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ABSTRACT

The bulk density and organic carbon concentration of kraft black liquor char during the char burning stage of combustion were determined following the completion of devolatilization and gasification of a packed bed of char particles. The specific volume of char was also determined from single particle swelling experiments in various gas atmospheres, temperatures, and velocities. The organic carbon concentration in kraft char averaged 7.8 kg/m^3 and was independent of fractional burnout of organic carbon at burnout levels greater than 10%. The bulk density of char went through a minimum value of 25 kg/m^3 at 10% conversion of organic carbon and gradually increased as the organic carbon was depleted. The specific volume was found to be independent of the heating flux to the char particle and dependent on temperature. Particles burnt in an atmosphere of O_2 had higher specific volumes than particles burnt in CO_2 or CO. In each gas environment, the specific volume stabilized as the experimental residence time exceeded 10-15 seconds for the single particle experiments.

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INTRODUCTION

Strong black liquor burns in air in three stages known as drying, devolatilization, and char burning [1,2]. Drying involves the evaporation of the water present in black liquor. During devolatilization the organic compounds in black liquor solids are thermally degraded to yield combustible gases and residual char. This char is a black, porous, and friable material consisting primarily of organic carbon and the inorganic salts Na_2CO_3, Na_2SO_4, and Na_2S. Approximately one-half of the carbon and most of the sodium contained in the incoming black liquor remain in the char after devolatilization [3]. On a molar basis, carbon is the dominant species and excess reactant in the char.

Knowing char density as a function of combustion time is necessary for accurately modeling physical and chemical processes occurring in the recovery furnace. Of particular importance are prediction of drop trajectories and determination of reaction kinetics. Unfortunately, reliable char density data are not readily available. Measuring the density of furnace char beds is complicated by the difficulty of acquiring samples from the furnace. Since the burning stages occur simultaneously, char bed composition varies with time. Laboratory measurements under controlled conditions would allow density measurements to be made during specific stages of liquor burning. Density measurements from lab generated chars are not available. However, swelling data for single droplets can be used to approximate the bulk density of black liquor char.

The objective of this paper was to use available swelling data to determine the bulk density of char during the devolatilization stage. To verify the available swelling data, single droplet experiments at IPST are reviewed. In addition, char measurements made during CO_2 gasification experiments are used to illustrate how char density changes during the char burning stage of combustion.

Review of Existing Char Density Data from Furnace Sampling

Richardson and Merriam[4] measured the density of char samples collected from recovery furnaces. Density was calculated for char bed samples by first determining the volume of the char by dimensional measurement in the case of solid samples or by the space occupied in a graduated beaker in the case of loose fluffy samples. The weight of the samples was then measured. In the case of the solidified smelt, volume was determined by water displacement after the sample had been weighed. The results of the calculations are summarized in Table 1.

Table1: Char and Smelt Density of Samples Collected from Recovery Furnace Char Beds[4].

	Mill A			Mill B
Material	Char	Char	Smelt	Char
Density (kg/m^3)	465	865	2,083	1,320

Smelt density values, by Richardson and Merriam [4], are compared to the density of melts of Na_2SO_4, Na_2CO_3, and Na_2S mixtures in Table 2. There is fair agreement among the density measurements of the various investigators.

Table 2: Density of Kraft Smelt and Melts of Na_2S, Na_2CO_3, and Na_2SO_4

Material, Mole Fraction	Density, kg/m^3	Temperature, °C	Investigators
Kraft Smelt	2,083	NA	Richardson and Merriam[4]
Na_2CO_3	1,910	1,000	Krause et al.[5]
30%Na_2S-70%Na_2CO_3	1,870	1,000	Krause et al.[5]
Na_2CO_3	1,917	971	Wozniak[6]
Na_2SO_4	2,018	988	Wozniak[6]
20%Na_2S-80%Na_2CO_3	1,885	967	Magnusson and Warnqvist[7]

Char density values reported by Richardson and Merriam [4] appear to be high when compared to existing char swelling data. For example, Miller [8] reported that the maximum swollen volume at 700°C for 65-100% solids black liquor ranged from 40-80 cc/g dry solids. This value corresponds to a bulk density of 7.5-15 kg/m^3, assuming the char particles are spherical and are packed together such that the bed void fraction is 0.40. Additionally, Richardson and Merriam's measurements do not indicate the variation of char density with combustion time.

Swollen Volume Data to Predict Bulk Bed Density

Spent pulping liquors characteristically swell extensively during combustion. [5,7,9,10,11] Frederick, Noopila, and Hupa [10] summarized individual black liquor droplet swelling as follows: The droplet swells slightly as it enters the furnace, but then the diameter remains nearly constant for the remainder of the drying stage. During devolatilization, the droplet swells rapidly to a maximum value. Maximum swelling coincides with the end of devolatilization. In the char burning stage, the droplet diameter decreases as char is converted to gases; only a smelt bead remains at the end of this stage.

Traditionally, the extent of swelling has been quantified by a swelling factor or by a specific swollen volume. Frederick et al. [10] note that the swelling factor, defined as the ratio of the diameter of a swollen particle to its initial diameter is commonly used when referring to swelling during drying. In addition, specific swollen volume, the maximum volume attained by the droplet during swelling divided by the initial dry solids mass of the droplet, is used when referring to swelling during devolatilization.

Miller [8] investigated the swelling of kraft black liquor during the drying and devolatilization stages of combustion. He investigated the effect of process variables such as pyrolysis temperature, solids content, heating rate, and particle size. Black liquor particles were heated by a hot flowing N_2 gas stream. For the investigated range of 300-900°C, maximum swollen volume occurred at a temperature of 500°C. The period of black liquor swelling corresponded to the evolution of pyrolysis gases; however, there was no correlation found between the amount of pyrolysis gases evolved and the change in char volume. The initial solid content of black liquor had a small influence on the swelling of black liquor (liquors below 80% initial solids content swelled more than liquors above 85% solids). The heating rate was found to affect the rate of swelling but not the final volume. Initial particle size (1-4 mm in diameter) had no effect on the swollen volume per unit particle weight.

Frederick et al. [10] also studied swelling during drying and devolatilization. Swelling during drying was found to be insensitive to furnace conditions and droplet size. Swelling during drying was, on average, constant for all liquors for which data were available. Although swelling during devolatilization was clearly liquor dependent, this swelling was not dependent on droplet size or, for two of the three liquors measured, on the initial dry solids content. Under otherwise identical conditions, droplets swelled to approximately the same extent in air or high concentrations of CO_2 or H_2O vapor in N_2 as noted in Table 3. Swelling was greater in N_2 and greatest at reduced O_2 concentrations. No explanation was offered to the enhanced swelling at low oxygen content.

Frederick et al. [10] stated that low-temperature swelling measurements (400-500°C) were not relevant when dealing with recovery boiler combustion problems. For example, their analysis showed that there was no correlation between the swelling measurements at 420°C and those made at recovery furnace temperatures (800°C). Similar data at 700°C and 800°C correlated well with each other. They therefore recommended that swelling measurements be made at temperatures representative of actual furnace conditions. Frederick et al. [10] noted that swelling decreases with increasing furnace temperatures, over the range 600-900°C, for three different liquors. They concluded that droplets swell less at higher temperatures encountered in recovery furnaces.

Table 3: The Effect of Gas Atmosphere on the Swelling of Black Liquor Droplets at 800°C for a Softwood Kraft Liquor[10]

Gas Composition	Swollen Volume[10], cm^3/g	Bulk Density for a Bed Void Fraction of 0.40, kg/m^3
N_2	100-166	3.6-6.0
4-12% O_2/88-96% N_2	113-355	1.7-5.3
21% O_2/79% N_2	45-87	6.9-13.3
20% CO_2/80% N_2	39-47	12.8-15.4
20% H_2O/80% N_2	41-81	7.4-14.6

Frederick et al. [10] noted that liquor particles contracted during char burning. They suggested that the particles shrink as carbon at the surface is burned away and the remaining inorganic smelt contracts under surface tension forces. Experimental data showing particle diameter decreasing with combustion time agreed well with model predictions made by assuming that external mass transfer controls the rate of char combustion.

