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**THE INFLUENCE OF COMPOSITION ON THE SWELLING OF
KRAFT BLACK LIQUOR DURING PYROLYSIS**

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KRAFT BLACK LIQUOR DURING PYROLYSIS**

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ABSTRACT

During the drying and pyrolysis phases of kraft black liquor combustion, significant swelling of individual liquor particles occurs. Swollen volumes can reach 20 to 30 times the original volume during combustion. The swelling process can conceivably affect the combustibility of black liquor and the amount of carryover in a recovery furnace.

The composition of black liquor was found to have a large influence on swelling. A combination of sugar acids and kraft lignin swelled to a larger extent than when either component was pyrolyzed separately. A 1:1 ratio of these two components resulted in maximum swelling for the various ratios tested. The molecular weight of kraft lignin had an effect on swollen volume with higher molecular weight fractions producing lower swelling chars.

Other components were found to reduce the swelling of black liquors. Extractives interfered with the swelling by appearing to change the deformable properties of the pyrolyzing material. Inorganic salts acted as a diluent.

Analysis of the surface characteristics of chars revealed that good swelling chars were composed of small bubbles 50 to 150 microns in diameter. Poor swelling liquors did not exhibit this phenomenon. The formation of bubbles was found to be initiated at 240°C, which closely corresponded to the thermal decomposition temperature of a sugar acid. Kraft lignin appeared to have a major influence on the viscous properties of the pyrolyzing particle. The composition of black liquor determines to a large extent the surface active and viscous forces present in black liquor; these forces are believed to be responsible for the extent to which kraft black liquors deform and swell during pyrolysis.

INTRODUCTION

The kraft process is the dominant pulping process today for paper grade pulps. Kraft pulp represents 74% of North American market pulps (1). An advantage of kraft pulping is the efficient recovery of the chemicals and the energy value from its spent pulping liquor. This aqueous solution from the process, kraft black liquor, contains dissolved organic and inorganic solids. In the recovery process, kraft black liquor is concentrated to approximately 65% solids content and combusted. The burning of organics contained in kraft black liquor provides a significant amount of energy, which is used to produce steam. The resulting char is then smelted to recover the inorganic chemicals for reuse in the pulping process. Both steam generation and smelting occur in the same process unit, the recovery boiler.

Kraft recovery boilers typically operate at full solids capacity, leaving little leeway for

upsets. Any interruption in the furnace operation can have an immediate detrimental effect on the operation of an entire mill. Steady-state combustion in the recovery furnace is thus of particular importance in maintaining efficient pulp production.

A blackout is defined as the loss of liquor ignition in the recovery boiler and can result in a significant amount of recovery boiler downtime. Some mills have experienced blackouts which appear to be linked to variations in the properties of black liquor (2). The cause of this poor combustion could not be determined from conventionally measured properties (heat value, solids content, specific gravity, and viscosity). Reduced swelling of black liquor has been observed in liquors exhibiting poor combustion characteristics (3,4).

Black liquor swelling is an important process during combustion. Swelling of black liquor particles increases the surface area available for reaction with oxygen and thus improves the combustibility of black liquor. Changes in the swelling of black liquor would alter the flight paths of black liquor particles in a recovery furnace. Excessive swelling of particles can lead to increased entrainment of black liquor char in air. The char becomes deposited on the upper portions of a recovery furnace and leads to increased downtime. These factors indicate that the potential exists for an optimum amount of black liquor swelling during combustion to maintain efficient recovery furnace operation.

Unfortunately, there are limited data on black liquor swelling during pyrolysis (3-6). Studies performed to date have been limited either by empirical analysis, low temperatures or the inability to monitor the swelling process as a function of time.

The present study was undertaken to investigate the swelling characteristics of kraft black liquor during pyrolysis. The objectives were to quantify the swelling and to determine the factors which contribute to swelling. The variables thought to be of importance in swelling were the heating rate, gas temperature, moisture content of the particle, particle size, and the black liquor composition.

An earlier paper discussed the effect of heating rate, particle size, pyrolysis temperature, and moisture content on the swelling of kraft black liquors during pyrolysis (7). The present paper discusses the effect of black liquor composition on the swelling of kraft black liquor. The components studied were kraft lignin, sugar acids, extractives, and the inorganic salts. Additional work involving the effect of initial black liquor solid content on swelling will also be discussed.

APPROACH

The reactor used for this study allowed one to view the swelling of black liquor particles during evaporation and pyrolysis. It is shown in Fig. 1. Details of the experimental apparatus, the experimental procedures, and the material preparation can

be found in the appendix. Black liquor particles were placed on a wire which was connected to a microbalance. The particles were heated by flowing a hot nitrogen gas stream past the particle. Heat transfer occurred primarily by convection, with some radiative heat transmitted to the particle from the surrounding reactor walls. Heat fluxes in the reactor were calculated from experimentally determined evaporation rates of water from small metal cups. Heat fluxes which were comparable to those found in commercial recovery furnaces (100 kW/m^2) could be attained at 900°C (7).

