 7.5K (▲) and char 7.5N (■)
Figure 14. A plot of experimental rate of gasification of char 7.5K (III) and char 7.5N (IV) vs. fraction of carbon gasified at 700°C.
Figure 15. A plot of experimental rate of gasification of char 7.5K (V) and chars 5K (VI) vs. fraction of carbon gasified at 700°C.
Figure 16. A plot of experimental rate of gasification of the 7.5N (VII) and char 5N (VIII) vs. fraction of carbon gasified at 700°C.
the high concentration of the catalysts deposited on the char surfaces. Also, there is a constant transformation of the active species to stable aromatic structures which also slows down the gasification reactions.

Figures 17a and 17b show experimental and simulated graphs for two chars 7.5K. Figures 18a and 18b show experimental and simulated graphs for two chars 7.5N. The graph show a large deviation of the simulation curve from the experimental curve. This could be due to, as explained earlier, the blocking of the pores, thereby making the CO\textsubscript{2} inaccessible to the reactive sites. The values of K\textsubscript{1}, k\textsubscript{2}, k\textsubscript{3} and K\textsubscript{4} are shown on table 2.
Figure 17a. A plot of experimental rate of gasification of char 7.5K vs. fraction of carbon gasified ( — ) and simulated graph (----) at 700°C
Figure 17b. A plot of experimental rate of gasification of char 7.5K vs. fraction of carbon gasified (-----) and simulated graph (-----) at 700°C.
Figure 18b. A plot of experimental rate of gasification of char of 7.5N vs. fraction of carbon gasified (— — ) and simulated graph (----) at 700°C.
Figure 18a. A plot of experimental rate of gasification of char 7.5N vs. fraction of carbon gasified (---) and simulated graph (-----) at 700°C
<table>
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<td>0.510</td>
<td>5.801</td>
<td>0.0126</td>
<td>0.69</td>
</tr>
<tr>
<td>Chars 7.5K</td>
<td>0.00040</td>
<td>0.505</td>
<td>5.801</td>
<td>0.0098</td>
<td>0.69</td>
</tr>
<tr>
<td>Chars 7.5N</td>
<td>0.00035</td>
<td>0.321</td>
<td>8.005</td>
<td>0.0126</td>
<td>0.69</td>
</tr>
<tr>
<td>Chars 7.5N</td>
<td>0.00036</td>
<td>0.391</td>
<td>8.051</td>
<td>0.0126</td>
<td>0.69</td>
</tr>
</tbody>
</table>

The values of $K_1$, $K_2$, $K_3$ and $K_4$ for chars 7.5K and chars 7.5N.
4. **MECHANISTIC PROPOSAL**

There are a number of ways to explain catalysis of the C-CO$_2$ reaction, the salients of which are reviewed above. It has been found that intercalation compounds prepared from activated carbon and potassium are unstable (67). In view of the fact that potassium intercalated compounds are thermally unstable below 700°C, it seems unlikely that during gasification, potassium exists as an intercalated compound. From the esr analysis it was suggested that the broad esr line was due to exchange between spins associated with aliphatic and aromatic carbon. The aliphatic portion results from the presence of K-O-C bonds. Thus any metallic potassium produced during the heating up of K$_2$CO$_3$ and carbon will react on the char surface to form stable potassium oxygen-containing compounds. It seems unlikely that intermediate metallic potassium acts as the active species during gasification.

Also, in view of the fact that K$_2$CO$_3$ decomposes around 550°C in the presence of carbon, the first step in McKee (22) mechanism is unlikely to occur. The most likely mechanisms are those involving potassium or sodium oxygen-containing compounds. This leads to the following formulation for the reaction mechanism.

\[
\text{M}_2\text{O} + \text{CO}_2 = \text{M}_2\text{CO}_3 \tag{30}
\]

\[
\text{M}_2\text{CO}_3 + \text{C} = \text{M}_2\text{O} + 2\text{CO} \tag{31}
\]

This gives an overall reaction
The two-step cycles are thermodynamically feasible. The first step is transitory intermediate, while the second step is rate determining in the overall C-CO$_2$ reaction. At present the mechanistic proposal should be considered as speculative. From the thermodynamic standpoint, it seems unlikely that the mechanistic proposal differs very much from either those of Mims and Pabst (32) or Kaptein et al. (34).

After pyrolysis the catalysts exist mainly in the oxide form. During gasification, CO$_2$ reacts with the M$_2$O to produce M$_2$CO$_3$ which is quickly reduced by carbon leading to the formation of CO$_2$ and M$_2$O.

This mechanism can be used to explain C-H$_2$O, C-O$_2$ and C-H$_2$ reactions.
CONCLUSION AND SUMMARY

The esr spectra recorded for chars 5K, chars 5N and chars R show a single symmetrical line at all temperature used in this experiment. The esr measurements indicate that chars 5K and chars 5N have higher unpaired spin concentrations at 400°C and 500°C than chars R, whereas at 600°C and 700°C chars R have higher unpaired spin concentration than chars 5K and chars 5N. The higher unpaired spin concentration in chars 5K and chars 5N at 400°C and 500°C was associated with the ability of the catalysts to facilitate the dehydration, depolymerization and decomposition processes, and thereby enhance the formation of unpaired spins. The lower unpaired spin concentration in chars 5K and chars 5N at 600°C and 700°C relative to chars R was associated with the rapid pairing up of the unpaired spins. Some of the unpaired electrons may be trapped in the surface complexes.

The peak-to-peak line widths recorded for chars 5K and chars 5N at 400°C and 500°C were lower than those of chars R. This observation was associated with exchange narrowing effect, due to the higher unpaired spin concentration in chars 5K and chars 5N. Due to the lower unpaired spin concentration, the small line widths recorded for chars R were associated with electron spin-electron spin dipolar interaction.