EXPERIMENTAL

Fixed Bed Experiments

Density measurements were calculated for char made from black liquor received from a Southeastern U.S. kraft mill pulping a mixture of hardwood and softwood. Partially devolatilized char particles were formed by injecting single black liquor droplets into upward flowing air in the IPST drop tube furnace described by Clay et al.[12] The drop tube furnace temperature was approximately 950°C; the initial black liquor droplet diameter was 2 mm; the initial black liquor density was 1420 kg/m^3; the particle retention time was approximately 2 seconds; the mean char particle diameter was 7.7 mm; and the bulk density of the manufactured char was 31.0 kg/m^3. Partially devolatilized particles were fully devolatilized by further heating at the gasification reaction temperature in a cylindrical fixed bed reactor (7.1 cm diameter by 15.2 cm depth), shown in Figure 1.[13] This was accomplished at atmospheric pressure with a mixture of 95%N_2/5%CO flowing through the fixed bed at approximately 5 standard L/min. During kraft char pyrolysis, Li [14] found that the addition of CO to the inert gas environment suppressed Na_2CO_3 decomposition up to a temperature of 800°C. The CO and CO_2 concentrations in the product gases were measured continuously using an infrared analyzer. Devolatilization was considered to be complete when CO and CO_2 concentrations in the product gas approached the levels of CO and CO_2 in the feed (5% and 0%, respectively).

To determine the density of the char as a function of organic carbon depletion, the char was gasified with CO_2 to deplete the organic carbon. CO_2 gasification was chosen over combustion in oxygen or air because gasification rates are much slower than combustion rates; thereby, the gasification process is easier to control. For char gasification, the devolatilization temperature was chosen to be the same as the gasification temperature. This choice of devolatilization temperature was made primarily for convenience, as gasification of the char was initiated immediately upon completion of devolatilization. Gasification was initiated by replacing the CO in the carrier gas with a desired level of CO_2. The char was gasified at 600°C, 700°C, and 800°C. The organic carbon concentrations and bulk densities of the black liquor char were determined from the volume, mass, and weight fraction of carbon in the residual chars from preheat experiments and CO_2 gasification experiments.

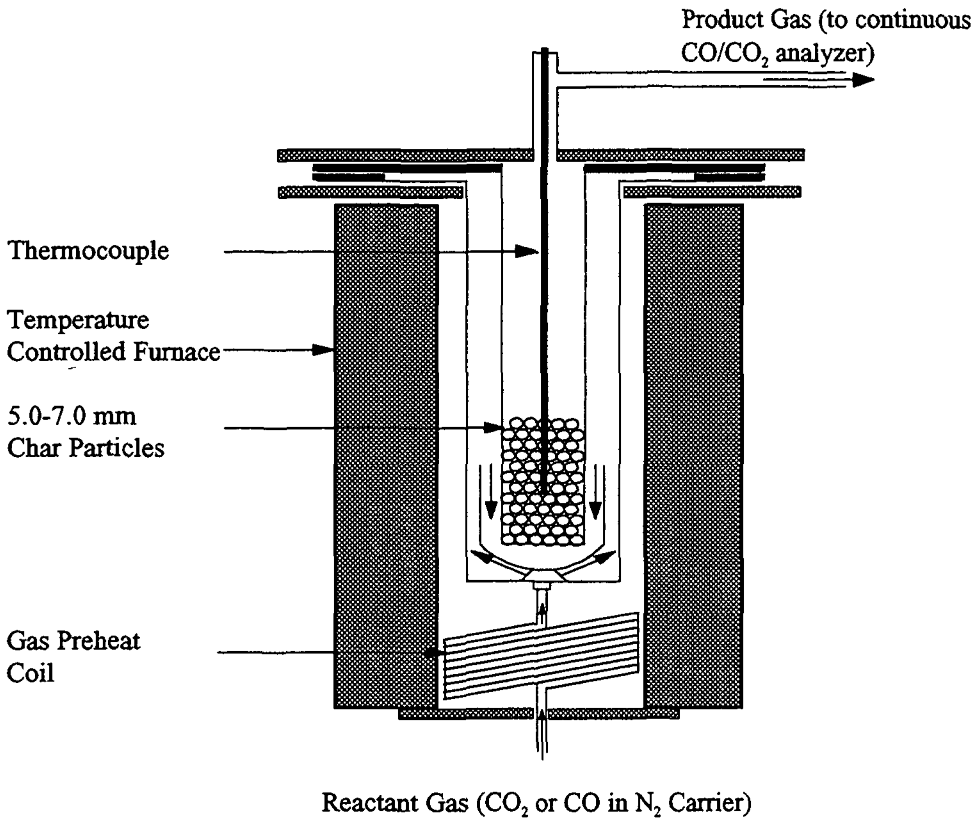

Figure 1: Schematic for Fixed Bed Reactor Used for CO_2 Gasification of Black Liquor Char[13].

Single Particle Experiments

Individual droplets of kraft black liquor were exposed in a single particle reactor, shown in Figure 2, to various gas conditions ($CO_2/CO/N_2$, CO/N_2, O_2/N_2), temperatures (500°C, 600°C, 750°C, 900°C), residence times (3, 7, 10, 15, 20, 30, and 40 seconds), and gas velocities (0.61 m/s and 1.83 m/s).[15] During these experiments, individual droplets of black liquor were formed on nichrome wires and inserted into the quartz reaction chamber of the furnace. After the specified residence time, the char was withdrawn from the pyrolytic environment into a quench stream and allowed to cool. A constant average velocity in the quartz reaction chamber was maintained for different furnace temperatures by adjusting the gas flow rate. Each experiment typically consisted of two replicate weight loss determinations at three different particle residence times. Composite samples of five fully-intact char particles were accumulated for each weight determination. Control of the exposure time was very good; for a given determination, the standard deviation of the average exposure time ranged from 0.1 to 0.3 seconds.[15]

Droplet combustion and pyrolysis behavior was recorded on videotape. A Tracor Northern TN-8502 image analyzer was used to determine the char particle size . The image analysis procedure was initiated by acquiring the image directly from the video display. This original image consisted of a continuously varying grey picture. Upon acquisition of the image, this original grey image was sampled at discrete points and the light intensity of the image was converted to an integer value varying from black(0) to white(255). Next, the original grey level image was processed to reduce the background to a more uniform grey level. The next step involved a process called binary thresholding which created a two-state map of the grey image resulting in a binary image which is defined as a black and white representation of the grey image. Once the binary image was produced, the image was further enhanced by filtering the binary image. Finally, the computer analyzed the binary image to determine the average projected area diameter. The droplet volume was calculated from the average droplet diameter.

It should be clearly noted that the swelling reported in this study is on a different basis than earlier work. [5,7,9,10,11] Swelling has been traditionally expressed as a swelling factor or as the specific swollen volume; however, these definitions do not allow the specific volume per mass of char to be determined throughout the stages of combustion. Knowing the specific volume of char allows the data to be converted to density as a function of time. In this study, specific volume is defined as the particle volume divided by the particle mass at the time of measurement.

