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Swelling of Kraft Black Liquor.

An Understanding of the Associated Phenomena During Pyrolysis

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SWELLING OF KRAFT BLACK LIQUOR

An Understanding of the Associated
Phenomena During Pyrolysis

A thesis submitted by

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ABSTRACT

During the drying and the pyrolysis phases of kraft black liquor combustion
significant swelling of individual liquor particles occurs. Swollen volumes
during combustion can reach 20-30 times the original volume. The swelling pro-
cess can affect the combustibility of black liquor and the amount of char carry-
over in a recovery furnace. Very little quantitative data are available on black
liquor swelling. The objectives of this thesis were to quantify the swelling of
black liquor during pyrolysis in a nitrogen atmosphere and to determine what
factors were responsible for swelling.

The first part of the investigation studied the process variables: pyrolysis
temperature, solid content, heating rate and particle size. A temperature of
500°C resulted in maximum swelling for the investigated temperature range of 300-
900°C. The swelling of black liquor occurred during 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. Par-
ticle size (1-4 mm in diameter) had no effect on the swollen volume per unit
particle weight.

The effect of black liquor composition (kraft lignin, sugar acids, extrac-
tives, and inorganic salts) was studied. An interaction between sugar acids and
kraft lignin was responsible for swelling (neither component swelled signifi-
cantly when pyrolyzed separately). The extractives interfered with the swelling
mechanism of black liquor, while inorganic salts acted as a diluent.

The swelling behavior of black liquor appeared to be dictated by the surface
active and viscous forces present in black liquor during pyrolysis. Surface

active forces were evidenced by the formation of small bubbles (50-150 microns in diameter) which appeared necessary for highly swollen chars. Low swelling chars did not exhibit this phenomenon. Bubble formation began at 250°C, which closely corresponded to the thermal decomposition temperature of sugar acids. The sugar acids formed bubbles when pyrolyzed but did not swell significantly during pyrolysis. Kraft lignin appeared to enhance the swelling of the sugar acids by increasing the viscosity and stabilizing the bubbles during pyrolysis.

INTRODUCTION

The kraft process is the dominant pulping process today for paper grade pulps. Kraft pulps represent 74% of the North American market pulps.[1] An advantage of kraft pulping is an efficient recovery process for the chemical 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 the 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 solids 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 a recovery boiler and can result in a significant amount of recovery boiler downtime. Some mills have experienced blackouts which appeared 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). Black liquor has been observed to swell significantly when heated above 300°C. A reduction in the swelling of black liquor during combustion would decrease the amount of surface area available for

reaction and presumably adversely affect the combustibility of black liquor. Reduced swelling of black liquor has been observed in liquors exhibiting poor combustion characteristics.[3,4]

Combustion of kraft black liquor takes place by spraying the liquor (droplet size - 1 to 10 mm in diam.) into the recovery furnace. Changes in the swelling characteristics alter the flight paths of particles in the recovery furnace. An increase in the amount of swelling during combustion can cause an undesirable amount of black liquor char to become entrained in air and deposit in the upper portions of the furnace. This occurrence can lead to increased downtime in a recovery furnace.

The degree of black liquor swelling can be an important variable for the efficient combustion of black liquor in a recovery furnace. The potential exists for an optimum amount of black liquor swelling which depends on both the liquor characteristics and the operating conditions of a recovery furnace.

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. A fundamental understanding of the black liquor swelling process during pyrolysis and combustion does not exist.

The present study was undertaken to investigate the swelling characteristics of kraft black liquor during pyrolysis, including heat fluxes which approximate those found in commercial recovery furnaces. The objectives were to quantify the swelling during pyrolysis and to determine the factors which are responsible for the extent of swelling.

LITERATURE REVIEW.

KRAFT BLACK LIQUOR COMPOSITION

Kraft black liquor is a by-product of the kraft pulping process. Kraft black liquors are viscous, dark-brown liquids resulting from the partial dissolution of wood with an aqueous solution of sodium hydroxide and sodium sulfide. An elemental analysis of typical softwood kraft black liquor solids is given in Table 1.