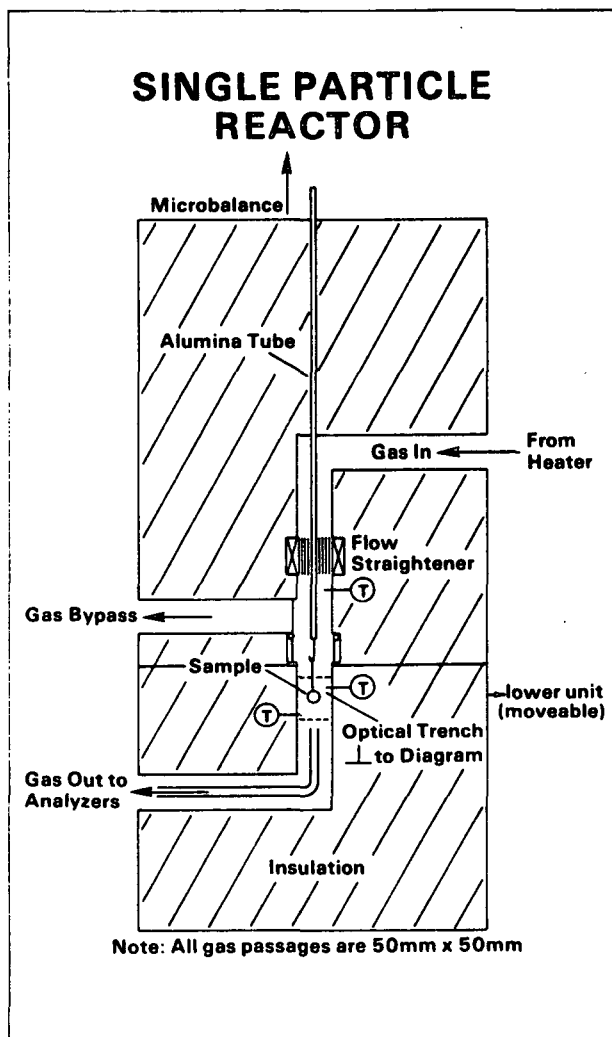


Fig. 1 Schematic of single particle reactor.

An optical port was available for viewing and taking photographs of the black liquor particles. The volume of the particles could be inferred from the projected area of the particle measured from photographs. The volume measurements given in the text were divided by the original dry solids weight of the particle; this way, particles differing in particle size and moisture content and that were pyrolyzed at different temperatures are compared on initial dry solid weight basis. A gas sampling

line below the particle allowed for the analysis of CO , CO_2 and H_2O . Data acquisition was performed by a microcomputer with an analog/digital interface.

The process variables were studied in an earlier paper (7). The particle size (1-4 mm in diam.) had no effect on the maximum particle volume. The heating rate could be changed qualitatively by changing the gas flow rate in the reactor. An increase in the heat flux shortened the time of pyrolysis but had no effect on the maximum volume attained; thus, the heating rate effectively changed the rate of swelling.

The effects of the gas temperature and of the moisture content are shown in Fig. 2. The swollen volume of black liquor particles attained a maximum at 500°C . Moisture present in black liquor increased swelling during pyrolysis between 400 to 600°C . The effect of moisture on swelling was not additive, as 65 and 80% solids black liquor behaved similarly. The swelling was found to occur during the evolution of pyrolysis gases; however, there was no correlation found between the amount of pyrolysis gas evolved and the amount of swelling.

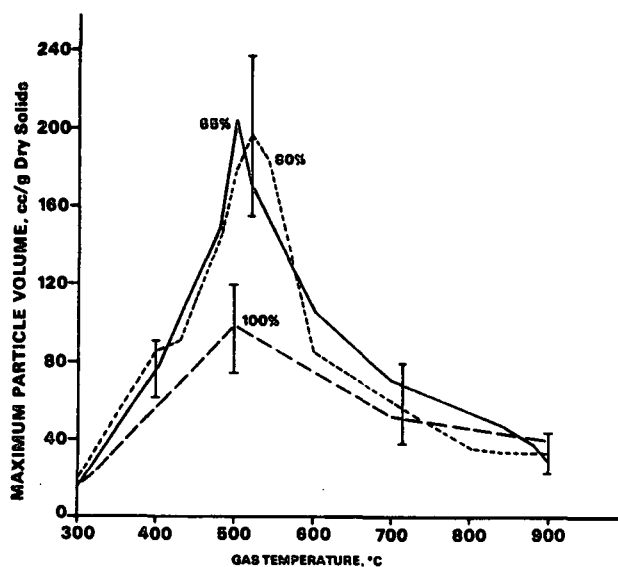


Fig. 2 Maximum particle volume vs. gas temperature for 65, 80 and 100% solids black liquors. Brackets indicate ± 1 std. deviation.

The compositional variables studied were kraft lignin (KL), sugar acids (SA), inorganic salts, and extractives. Kraft lignin was precipitated from the black liquor by acidification to pH 2.5 with $1\text{N H}_2\text{SO}_4$. After removal of kraft lignin and some of the inorganics, the solution contained the sugar acids from black liquor. The isolated kraft lignin and sugar acid solutions were in their acidic form. To simulate the alkaline conditions of kraft black liquors the pH was raised to 12 by using 1N NaOH . A 20% by weight solution of sodium sulfate was used to simulate the inorganic salts found in black liquor. The effect of extractives on the swelling of black liquor was studied in two ways: 1) the

extractives were isolated and added back to black liquor and 2) the black liquor from cooks of extractive-free wood were compared to black liquor derived from wood containing extractives.

The pyrolysis of black liquor could be tested by placing black liquor on a small wire. The sugar acids were not viscous enough to remain attached to the wire during pyrolysis. Small metal cups were used to hold the material during pyrolysis. The metal cups were found to reduce swelling but influenced the various samples in the same manner.

RESULTS

Preliminary tests revealed that a combination of kraft lignin and sugar acids swelled to a greater extent than either component tested separately. The extractives and inorganics were found to reduce swelling. Figure 3 shows the influence of pH and sugar acid/kraft lignin ratio on swelling at 500°C. Table 1 shows that the synergistic effect of KL and SA on swelling also occurred at 900°C.

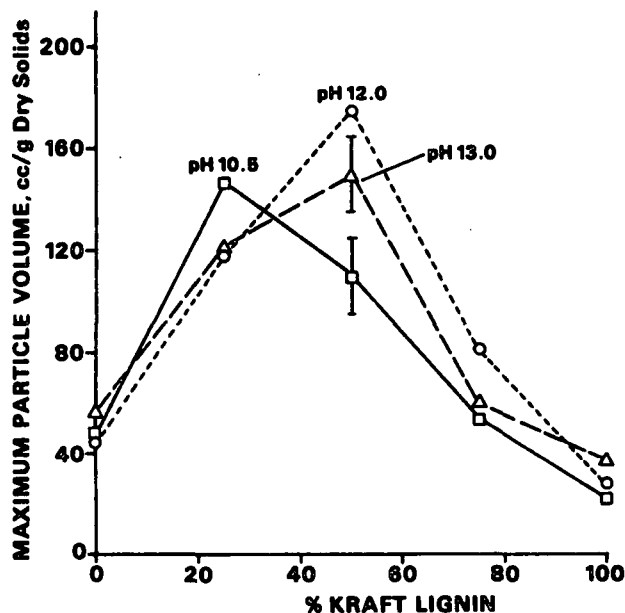


Fig. 3 Maximum particle volume of kraft lignin/sugar acid mixtures at different pH, pyrolyzed at 500°C. Brackets indicate ± 1 std. deviation.