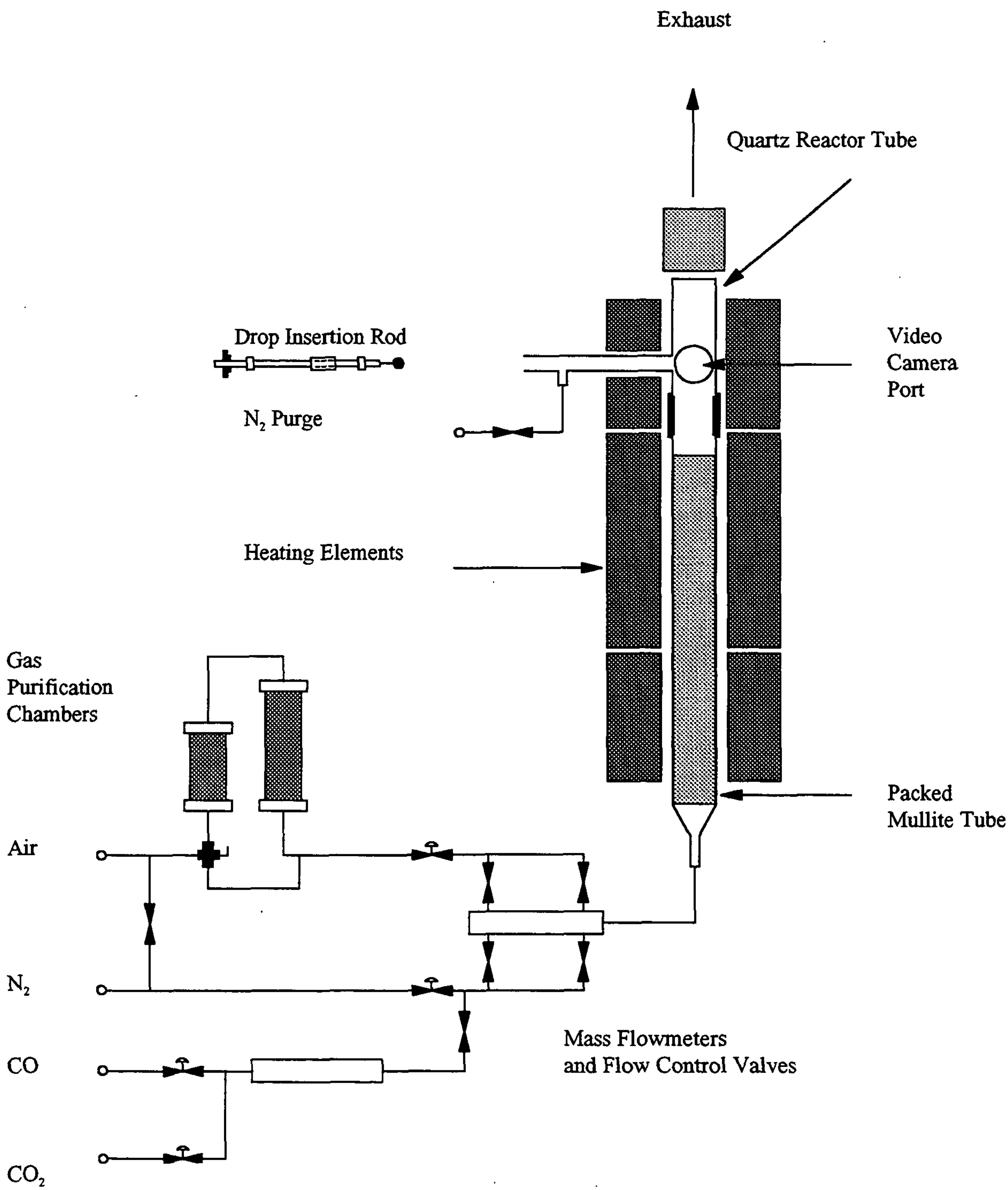

Figure 2: Schematic for Single Particle Reactor Used for Swelling Experiments[15].

EFFECT OF CO_2 GASIFICATION ON CHAR DENSITY

The data shown in Figure 3 indicate that organic carbon concentration decreased upon the initiation of gasification and leveled off as gasification proceeded. Averages and standard deviations of groupings of the data represented in Figure 3 are as follows: 10.8±1.36 kg carbon/m^3 at 0% fractional conversion of organic carbon, 7.33±0.508 kg carbon/m^3 at 10% fractional conversion of organic carbon, 5.52±1.79 kg carbon/m3 at 40-56% fractional conversion of organic carbon, and 6.87±2.59 kg carbon/m^3 at 54-95% fractional conversion of organic carbon. The average carbon concentration was 7.8 kg/m^3 for the range of fractional conversion from 0.00 to 0.97. Initial organic carbon concentration was statistically higher (at the 99% confidence level) than the organic carbon concentration of char after 10% conversion. The organic carbon concentration in kraft char was independent of fractional conversion at burnout levels greater than 10%.

Of necessity, the organic carbon concentration will approach zero as the conversion of organic carbon approaches 100%. Organic carbon concentration did not decrease linearly as a function of the fractional conversion of organic carbon. At 95% conversion of organic carbon, the concentration of organic carbon was approximately 6 kg carbon/m^3; therefore the organic carbon concentration is greatly reduced between conversions of 95% and 100%.

A review of the bulk density provides additional insight into the char behavior. As shown in Figure 4, the char density reaches a minimum value of 25 kg/m^3 at a fractional burnout of organic carbon of approximately 10%. Char bulk density calculated from data reported by Miller[8] is of the same order of magnitude as the bulk density reported in this study. Char density gradually increases as the organic carbon is depleted. This increase is statistically valid at the 99% confidence limit. The low char density values at organic carbon conversions of approximately 10% resulted from particle volumes remaining constant while the char mass was only slightly decreasing. In contrast, at higher conversions of organic carbon, the particle volume decreased steadily as the organic carbon was depleted. The char density increases at higher fractional conversion because the inorganic salts coalesce as the organic carbon is depleted.

Richardson and Merriam [4] have provided the only other char density measurements directly applicable to the char burning stage of black liquor combustion. Char density values of Richardson and Merriam are at least an order of magnitude greater than the density values reported in this study. Char samples for this study were taken from a uniform bed of previously pyrolyzed char particles, in contrast to the nonuniform recovery furnace bed from which Richardson and Merriam collected their char samples. The high char density values reported by Richardson and Merriam are probably the result of sampling a mixture of smelt and char rather than pure char. This hypothesis is supported by considering that the char density measured by Richardson and Merriam (465-1320 kg/m^3) is less than the smelt density measured by Richardson and Merriam (2083 kg/m^3) and much greater than the density of fully devolatilized char measured in this study (55 kg/m^3).

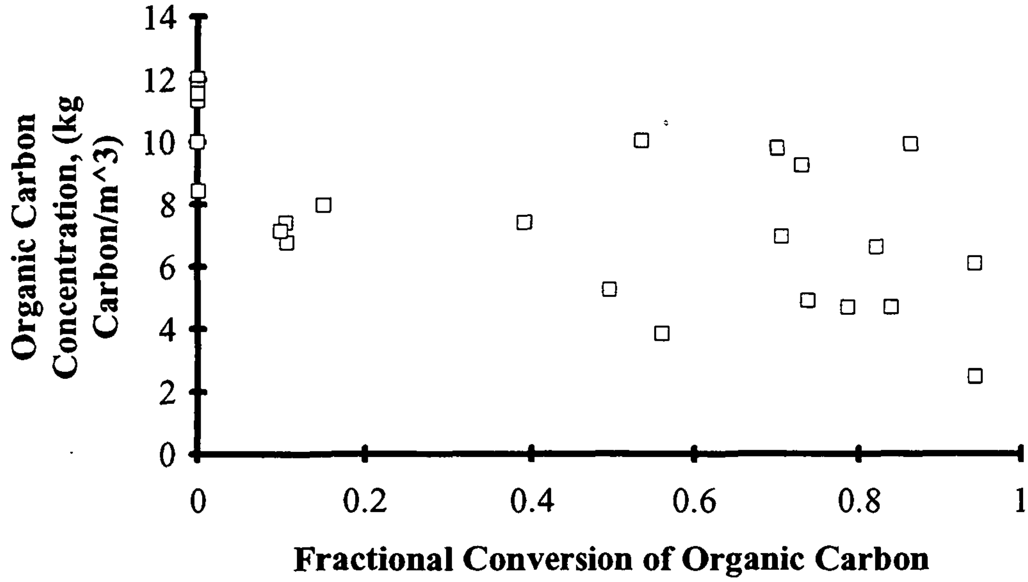

Figure 3: Concentration of Organic Carbon as a Function of Fractional Conversion of Organic Carbon.

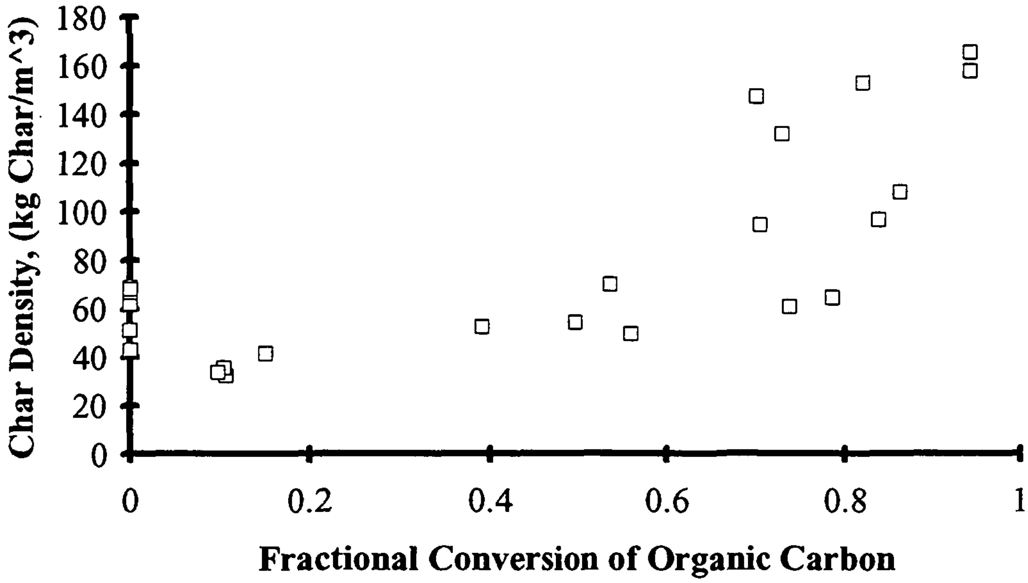

Figure 4: Bulk Density of Char as a Function of Fractional Conversion of Organic Carbon.