At 600°C and 700°C the line widths recorded for chars R were smaller than those of chars 5K and chars 5N. This observation was associated with the breakdown of the exchange narrowing effect, electron spin-electron spin dipolar interaction, and the interaction between the
unpaired spins and the conduction electrons. From the esr study it is possible that aliphatic fragments exist in chars 5K and chars 5N at 700°C. Also electron spin-electron spin interaction exist in treated cellulose sample at 600°C and 700°C but not at 400°C and 500°C.

Carbon weight loss as a function of time was obtained from the thermogravimetric studies and measurements of isothermal kinetics of the samples prepared at 700°C for 10 minutes. The carbon weight loss curves were converted to fraction of carbon gasified curves. The fraction of carbon gasified data are then used to test the kinetic equation.

The catalysis of CO₂-chars 5K and CO₂-chars 5N reactions show substantial increase in the rate of gasification. It was found that K₂CO₃ show a better catalytic effect than Na₂CO₃. The net effect of the catalysts on the kinetic equation is to change the values of K₁, k₂, k₃ and K₄. The values of K₁, k₂, k₃ and K₄ are shown in table 1 and 2.

The rates of gasification of chars 5K and chars 5N go to zero before complete gasification is achieved. The reason why the rates of reaction go to zero before complete gasification is due to the blocking of the pores by high concentration of the potassium or sodium oxygen compounds. Also, the stable polyaromatic structures formed during gasification can slow down the rate of reaction.
The gasification process is considered to be due to the consumption of active species (aliphatic). The reason why chars R did not show any significant gasification is probable due to its highly cross-linked polymeric structures which may be inert to oxidation by CO$_2$. The kinetic equation also is tested for chars 7.5K and chars 7.5N. Chars 7.5K and chars 7.5N show higher reaction rates than chars 5K and chars 5N. However, the rate of reaction for chars 7.5K and chars 7.5N go to zero earlier than those of chars 5K and chars 5N. This observation is due to the high catalyst to carbon ratio during gasication.

The reason why K$_2$CO$_3$ treated samples have better catalytic activity than Na$_2$CO$_3$ treated samples is not clear. Further experiments need to be done before a concrete explanation can be established.

A different mechanism based on oxygen atom transfer is proposed. This mechanism can be used to explain other gasification processes. This mechanism is offered as an alternative to other mechanisms.
EXPERIMENTS

Whatman cellulose powder (ash content of 0.0150%) was used as representative of cellulose. Cellulose was soaked in \( \text{K}_2\text{CO}_3 \) and \( \text{Na}_2\text{O}_3 \) solutions over night. The samples were filtered and dried in a vacuum oven at 60°C. The samples were then ashed to determine the percentage of the inorganic additives. It was found that the \( \text{Na}_2\text{CO}_3 \) content was more than 5% whereas that of \( \text{K}_2\text{CO}_3 \) was less than 5%. The solutions were adjusted to add 5% of the additives to cellulose. Another set of samples containing 7.5% of the additives also were prepared. All the samples were pyrolyzed in a preheated convectonal quartz tube furnace. The pyrolysis was carried out under nitrogen (flow rate of 60ml/min) for 1.5, 5.0, 10.0, 30.0 and 60.0 minutes in the temperature range 400°C to 700°C at 100°C interval. About 500 mgs of the samples was weighed into porcelain boat and allowed to be purged in nitrogen for 10 minutes in the cool part of the tube. After 10 minutes the boat was pushed to the heated area and pyrolyzed for the desired time. Any traces of oxygen in the nitrogen were removed by passing the nitrogen through a high capacity 'oxy-trap' (Alltech Associates) and then through copper turnings heated at 700°C. After pyrolysis the porcelain boat was pulled back to the cool region and allowed to cool to room temperature under nitrogen. The chars were stored in dessicator under reduced pressure until used. To avoid any slight oxygen chemisorption onto the char surface, chars were used within 48 hours after preparation.
The ESR measurements were made at room temperature and under vacuum with Varian E-3 ESR spectrometer equipped with a single cavity. In order to compare the ESR measurements directly all the electronic and magnetic parameters were fixed. To avoid saturation in the chars, the microwave power was set at 1.0 mW, frequency of 9.35 GHz, magnetic field of 3330 gauss, scan rate of 25 gauss per minute and modulation amplitude of 0.68 gauss. About 5 mgs of the sample was weighed into a quartz tube of internal diameter 1/4 inch and placed in the cavity. The ESR spectra were monitored on a Tektronix 4051-E-01 microcomputer equipped with 12 bit ROM-band A/D converter. The signal was doubly integrated using trapezoidal quadrature. The unpaired spin concentration was calculated relative to standard 1% DPPH diluted with KBr. The line width was measured from the points of infection of the first derivative curve.

Thermogravimetric (TG) studies and measurements of isothermal kinetics of the samples prepared at 700°C for 10 minutes were carried out on a Perkin-Elmer TGS-2 thermogravimetric analyser interfaced with Tektronix 4051-E-01 microcomputer using a Hewlett-Packard model 3497A data acquisition/control unit. About 10 mgs of each sample was gasified in the atmosphere of CO₂. The sample was outgassed in nitrogen in the TG furnace while the furnace was heated to 700°C. When the temperature reached 700°C the flow was switched to CO₂ and the weight loss monitored continuously as a function of time. CO₂ flow was maintained at 90 ml/min. The weight loss as a function of time curves obtained were converted to fraction of carbon gasified as a function of time curves.
REFERENCES


15. Chatterjee, P.K. and Conrad, C.M., Textile