Table 1 Swelling of sugar acids (SA), kraft lignin (KL) and a KL:SA mixture (900°C, pH 12), pyrolysis occurred in small metal cups

| Component | SA | KL | SA:KL 1:1 |
|-----------------------------|----|----|-----------|
| Volume (cm ³ /g) | 19 | 15 | 76 |
| | 24 | 27 | 84 |
| | 22 | 21 | 59 |
| | 23 | 29 | 53 |
| Mean | 22 | 23 | 68 |

LSD - 15 cm³/g, least significant difference (LSD), 95% confidence

The data in the figures represent at least three replications; variability in the figures is represented by plus or minus one standard deviation. The least significant difference (LSD) statistic was the criterion used to determine whether the means of the experimental data presented in the tables were significantly different from one another. The LSD represented the difference required between two means to be able to detect a difference at the 95% confidence level.

Figures 4-6 show the release of carbon dioxide during the pyrolysis of SA, KL, and a 1:1 mixture of the two components. The dashed lines represent the time at which photographs had been taken. The volume of the particle is given above the dashed line. The solid line in Fig. 4 indicates the point at which the lignin solidified. The solid line in Fig. 6 indicates the point at which significant swelling started for the SA/KL mixture.

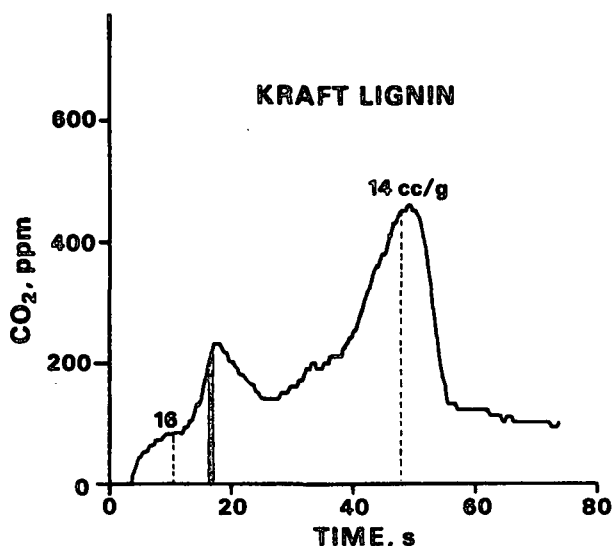


Fig. 4 Carbon dioxide vs. time for kraft lignin pyrolyzed at 500°C (99 mg, 46% solids). Photographs are indicated by dashed lines. Solid line indicates point at which material became a rigid structure.

A solution of kraft lignin was separated into three fractions by ultrafiltration. These lignin fractions were mixed with sugar acids in a 1:1 ratio (dry weight basis) and pyrolyzed at 500°C. The results are shown in Table 2.

Inorganic salts and extractives were added to black liquor. The effect of inorganic salts was determined by adding a 20% by weight solution of sodium sulfate to black liquor. The results are shown in Fig. 7. The solid line indicates the volume expected if the sodium sulfate acted as a diluent.

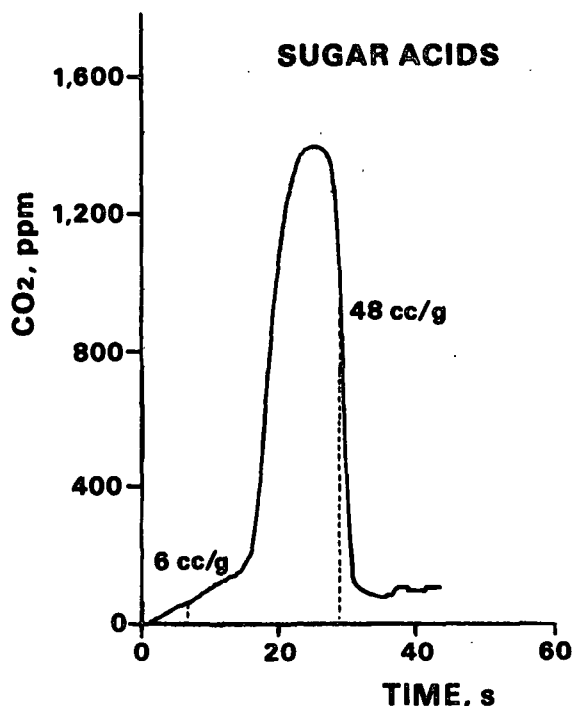


Fig. 5 Carbon dioxide vs. time for sugar acids pyrolyzed at 500°C (88 mg, 51%). Photographs are indicated by dashed lines.

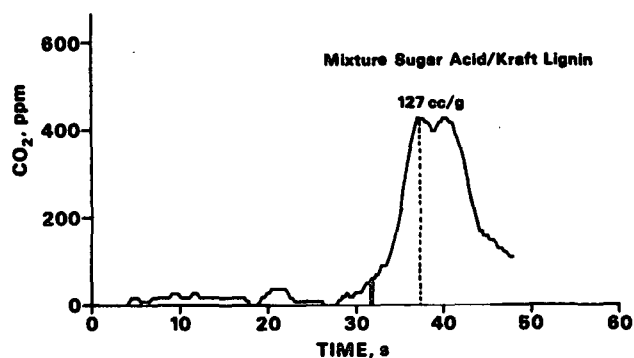


Fig. 6 Carbon dioxide vs. time for a 1:1 mixture of kraft lignin and sugar acids pyrolyzed at 500°C (123 mg, 48% solids). The solid line indicates point at which significant swelling began. The dashed line indicates the time at which a photograph was taken.