ANALYSIS OF SINGLE PARTICLE COMBUSTION RESULTS

The specific volume of single particles exposed in gas atmospheres of $5\%CO/95\%N_2$, $5\%O_2/95\%N_2$, and $20\%CO_2/5\%CO/75\%N_2$ was determined at various temperatures, gas velocities, and exposure times. The effects of these process variables on the specific volume was determined from these experiments.

The effect of temperature on specific volume, in an environment of $5\%CO/95\%N_2$, was studied over a temperature range of 600 to 900°C under otherwise identical conditions. As shown in Figures 5 and 6, specific volume increased with temperature at exposure times of 10 seconds and 30 seconds, respectively. Statistical analysis at the 99% confidence interval verified that the specific volume increased with temperature. In contrast, Frederick et al. [10] report that the swollen volume of droplets burnt in air swell less at higher temperatures for the temperature range encountered in real furnaces.

Miller [8] noted that the rate at which pyrolysis (CO_2) gases evolved from black liquor particles did not have an effect on the maximum particle volume attained. However, Miller also reported that at higher temperatures the CO_2 concentration in the pyrolysis product increased as the temperature increased. Although the increased CO_2 at higher temperature was most likely a result of Na_2CO_3 decomposition [13], the increased specific volume at higher temperatures reported in this study may be directly related to an increase in pyrolysis gas evolution. Unfortunately, pyrolysis gas composition was not measured during this study.

Gas composition influences the swelling of black liquor droplets. Under otherwise identical conditions, the data in Figure 7 show that the droplet swelling was the same in gas environments of 5%CO and $20\%CO_2/5\%CO$ when the furnace temperature was 600°C and the gas velocity was 0.61 m/s. Despite the difference in furnace temperature for particles exposed in $5\%O_2/95\%N_2$ (500°C), $5\%CO/95\%N_2$ (600°C), and $20\%CO_2/5\%CO/75\%N_2$ (600°C), the particle swelling was greatest at reduced oxygen concentrations as shown in Figure 8. The particles exposed in low O_2 concentrations had much greater volumes than particles exposed in CO or CO_2, yet the particle mass remained approximately constant. The reaction of O_2 with the char is exothermic and would cause the particle to be hotter than 500°C. Therefore, the true particle temperature may have been much greater than 600°C. As noted earlier, the specific swollen volume in an atmosphere of $5\%CO/95\%N_2$ increased as the temperature increased. A similar trend may occur in an atmosphere of $5\%O_2/95\%N_2$. Otherwise, the high specific volume encountered at low concentrations of O_2 may be because the relationship between swelling and temperature is opposite that experienced in $5\%CO/95\%N_2$. For example, Miller [8] reported that particles swollen in an atmosphere of N_2 went through a point of maximum swelling at 500°C.

Specific char volume as a function of exposure time was largely dependent on the furnace conditions. As shown in Figure 7, for temperatures of 600°C and gas velocities of 0.61 m/s the specific volume was greatest at low exposure times (<10 seconds) and decreased for times greater than 15 seconds in gas atmospheres of $5\%CO/95\%N_2$ and $20\%CO_2/5\%CO/75\%N_2$. Statistical analysis at the 99% confidence interval confirmed that the specific volume at 5 seconds residence time was significantly greater than the specific volume at higher residence times. Videotape observations revealed that the high specific volume at the low exposure time

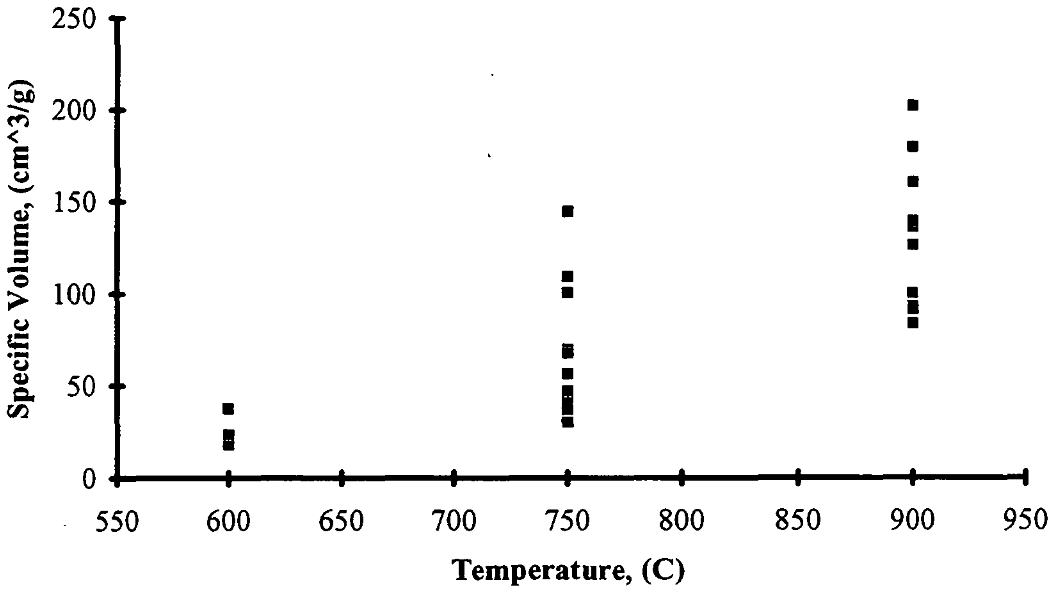

Figure 5: Specific Volume of Kraft Black Liquor Char as a Function of Temperature in 5%CO/95%N_2 at Exposure Time of 10 Seconds and Gas Velocity of 0.61 m/s.

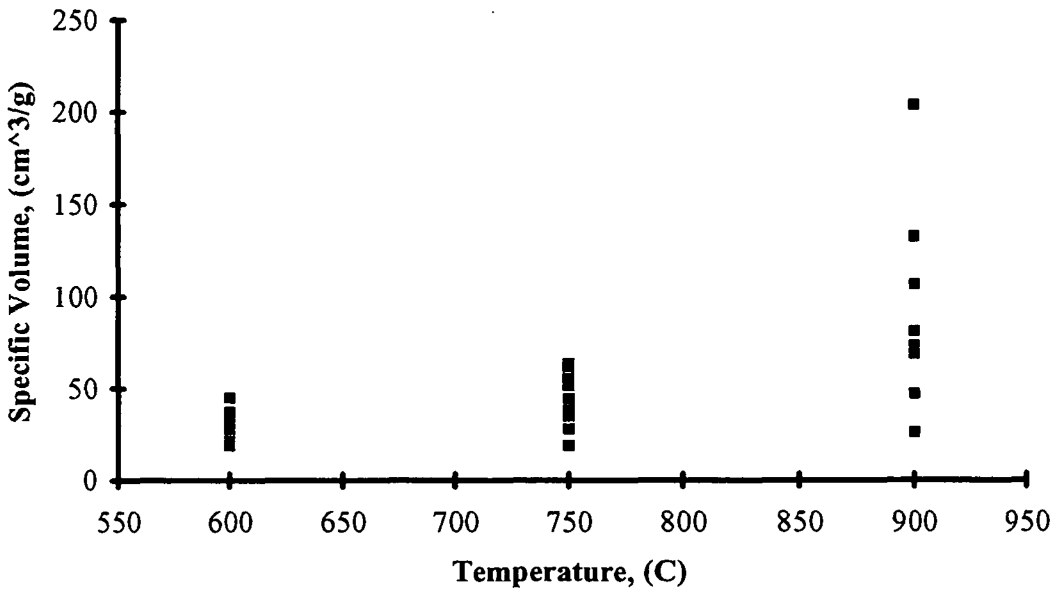

Figure 6: Specific Volume of Kraft Black Liquor Char as a Function of Temperature in 5%CO/95%N_2 at Exposure Time of 30 Seconds and Gas Velocity of 0.61 m/s.