The extractives were isolated by TAPPI Standard T264 om-82 with approximately 7% of the wood removed as extractives. Three black liquors differing in extractive content are shown in Table 3. The normal liquor represents a black liquor with no extractives removed. The extractive-free liquor represents black liquor obtained from extractive-free wood. A sample of extractive-free black liquor was mixed with the isolated extractives (7% by weight). Figure 8 shows the effect of extractives added to extractive-free black liquor over a

range of addition levels. The solid line indicates the volume expected if the extractives acted as a diluent.

Table 2 Effect of kraft lignin molecular weight on the swelling of a 1:1 KL:SA mixture; pyrolysis occurred in small metal cups

| MW of Kraft Lignin | High | Med. | Low |
|-----------------------------|------|------|-----|
| Volume (cm ³ /g) | 44 | 78 | 123 |
| | 68 | 88 | 109 |
| | 33 | 97 | 106 |
| | -- | 96 | 127 |
| Mean | 48 | 90 | 116 |
| LSD - 21 cm ³ /g | | | |

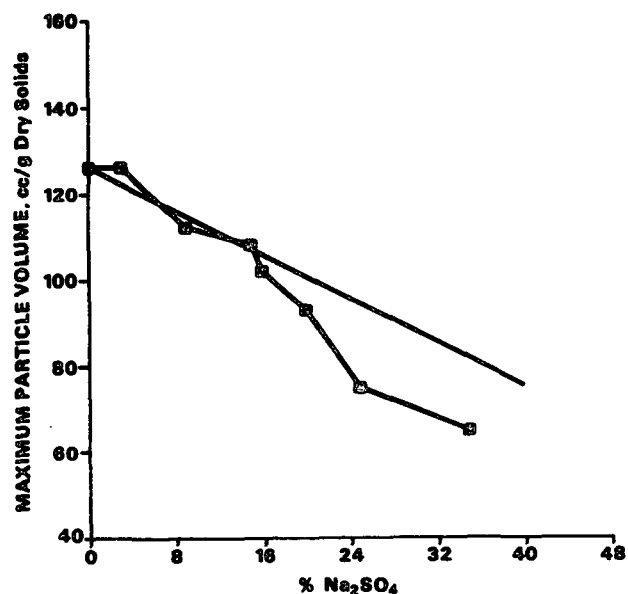


Fig. 7 Effect of Na₂SO₄ concentration on the maximum particle volume at 500°C. The solid line corresponds to Na₂SO₄ acting as a diluent to the swelling process.

Table 3 The effect of extractives on maximum particle swollen volume; pyrolysis occurred in small metal cups

| Type | Normal | Ext. Free | Ext. Free + 7% Ext. |
|-----------------------------|--------|-----------|---------------------|
| Volume (cm ³ /g) | 48 | 109 | 26 |
| | 47 | 60 | 19 |
| | 44 | 95 | 31 |
| | | 64 | |
| Mean | 46 | 82 | 25 |
| LSD - 26 cm ³ /g | | | |

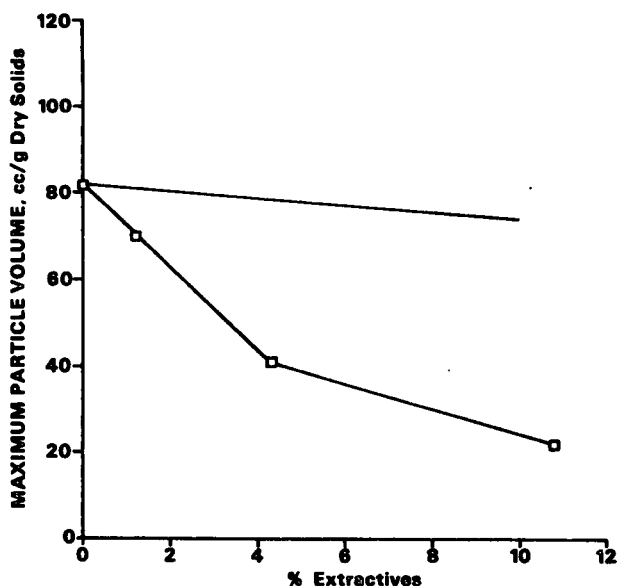


Fig. 8 Effect of extractive concentration on the maximum particle volume at 500°C. Solid line indicates relationship if the extractives were to act as a diluent and not participate in the swelling process.

Black liquors at a range of solids contents (65, 73, 86, 96 and 100%) were prepared for further study. The results are shown in Table 4. Three liquor samples (65, 86, and 100%) with distinctly different rheological properties were chosen for further study. The 65% black liquor was a viscous liquid, the 86% sample a tarry substance and the 100% sample a porous solid. The evolution of carbon dioxide and water vapor during pyrolysis of these black liquors is shown in Fig. 9.

Table 4 The effect of solids content on the maximum particle volume; pyrolysis occurred in small metal cups

| % Solids | 100% | 96% | 86% | 73% | 65% |
|-----------------------------|------|-----|-----|-----|-----|
| Volume (cm ³ /g) | 97 | 106 | 69 | 105 | 125 |
| | 79 | 91 | 63 | 101 | 115 |
| | 84 | 89 | 72 | 132 | 124 |
| | -- | 83 | 87 | 136 | -- |
| Mean | 87 | 95 | 68 | 113 | 121 |
| LSD - 17 cm ³ /g | | | | | |

DISCUSSION

The study of the process variables in an earlier paper (7) revealed that the evolution of the pyrolysis gases drove the swelling process. There was no correlation found between the amount of pyrolysis gases evolved and the change in volume for particles at a given temperature. The deformable properties of the black liquor during pyrolysis was hypothesized to determine the extent of swelling. The study of the compositional variables was initiated to further investigate this hypothesis.