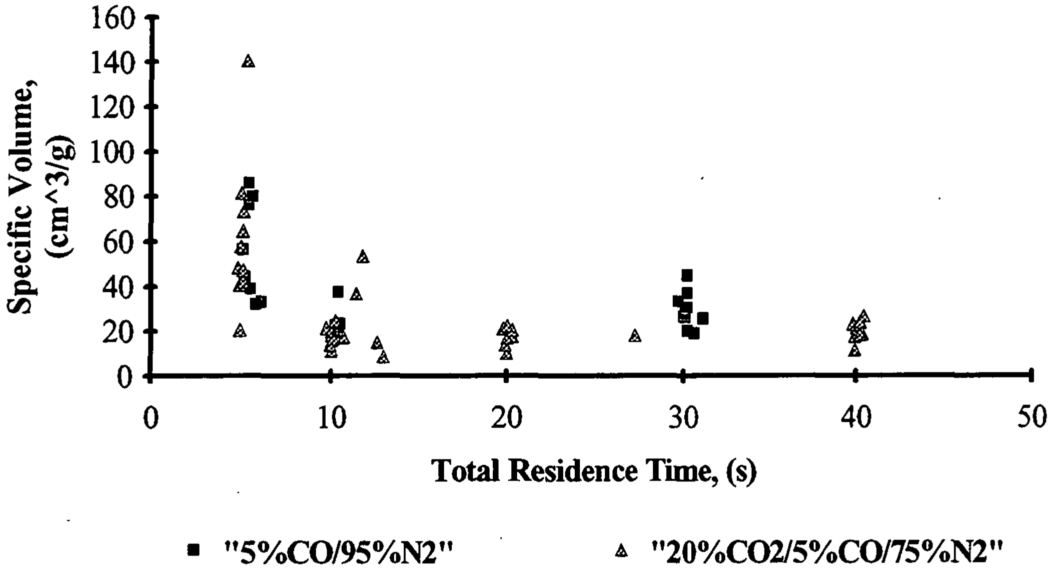

Figure 7: Specific Volume of Kraft Black Liquor as a Function of Total Residence Time at Gas Conditions of 600°C and 0.61 m/s.

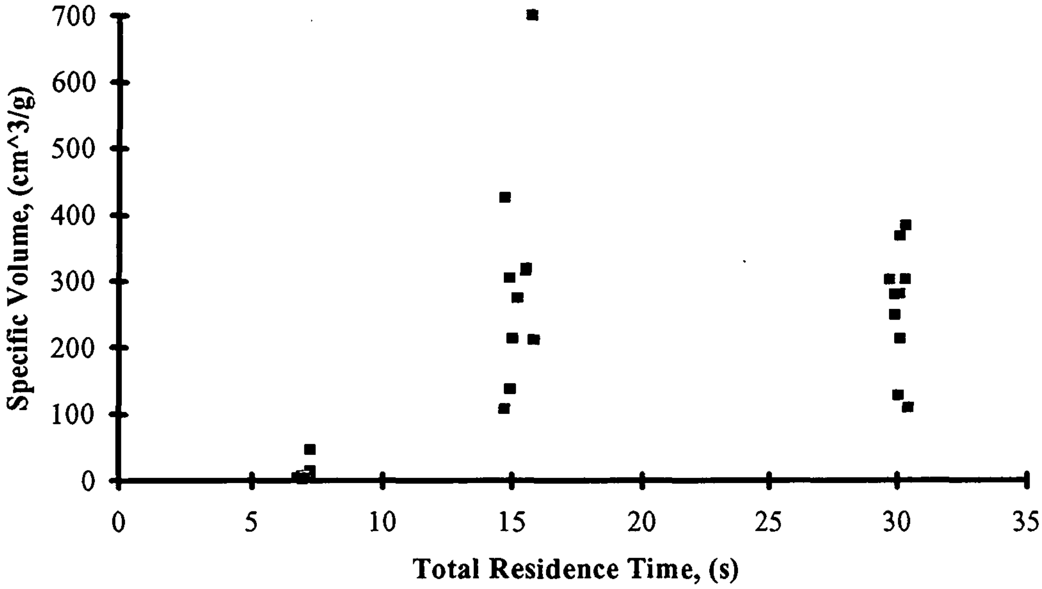

Figure 8: Specific Volume of Kraft Black Liquor as a Function of Total Residence Time in $5\%O_2/95\%N_2$ at 500°C and 0.61 m/s

was associated with the point of maximum volume that occurred at 3-7 seconds exposure time in an atmosphere of 5%CO/95%N_2 and 20%CO_2/5%CO/75%N_2. In contrast, Figure 8 shows that in an atmosphere of O_2 at 500°C and 0.61 m/s the specific volume increased from a minimum at 7 seconds exposure time, levelled off after 15 seconds, and remained constant up to exposure times of 30 seconds. This was also supported by an analysis of variance test at the 99% confidence interval. Video observations revealed that the maximum volume in low concentrations of O_2 did not occur until approximately 10-12 seconds exposure time, therefore, the data reported at low exposure times in Figure 8 were from before the time of maximum swelling. Specific volume data was not obtained at the point of maximum volume for any of the gas environments.

At higher temperatures of 750°C and 900°C in 5%CO/95%N_2, the specific volume reached a maximum at the lowest exposure times and remained constant over the range of exposure times as shown in Figures 9 and 10. This was supported by statistical analysis at the 99% confidence interval. A review of video images showed the point of maximum volume for pyrolysis at 750°C occurred after approximately 3 seconds elapsed time, this corresponds to data reported at the lowest exposure time. In addition, the point of maximum volume for 900°C occurred after 1 second exposure time; therefore, all the data reported in Figure 10 were after maximum swelling had occurred. As noted from these results, the time of maximum volume decreases as the temperature increases. The specific volume versus exposure time trends from pyrolysis in an atmosphere of 5%CO/95%N_2 at 600°C, 750°C, and 900°C agree with the swollen volume versus exposure time trends reported by Miller [8] for char exposed in an atmosphere of N_2 over a temperature range of 500°C-900°C.

The influence of gas velocity on swelling behavior was investigated by comparing the data at 0.61 m/s in Figure 9 to those at 1.83 m/s in Figure 11. There was no apparent affect of gas velocity on the specific volume of char devolatilized in an atmosphere of 5%CO/95%N_2. These data suggest that the conditions employed for devolatilization in 5%CO/95%N_2 were kinetically controlled rather than film mass transfer controlled. The change in gas flowrate (at constant gas temperature) was used to change the mass flux of gas to the particle. Since the char particle was heated predominantly by radiative heat transfer with convective heat transfer increasing with increased gas velocity, these results show that convection did not have a significant effect on the final swollen volume This finding agrees with Miller's [8] conclusion that swelling is independent of convective heat transfer.

Assuming that char particles are spherical and packed together with a bed void fraction of 0.40, the specific volume results for an atmosphere of 20%CO_2/5%CO/95%N_2 at 40 seconds exposure time, shown in Figure 7, correspond to an average bulk density of 30.8±8.21 kg/m^3 . These single particle results are in agreement with the density measured for char, gasified to a fractional conversion of 10% organic carbon in 5%CO_2/95%N_2, (ρ=25 kg/m^3) which was discussed earlier. The density results from this single particle study are approximately twice as high as the swollen volume results reported by Frederick et al. [10] for particles exposed to a gas environment of 20%CO_2/80%N_2 at 800°C. These differences may be due to differences in swollen volume versus specific volume or variations between liquors and experimental temperatures.