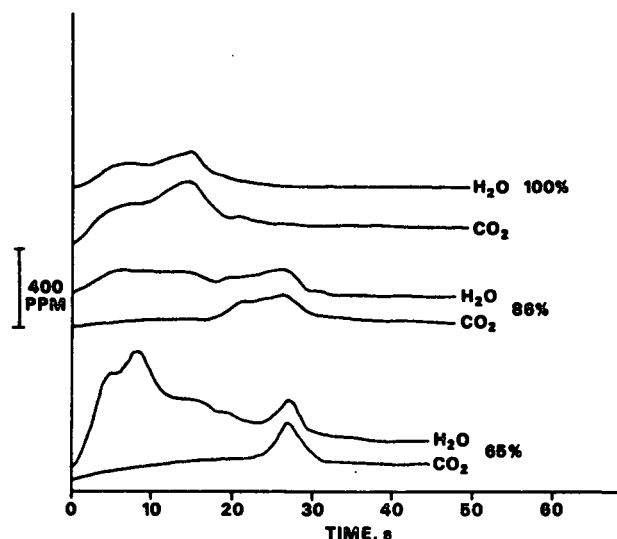


Fig. 9 The water vapor and carbon dioxide evolution curves of black liquor at 65, 86 and 100% solids (30-35 mg, 500°C).

An interaction between equal amounts (dry weight basis) of sugar acids and kraft lignin resulted in the highest swelling of black liquor regardless of the pyrolysis temperature (Fig. 3, Table 1). Figures 4-6 provide some evidence to explain the swelling behavior. Figure 4 shows that when a kraft lignin solution was pyrolyzed, it formed a rigid structure before a significant portion of the pyrolysis gases were evolved. The lignin solutions, when pyrolyzed showed some swelling during evaporation, but once the evaporation was complete no more swelling was observed.

Sugar acids evolved much more gas than kraft lignin as shown in Fig. 5. Expansion of the pyrolyzing sugar acids occurred throughout the pyrolysis process, similarly to black liquor. However, the sugar acids during pyrolysis were more fluid than black liquor and appeared to allow more of the gases to escape. The chars of sugar acids were spherical and composed of a very thin, fragile outside layer.

The combination of KL and SA in a 1:1 ratio (dry weight basis) produced the highest swollen volumes despite evolving a lower amount of pyrolysis gases than the sugar acids for an equivalent amount of starting material. The KL/SA mixtures appeared to have a higher viscosity than sugar acids during pyrolysis, which resulted in higher swollen volumes. The behavior and appearance of the chars from the KL/SA mixture were similar to those derived from black liquor.

The ionization of kraft lignin appears to be important for swelling. The highest swelling occurred when the lignin was fully ionized at pH 12. At pH 10.5 some of the higher molecular weight lignin precipitated out, which adversely affected the swelling at a 1:1 KL:SA ratio. Increasing the pH to 13 did not significantly influence the

swelling, indicating the sodium hydroxide was not directly involved in the swelling mechanism. The effects of pH above 10.5 on swelling were relatively small and were not studied further.

Polydispersity of kraft lignins has been repeatedly reported (8). The kraft lignin was separated into three fractions by ultrafiltration. The single fractions were then mixed with sugar acid solution to simulate black liquors. Liquor containing the higher molecular weight (HMW) fraction of kraft lignin was found to swell significantly less than liquors containing the lower molecular weight (LMW) fractions. A possible explanation for this occurrence was that the low molecular weight lignins increased the surface area available for association with the sugar acids.

Figure 7 shows that sodium sulfate acted as a diluent in the swelling of black liquor up to a 20% by weight addition level. The 25 and 35% data points are significantly different (95% confidence) from the diluent line, which indicated the sodium sulfate interfered with the swelling mechanism at these concentrations. An explanation for this occurrence is not obvious. The results suggest that under the conditions found in a recovery boiler [8-20%, $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CO}_3$ (9)] the inorganic salts act as a diluent and are not directly involved in the swelling mechanism.

The extractives significantly reduced the swelling behavior of black liquor. The evolution of carbon dioxide from pyrolyzing black liquor particles with and without extractives is shown in Fig. 10 and 11. The dashed lines indicate when photographs were taken, with the volumes indicated above the lines.

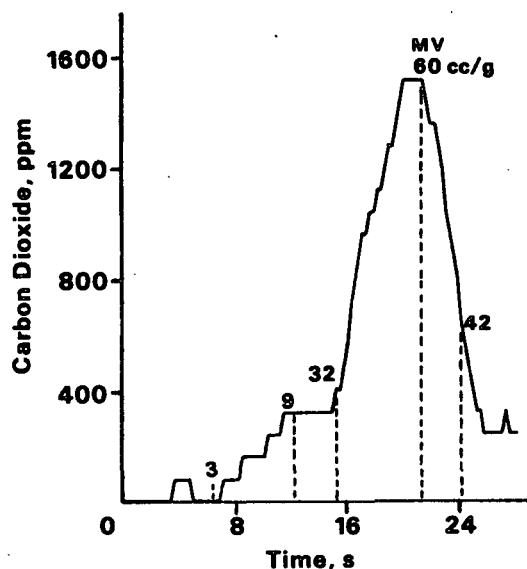


Fig. 10 Carbon dioxide evolution profile for an extractive-free black liquor particle (500°C 63%, 38.4 mg). Photographs indicated by dashed lines, with swollen volumes above them. MV indicates maximum volume.

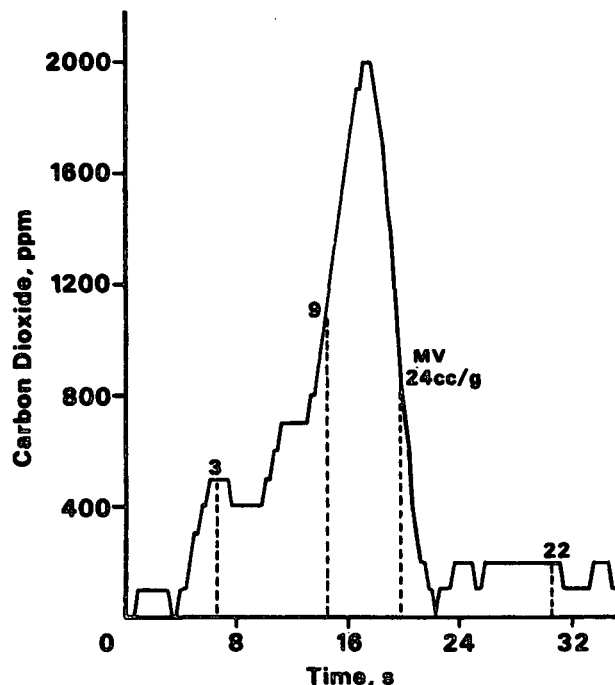


Fig. 11 Carbon dioxide evolution profile for an extractive free black liquor with 8% extractives added (63%, 30.0 mg, 500°C). Photographs indicated by dashed lines, with volumes indicated above them. MV indicates maximum volume.