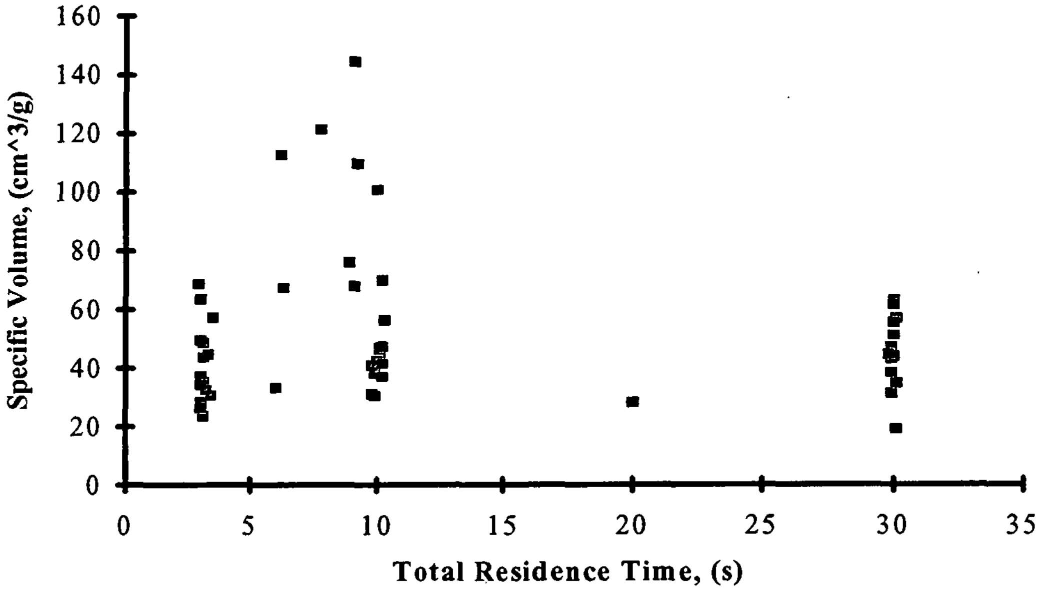

Figure 9: Specific Volume of Kraft Black Liquor as a Function of Total Residence Time in 5%CO/95%N_2 at 750°C and 0.61 m/s

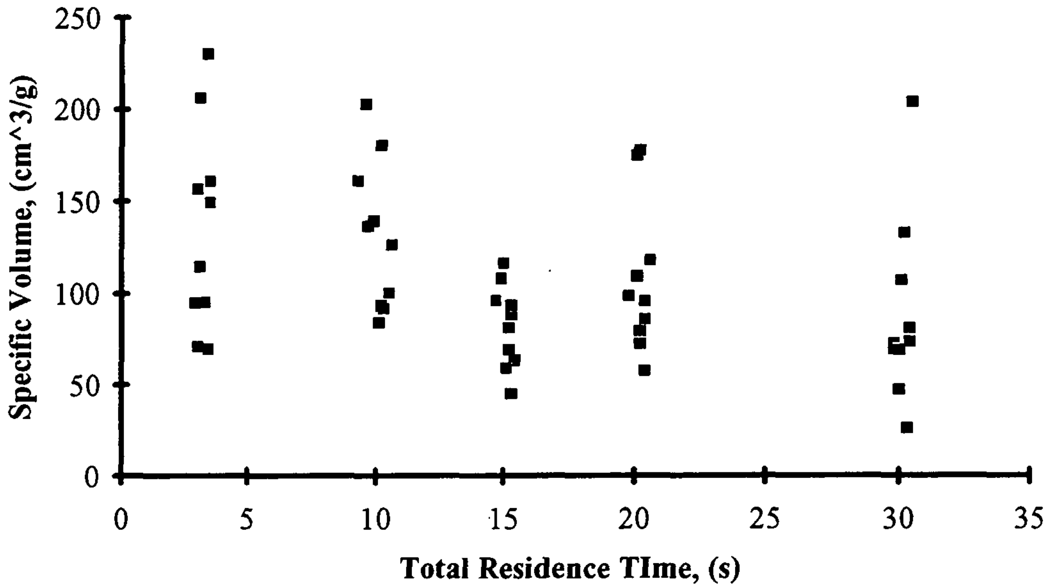

Figure 10: Specific Volume of Kraft Black Liquor as a Function of Total Residence Time in 5%CO/95%N_2 at 900°C and 0.61 m/s

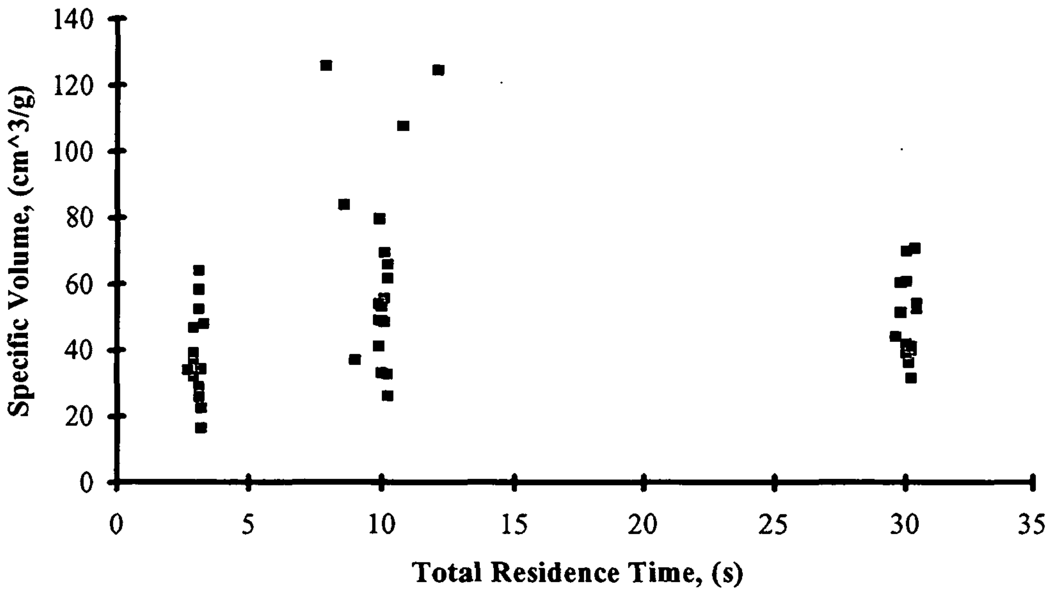

Figure 11: Specific Volume of Kraft Black Liquor Char as a Function of Total Residence Time in 5%CO/95%N_2 at 750°C and 1.83 m/s.

Observations of Drop Pyrolysis and Comparison of Char Photomicrographs

For the various experimental conditions, all drops exhibited the same behavior during drying. However, there were substantial differences in devolatilization observed at the different conditions. Particles produced in 5%CO/95% N_2 were porous and brittle. Swelling of these particles was uniform and spherical. Char formed during all experiments at 600°C shrank substantially after reaching maximum swollen volume; much less collapse was noted at 750 and 900°C.

As noted earlier, particles exposed to the oxygen-containing atmosphere at 500°C had higher specific volumes than particles exposed in other gas atmospheres. These drops underwent serpentine expansion and formed hollow char particles with delicate but resilient external films. The increased extent of swelling at low oxygen concentrations has been observed by others. [10] It is conceivable that the oxygen increases the resilience of the char surface by plasticizing the material. Chars produced in 20%CO_2/5%CO/75% N_2 at 600°C were identical in appearance to the samples from pyrolysis at 600°C.

The char surface structure was investigated under a Scanning Electron Microscope (SEM). Results are presented in micrographic form in Figures 12- 17. Figures 12-14 are example SEM photomicrographs of the residual char from liquor pyrolysis in 5%CO/95%N_2 at 600°C for gas velocity of 0.61 m/s at 600°C, 750°C, and 900°C, respectively. The concentration of "whiskers" or dendritic structures appeared to decrease as the temperature increased. The "whiskers" at 600°C evolved into "agglomerated platelets and whiskers" at 750°C and became "isolated agglomerates of whiskers and platelets" at 900°C. The surface changes observed may bare relationship to the earlier conclusion that specific volume increases with increasing temperature.

Figure 15 shows the char surface from liquor exposed in 5%CO/95%N_2 with gas velocity of 1.83 m/s at 750°C. In comparison to Figure 13, the "whiskers" are minimized and replaced predominantly by platelets at the higher gas velocity. The specific volume remained unchanged as the mass flux of CO to the particle was increased.

Figure 16 is an example SEM photomicrograph of the residual char from liquor exposed in 5%CO/20%CO_2/75%N_2 with gas velocity of 0.61 m/s at 600°C. The char in Figure 17 was produced from liquor exposed in 5%O_2/95%N_2 for gas velocity of 0.61 m/s at 500°C. Exposure in low concentrations of O_2 resulted in the greatest concentration of "whiskers." As the organic carbon is depleted from the surface of the char, the residual inorganics may appear in the form of these "whiskers". As the temperature is raised above the melting point of the inorganic salts (for example 750°C or 900°C), these "whiskers" may transform into platelets. In an atmosphere of CO_2 and CO, the "whiskering" effect is not as pronounced as observed in an atmosphere of CO; however, the formation of "platelets" is not as evident as that observed at higher temperatures in CO.