The particles in Fig. 10 and 11 swelled significantly through the pyrolysis reactions. An indication of the deformability of the char was the shrinking behavior of particles during the decrease in pyrolysis activity. The extractive-free liquor shrank about 30% after reaching maximum volume. The black liquor containing 8% extractives shrank less than 10% after reaching maximum volume. No difference existed in the amount of carbon dioxide given off by particles differing only in extractive content. This indicated the extractives influenced the swelling by changing the deformable characteristics of black liquor and did not influence the extent of volatilization reactions during pyrolysis.

Since the viscous properties of pyrolyzing materials could not be measured, the surface features of high and low swelling chars were analyzed with a scanning electron microscope (SEM). The objective of this effort was to determine any differences in char structure which might help explain the swelling phenomenon. The highly swollen chars were obtained from extractive-free black liquor and LMW KL:SA (1:1). The low swollen volume chars analyzed were black liquor with 8% extractives and HMW KL:SA (1:1). Figures 12-14 show three SEM photographs of chars from black liquor.

Figure 12 shows the formation of bubbles in an extractive-free black liquor particle that was quenched midway through pyrolysis. Figure 13 shows the collapsed bubbles of a char from the same black

liquor after pyrolysis was completed. The bubbles were approximately 50-100 microns in diameter. Analysis of LMW KL:SA systems showed the same type of bubble formation. The black liquor with extractives did not exhibit this feature as shown in Fig. 14. The HMW KL:SA also did not exhibit the formation of bubbles. The results indicated the formation of small bubbles could be necessary to produce highly swollen chars of kraft black liquor. Work with light microscopes confirmed that the structures observed in the SEM were bubbles. The formation of bubbles indicated surface tension could be playing an important role in swelling.



Fig. 12 SEM photograph of an extractive free black liquor quenched midway through pyrolysis.



Fig. 13 SEM photographs of char resulting from the pyrolysis are of an extractive-free black liquor.

The analysis of black liquors differing only in solids content was further investigated. Black liquor above 85% solids swelled to a lesser extent than black liquors below 80% solids for black

liquors pyrolyzed between 400 to 600°C. Figure 15 shows the swelling during pyrolysis of four particles each at a different solids content. For the discussion 86C will be used to designate a char particle pyrolyzed from an 86% black liquor sample.

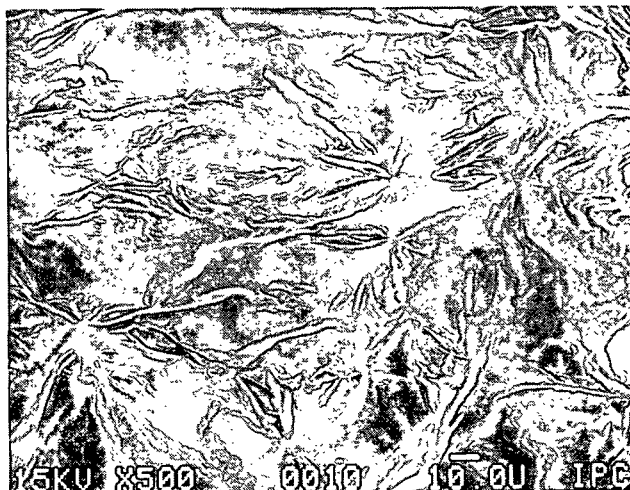


Fig. 14 SEM photograph of char resulting from the pyrolysis of black liquor containing 8% extractives.

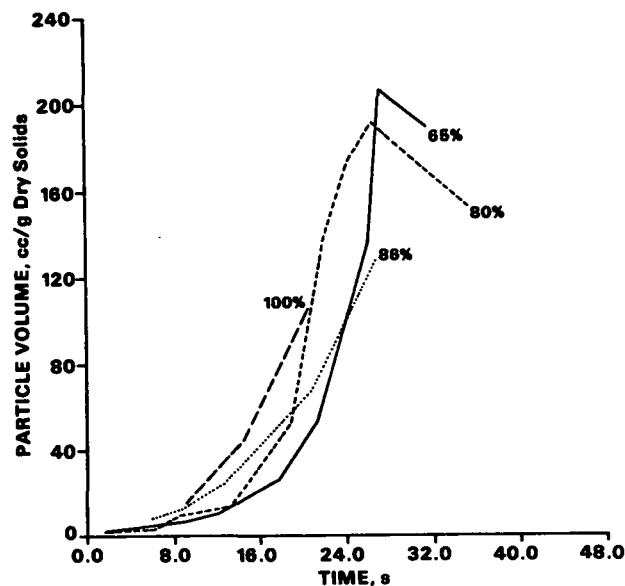


Fig. 15 Particle volume vs. time for black liquor particles differing in original solid content (500°C, 30-40 mg).

The higher swollen chars (65C and 80C) went through an evaporation stage which produced rapid expansions and contractions that were followed by rapid swelling rates. The black liquor with higher solid contents swelled to a larger extent early in the pyrolytic process but never attained the high swelling rates achieved by the lower solid content liquors. This resulted in higher swollen volumes

for the particles that went through a rapid evaporation phase relatively free from pyrolysis.

The carbon dioxide and water vapor release profiles of particles differing in solid contents are shown in Fig. 9. Evaporation and pyrolysis occur as separate processes when subjected to the heat fluxes found at 500°C. The solids content of the black liquors influenced not only the evaporation rate of black liquor but could also influence the subsequent pyrolysis and swelling processes. This was indicated by the broad water vapor (evaporation) and carbon dioxide (pyrolysis) peaks of the 86% solids black liquor (Fig. 9).

Analysis of the surface features of chars differing in solid contents revealed the formation of small bubbles. Thus, the differences in swelling behavior due to the original solids content of black liquor cause a more subtle difference in the pyrolysis of the material. Char particles were analyzed by CP/MAS ¹³C NMR to try and determine major chemical differences which might reflect the swelling behavior. The results of the NMR analysis are shown in Table 5.

Table 5 The swelling and structural characteristic of chars differing in original solids contents. Corrected structural intensities from CP/MAS ¹³C NMR. Pyrolysis at 500°C.

| % Solids | 65% | 73% | 86% | 100% |
|-------------------------|------|------|------|-------|
| Vol. cm ³ /g | 121 | 113 | 68 | 87 |
| Corrected Int. | | | | |
| Carboxyl | | | | |
| (165-220 ppm) | 10.2 | 11.3 | 8.2 | 8.6 |
| Aromatic | | | | |
| (90-165 ppm) | 61.4 | 60.0 | 65.2 | 61.1 |
| Aliphatic | | | | |
| (90- -30 ppm) | 30.6 | 30.3 | 29.2 | 32.31 |

The aliphatic content did not vary significantly between the chars. The aromatic content was higher for the 86C than the other chars (65C, 73C, 100C). The pyrolysis process was significantly slower for the 86C sample than the others, which may have led to the higher aromatic content. The slower pyrolysis of the 86C was evidenced by the broad pyrolysis peak in Fig. 9 relative to the other chars (65C, 100C).

The carboxyl content of the chars correlated well with the swelling characteristics of the chars. The higher swelling chars (65C and 73C) had a higher carboxyl content than the lower swelling chars (86C and 100C). The chars with similar swelling characteristics also had similar carboxyl contents (65C and 73C, 86C and 100C). The carboxyl content can be attributed to the sugar acid fraction of black liquor.

The ultrafiltration process separates lignin by size. The differences in size of the lignin are not true molecular weight differences but differences in the size of the aggregates of lignin molecules. Fractions of lignin isolated by ultrafiltration can have different physical and chemical

properties. In view of the possible importance of surface active functional group concentration per volume, these differences may influence the swelling behavior observed for the different "molecular weight" fractions of kraft lignin mixed with sugar acids. More work is required to clarify the effect of kraft lignin molecular weight on the swelling behavior of kraft black liquor during pyrolysis.

A hot stage microscope was used to study the swelling behavior of black liquor up to 300°C. The formation of small bubbles occurred at approximately 240°C for both black liquor and a solution of sugar acids. Decomposition of a sugar acid at 250°C was found to occur by Shafizadeh *et al.* (10).

Kraft lignin appeared to control swelling by having a major influence on the viscous properties of KL:SA mixtures. The formation of bubbles occurred at low temperatures and was associated with the decomposition of sugar acids. Higher temperatures resulted in higher swollen volumes which appeared to be related to a more deformable material.

As the pyrolysis temperature was increased past 500°C the swollen volume of chars decreased. This was most likely due to an increase in the rate of char formation. Particles subjected to a nitrogen gas stream at 900°C for a few seconds were taken out and examined. The inside of the particles were still a viscous fluid surrounded by char. The particle size was approximately 3 mm in diameter (comparable to what may be found in a commercial recovery furnace). This indicated that phenomena occurring at lower temperatures (< 500°C) were responsible for the swelling behavior at higher temperatures.

SUMMARY OF FINDINGS

Kraft lignin and sugar acid mixtures swelled more during pyrolysis than either component tested separately. A 1:1 mixture of these two components resulted in the highest swollen volumes of black liquor chars for a given temperature. The addition of extractives interfered with the swelling mechanism. The addition of sodium sulfate, which represented inorganic salts, acted as a diluent up to a 20% by weight addition level.

The formation of bubbles (50-100 microns in diameter) appeared to distinguish highly swollen chars (extractive-free black liquor, LMW KL:SA) from low swollen chars (black liquor with extractives, HMW KL:SA). A correlation was found between the swelling behavior and the carboxyl contents of chars pyrolyzed from black liquors differing only in moisture content. The formation of bubbles was found to initiate at 240°C for black liquor and a sugar acid solution. These observations indicated surface active forces play an important role in the swelling of black liquor during pyrolysis. The analysis of extractive content, kraft lignin molecular weight, and the pyrolysis temperature indicated viscous forces also play an important role in black liquor swelling.

CONCLUSIONS

The rheological properties, although not measured directly, appeared to determine the extent of

swelling during black liquor pyrolysis. An interaction between the sugar acids and kraft lignin in black liquor was responsible for the swelling behavior during pyrolysis. The decomposition of saccharinic acids below 300°C resulted in the formation of bubbles (50-150 microns in diam.); this process appeared to be necessary for highly swollen chars. Kraft lignin appeared to influence swelling by affecting the viscous properties of black liquor during pyrolysis. Pyrolytic decomposition of organic materials at relatively low temperatures (230-500°C) was responsible for the swelling behavior of black liquor at higher temperatures (500-900°C).

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APPENDIX

Apparatus

A schematic of the single particle reactor is shown in Fig. 1. The particles were heated by a gas stream in a 50 mm x 50 mm channel. The reactor consisted of a movable lower unit and a stationary upper unit. The hot gas flowed from an electric heater through two bends, past a flow straightener and down to the particle. The gas flow could be diverted by a damper ahead of the particle. The temperature was controlled by the setpoint of the thermocouple (SP) which was located above the damper. Two thermocouples (BD) and (BS), which were located above and below the sample, were used to determine the gas temperature at the particle location.