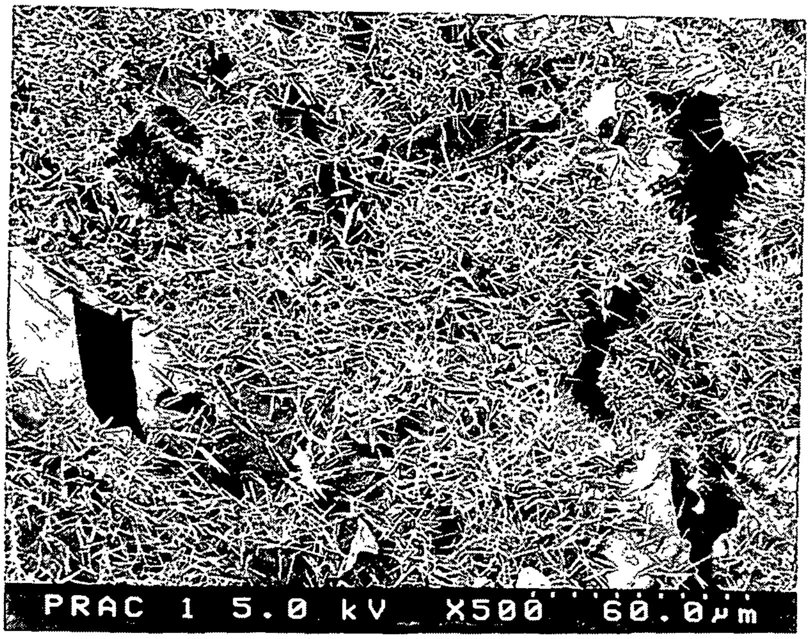

Figure 12: Scanning Electron Micrograph of Kraft Black Liquor Char Exposed in 5%CO/95%N_2 at 600°C and 0.61 m/s.

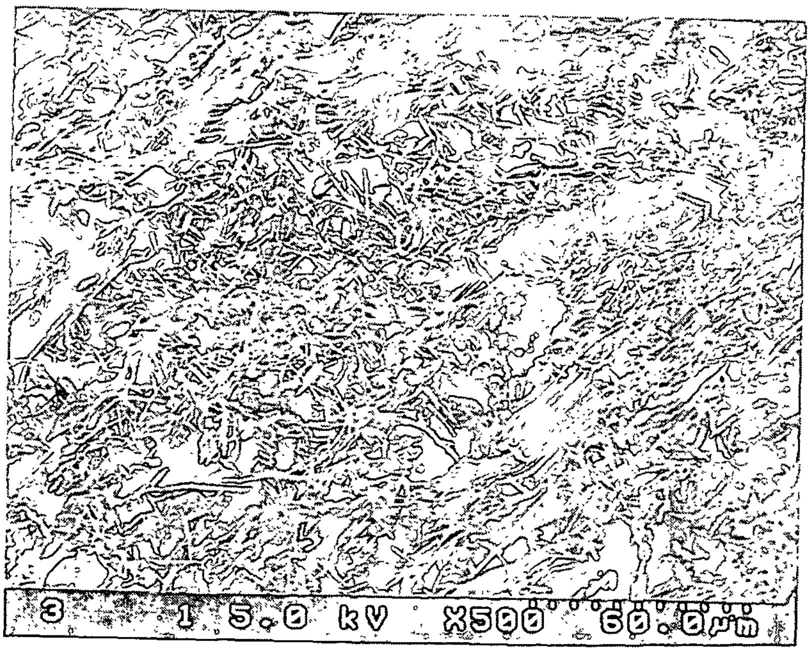

Figure 13: Scanning Electron Micrograph of Kraft Black Liquor Char Exposed in 5%CO/95%N_2 at 750°C and 0.61 m/s.

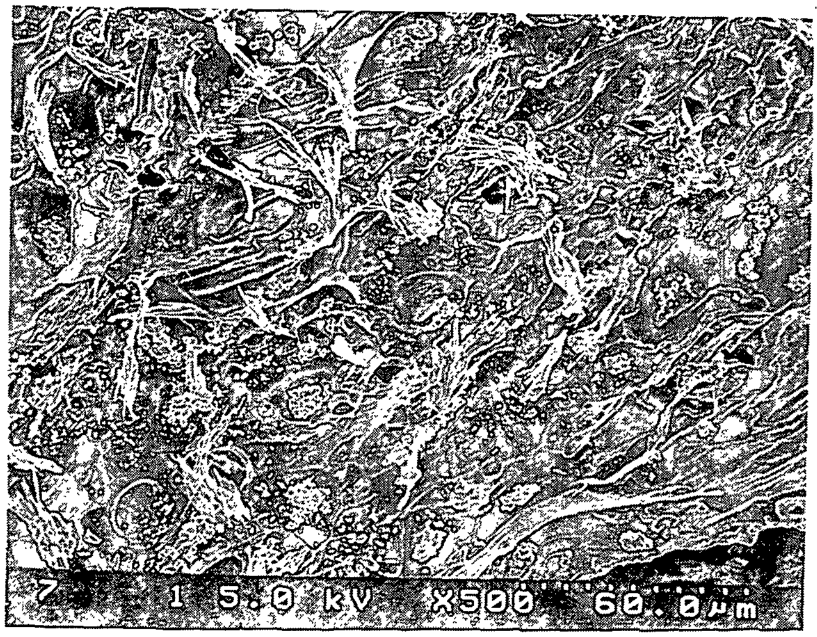

Figure 14: Scanning Electron Micrograph of Kraft Black Liquor Char Exposed in 5%CO/95%N_2 at 900°C and 0.61 m/s.

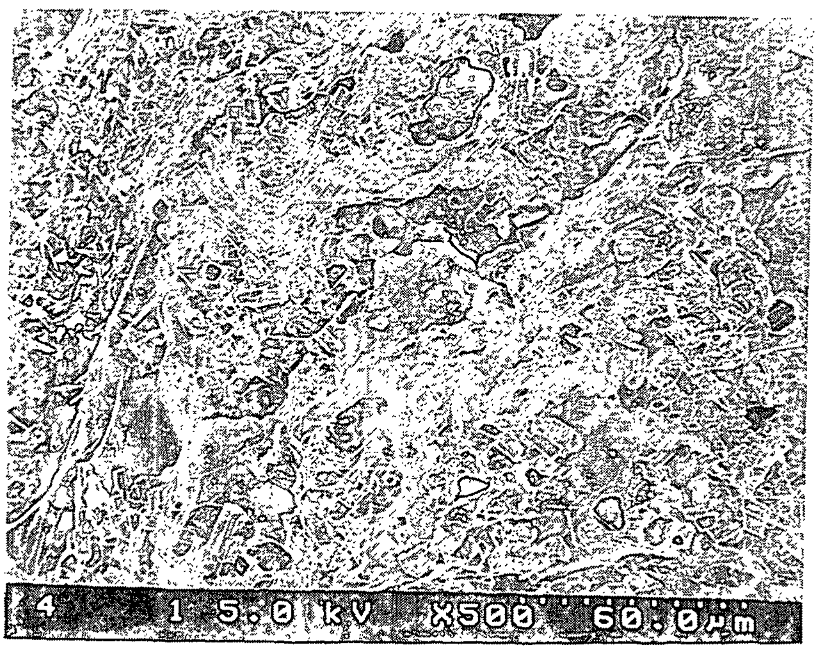

Figure 15: Scanning Electron Micrograph of Kraft Black Liquor Char Exposed in 5%CO/95%N_2 at 750°C and 1.83 m/s.

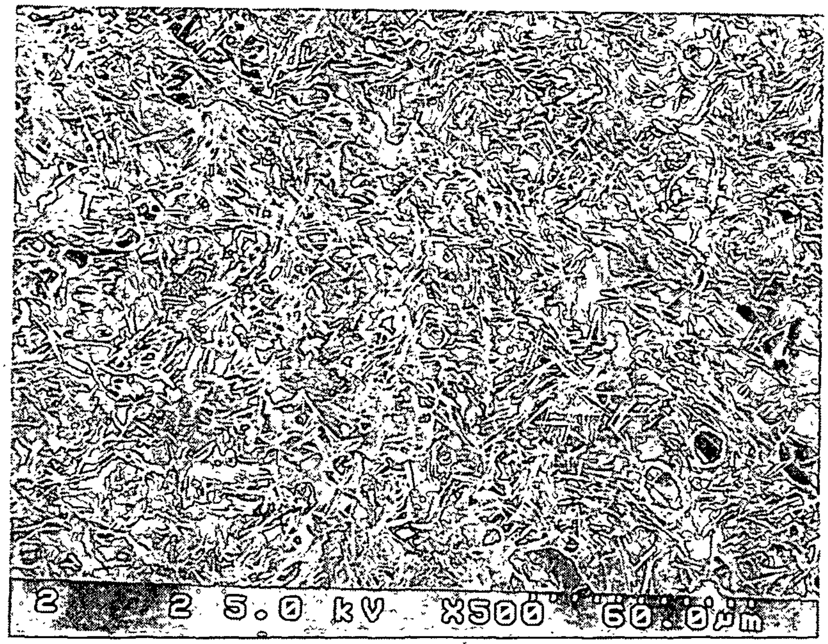

Figure 16: Scanning Electron Micrograph of Kraft Black Liquor Char Exposed in $5\%CO/20\%CO_2/75\%N_2$ at 600°C and 0.61 m/s.