The particle was attached to a Cahn 2000 microbalance via a wire enclosed in an alumina tube. A gas sampling line located right below the particle was used to withdraw gas samples at a constant flow rate. An Infrared Industries Inc. Model 702 gas analyzer was used to monitor the evolution of CO₂ and CO. The system had a 4.0 second delay time and a first order time constant of 3.6 seconds. A Beckman Industries Model 865 infrared H₂O analyzer monitored the water vapor content of the gas stream. When the H₂O unit was installed, there was a 2.7-second delay time between units. The water vapor meter had a first order time constant of 3.0 seconds. An optical trench allowed the particle to be viewed and photographed. A 35-mm camera equipped with a zoom lens and an autowinder was used to take photographs.

The analog signals from the instruments were converted to digital signals and stored on disk by a data acquisition system. Computer programs were written that stored the following information: time, particle mass, gas temperature, CO, CO₂, and H₂O concentration and a camera switch reading. The data could be collected about seven times a second. The camera switch reading recorded by the computer was simply an on-off switch connected to the camera switch; in this way one could automatically record the times at which photographs were taken.

A test consisted of the following sequence of events: 1) switching the gas stream from air to nitrogen, 2) diverting the gas stream to the gas by-pass duct, 3) lowering the lower compartment, 4) starting the data acquisition program, 5) attaching the particle to the microbalance, 6) raising the lower compartment and 7) switching the gas flow to the particle. Zero time was defined as the time at which the temperature measured at thermocouple (BD) began to rise.

Preparation of the Black Liquor Samples

Black liquors were obtained from kraft laboratory cooks of loblolly pine chips. The cooking conditions are given in Table 7. The black liquor was concentrated to approximately 25% solids on a hot plate, and the soap residues were skimmed off

before evaporation in a rotary vacuum evaporator. Some of the liquors used for the study of the effect of extractives on swelling were not skimmed. These black liquors were evaporated in a rotary vacuum evaporator under a 95 kPa vacuum in a water bath at 80°C.

Table 7 Kraft cooking conditions - loblolly pine

| | | | |
|----------------|-------|---------------|--------|
| Sulfidity | 25% | Time to temp. | 90 min |
| Eff. alkali | 16% | Time at temp. | 94 min |
| Liquor/wood | 4 | Cooking temp. | 173°C |
| H-factor | 2000 | | |
| Results | | | |
| Yield | 45.7% | | |
| Kappa no. | 25.7 | BL solids | 16.5% |

Black liquor was evaporated in the rotary vacuum evaporator until a solids content of approximately 65% had been reached. Samples between 73 and 96% solids were obtained by placing black liquor at 65% solids in an oven under a 95 kPa vacuum at 90°C. Samples were taken out periodically so that a range of moisture contents were obtained. A 100% dry solids black liquor was obtained by allowing the liquor to dry overnight.

Loblolly pine was extracted according to TAPPI Standard T264 om-82. The first extraction lasted 8 hours and consisted of a 1:2 volume basis of 95% ethyl alcohol and benzene. Next, the wood was extracted with 95% ethyl alcohol for four hours. Finally, the chips were placed in boiling distilled water for one hour.

The first extractives were concentrated to about 60% in a rotary vacuum evaporator at 95 kPa vacuum at 60°C. This solution was mixed with black liquor. The solvent mixture (alcohol-benzene) was found to have no effect on the swelling of black liquor.

Measurement of Black Liquor Char Volume

An indirect measurement of particle volume was sought in order to gain a better understanding of the kraft black liquor swelling. The analysis of photographs with a planimeter was used initially and found to be acceptable. A planimeter was used to measure the projected area of a particle obtained from a photograph. A spherical volume was calculated by assuming that the area represented a circle. The volume calculated was used for the black liquor char volume. A photograph of a ball bearing in the reactor was used for calibration purposes. This method was compared to a direct measurement technique developed earlier (7). The two methods agreed with each other by approximately $\pm 5\%$ for a number of char particles tested which varied in size and shape.

Preparation of the Components of Black Liquor

A loblolly pine kraft black liquor at approximately 17% solids was heated on a hot plate to approximately 30% solids. Any soap formed during the evaporation was skimmed off. The black liquor solution was then diluted with distilled water to approximately 15% solids. The pH was gradually lowered to pH 2.5 with 1N H₂SO₄. The solution was centrifuged for an hour at 2000 rpm. The precipitated kraft lignin was washed and centrifuged two times.

The remaining filtrate was concentrated (almost to dryness) in a rotary vacuum evaporator at 95 kPa and 80°C. Acetic acid corresponding to double the volume of the sugar acid solution was added and allowed to stand overnight. The precipitated inorganic material was removed. After vacuum evaporation a syrupy product was obtained. Distilled water was added to give about a 30% solution.

The solution was then passed through a column of Dowex 50-X8 (H⁺) ion exchange resin (100 cm³ of resin to 250 cm³ solution). The solution was then mixed with Dowex 3 (OH⁻) for approximately 10 minutes (50 cm³ of resin to 250 cm³ of solution). The solution was next passed through a column filled with adsorbent resin (Amberlite XAD-8, 250 cm³ resin to 50 cm³ solution). The solution was then placed in a beaker with Amerlite XAD-2 and allowed to stand overnight. This solution was then evaporated in a rotary vacuum evaporator to approximately 30% solids. The procedure basically follows that given by Alen and Sjoström (11,12) yielding what was termed the "crude" hydroxy or sugar acid fraction.

The ultrafiltration of the isolated kraft lignin was performed at the University of Maine at Orono. The sample of kraft lignin was made alkaline (pH 13) by the addition of 1N NaOH and diluted to a 1% solids solution. The lignin solution at 60°C was put through the filtration process for a few minutes.

The concentrate retained on the 50,000 MWCO membrane represented the high molecular weight fraction. The medium molecular weight fraction consisted of those lignins which passed through the 50,000 MWCO membrane but were retained by the 20,000 MWCO membrane. The lignin which passed through the 20,000 MWCO membrane was used for the low molecular weight fraction.

When the materials were concentrated to a higher solids content (> 20%), none of the samples swelled to a large extent. Upon concentration the caustic levels (inorganics) were too high for swelling to occur. The samples were acidified, washed and then brought back up to a pH of 12. This produced samples which swelled upon pyrolysis.

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