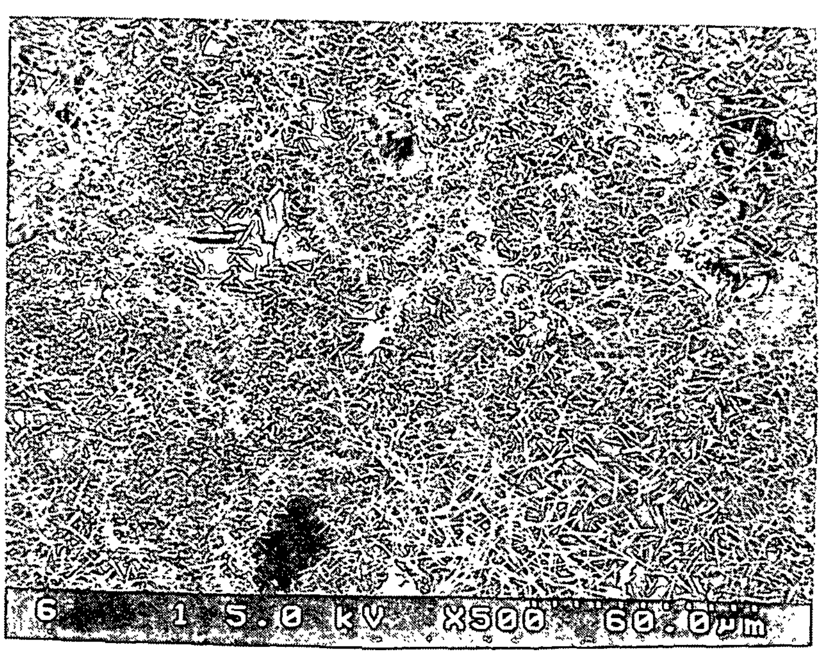

Figure 17: Scanning Electron Micrograph of Kraft Black Liquor Char Exposed in $5\%O_2/95\%N_2$ at 500°C and 0.61 m/s.

SUMMARY & CONCLUSIONS

The bulk density of kraft black liquor char was determined by measuring the volume and mass of the residual char following the completion of devolatilization and gasification experiments. This study provides the first indication of organic carbon concentration and char bulk density as a function of organic carbon depletion during the char burning stage of black liquor combustion. The organic carbon concentration in kraft char averages 7.8 kg/m^3 and is independent of fractional conversion of organic carbon at burnout levels greater than 10%.

Char bulk density went through a minimum of 25 kg/m^3 at 10% conversion of organic carbon and gradually increased as the organic carbon was depleted. The char density increased at higher fractional conversion due to inorganic salt coalescence as the organic carbon was depleted. The bulk density from this study is more representative of the actual furnace char density than the high smelt containing values reported by Richardson and Merriam.

Char specific volume, defined as the particle volume divided by the particle mass at the time of measurement, was determined from single particle swelling experiments in gas atmospheres of 5%CO/95%N_2, 5%O_2/95%N_2, and 20%CO_2/5%CO/75%N_2. Char specific volume was found to be independent of the mass flux of gas to the char particle. In addition, char specific volume decreased with increasing temperature when exposed in 5%CO/95%N_2. Particles exposed for longer than 10-15 seconds to an atmosphere containing low concentrations of O_2 had higher specific volumes than the particles reacted in CO or CO_2. The effect of particle exposure time on specific volume was strongly dependent on the gas atmosphere. For particles exposed in high concentrations of CO_2 or low concentrations of CO, the particle specific volume was greatest at lower exposure times. In contrast, in low concentrations of O_2 the swelling was lowest at the lower exposure times. However, in all gas environments the swelling leveled off at exposure times greater than 15 seconds. Bulk density for char beds which were predicted from the single particle measurements in an environment of 20%CO_2/5%CO/75%N_2; these results were in agreement with the density measured for char gasified in the fixed bed reactor in 5%CO_2/95%N_2.

Scanning Electron Microscope images of residual chars revealed differences in surface morphology for the various furnace conditions. As the organic carbon was depleted from the surface of the char, the residual inorganics appeared in the form of dendritic structures or "whiskers". As the temperature is raised above the melting point of the inorganic salts (for example 750°C or 900°C), these "whiskers" transformed into platelets.

Previously char swelling has been characterized by measured swollen volume normalized by initial droplet mass or as a ratio of swollen size to initial size. The results of this study provide for the first time an indication of how actual char density changes with gasification conditions and exposure time during the char burning stage of black liquor combustion.

LITERATURE CITED

1. GRACE, T.M.; CAMERON, J.H.; and CLAY, D.T., "Role of the Sulfate-Sulfide Cycle in Char Burning: Experimental Results and Implications," TAPPI 69(10): 108-113 (1986).

2. ADAMS, T.N. and FREDERICK, W.J., Kraft Recovery Boiler-Physical and Chemical Processes, The American Paper Institute (1988).

3. GRACE, T.M.; CAMERON, J.H.; and CLAY, D.T., Char-Burning Project 3473-6, The American Paper Institute (February 22, 1985).

4. RICHARDSON, D.L. and MERRIAM, R.L., "Study of Cooling and Smelt Solidification in Black Liquor Recovery Boiler," Phase I report, prepared for the American Paper Institute, Arthur D. Little, Inc., Cambridge, MA, Feb. 1977.

5. KRAUSE, H.H.; SIMON, R.; and LEVY, A., Final Report on Smelt-Water Explosions to the Fourdrinier Kraft Board Institute, Inc., Battelle Columbus Laboratories, Jan. 1973.

6. WOZNIAK, J., Measurement of the Physical Properties of Sodium Sulfide-Sodium Carbonate Melts," Appleton, WI, The Institute of Paper Chemistry, (1985).

7. MAGNUSSON, H. and WARNQVIST, B., "Properties of Sodium Sulfide-Sodium Carbonate Melt," SVENSK PAPPERSTIDNING 78(18): 614-616 (1975).

8. MILLER, P., "Swelling of Kraft Black Liquor-An Understanding of the Associated Phenomena During Pyrolysis," Ph.D. Dissertation, Appleton, WI, The Institute of Paper Chemistry, (1986).

9. HUPA, M.; SOLIN, P.; and HYOTY, P., "Combustion Behaviour of Black Liquor Droplets," Proc. 1985 Intl. Chem. Recovery Conf., New Orleans, 1985, p. 335-344.

10. FREDERICK, W.J.; NOOPILA, T.; and HUPA, M., "Swelling of Spent Pulping Liquor During Combustion," Journal of Pulp and Paper Science 17(5): 164-170 (1991).

11. MILANOVA, E. and KUBES, G.J., "The Combustion of Kraft Liquor Chars," J. Pulp Pap. Sci. 12(6): J187 (1986).

12. CLAY, D.T.; GRACE, T.M.; KAPHEIM, R.J.; SEMERJIAN, H.G.; MACEK, A. and CHARAGUNDLA, S.R., "Fundamental Studies of Black Liquor Combustion," Report No. 1-Phase 1, U.S. DOE Report No. DE85013773 (Jan. 1985).

13. Lee, S. R. and Nichols K. M. "CO_2 Gasification of Kraft Black Liquor Char in a Fixed Bed Reactor," Submitted for Publication to Journal of Pulp and Paper Science, 1992.

14. LI, J., "Pyrolysis and CO_2 Gasification of Black Liquor Char," M. Eng. Thesis, Montreal, McGIll Univ., (Feb., 1986).

15. Verrill, C. L., "Inorganic Aerosol Formation During Black Liquor Drop Combustion," Ph.D. Dissertation, Atlanta, Institute of Paper Science and Technology, (September 8, 1992).

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