Table 1. Elemental analysis of a typical softwood kraft black liquor (weight percent of dry liquor solids).[7-10]

Carbon	36-42%
Hydrogen	4-5
Oxygen	32-36
Sulfur	4-5
Sodium	18-20

During kraft pulping approximately 50% of the wood enters into solution. This dissolved wood originates primarily from hemicellulose, cellulose, and lignin fractions of wood, with a small amount originating from extractives. The composition of typical softwood kraft black liquor is presented in Table 2.

The lignin in black liquor is degraded from its natural state in wood and is often termed kraft lignin. The kraft lignin is very heterogeneous and is formed by combinations of phenyl propane units. Five fractions of kraft lignin were isolated by ultrafiltration[11]. Table 3 shows some analytical data on the kraft lignin fractions. Separation of kraft lignin solutions by ultrafiltration

utilize membranes differing in molecular weight cut off (MWCO). Since lignin molecules form aggregates in alkaline solutions, the MWCO does not correspond to the true molecular weight of the lignin (Table 3).

Table 2. Softwood black liquor composition (% dry solids).[7,8,12]

Alkali lignin	35-40%
Sugar acids	25-30
Extractives	3-5
Acetic acid	5
Formic acid	3
Methanol	1
Sulfur	3-5
Sodium	15-20
Sodium sulfate	1-8
Sodium carbonate	6-12
Active alkali as Na_2O	4-9

Lignin is stabilized and solubilized in black liquor because of the presence of ionized hydrophilic groups, mainly phenolic and carboxylic groups. The ionized groups prevent the macromolecules from agglomerating and precipitating. The state of ionization of these solubilizing groups is dependent on pH. The dissociation constants for the phenolic hydroxyl groups have pK's of 9.4-10.8, while those for the carboxyl groups are about 5. If the pH of the black liquor is in the range of the pK of the phenolic hydroxyl group, lignin precipitation will occur. The effect is illustrated in Fig. 1.

Table 3. Analytical data of kraft lignin fractions.[11]

Fraction No.	Yield, %	Mol. Wt., $\overline{M}w$	Phenolic Hydroxyl, meq/g	ε_{280}[a] x 10^{-3}	C_9 Unit Wt.[b]	MWCO
1	0.4	670	3.83	4.94	183	<10,000
2	8.5	920	3.34	4.82	182	>10,000
3	62.8	2,560	3.13	4.85	183	>20,000
4	16.9	7,200	3.15	4.75	182	>50,000
5	11.8	>13,000	3.10	3.37	182	>100,000
Weight Average		4,430	3.16		183	

[a]Absorptivity, expressed by 1 (unit wt.)$^{-1}$cm^{-1}.
[b]C_9 unit formulae:
1 $C_9H_{8.21}O_{2.06}S_{0.18}$ $(OCH_3)_{0.63}$ $(CO_2H)_{0.33}$
2 $C_9H_{8.43}O_{1.96}S_{0.14}$ $(OCH_3)_{0.70}$ $(CO_2H)_{0.29}$
3 $C_9H_{8.22}O_{2.10}S_{0.13}$ $(OCH_3)_{0.80}$ $(CO_2H)_{0.18}$
4 $C_9H_{8.51}O_{2.13}S_{0.10}$ $(OCH_3)_{0.80}$ $(CO_2H)_{0.12}$
5 $C_9H_{8.8}O_{2.35}S_{0.09}$ $(OCH_3)_{0.81}$

The degraded carbohydrates are found in the form of sugar acids in black liquor. Table 4 shows the composition of sugar acids in a typical softwood black liquor. Relatively little information is present on the behavior of these substances in black liquor.

The extractives can be considered to be made up of three groups: resin acids, fatty acids and neutrals (sterols, terpene alcohols). The fatty and resin acids in black liquor are sodium salts.

The inorganic fraction of black liquor is difficult to define. The sodium is associated with alkali lignin, hydroxy acids, extractives, and the inorganic ions. Approximately 10% of the sulfur appears in organic compounds as thiolignin, methyl mercaptan, methyl sulfide, and methyl disulfide. The other 90% appears in the inorganic compounds: sulfide, polysulfides, thiosulfate, sulfite, and sulfate.[7,8]
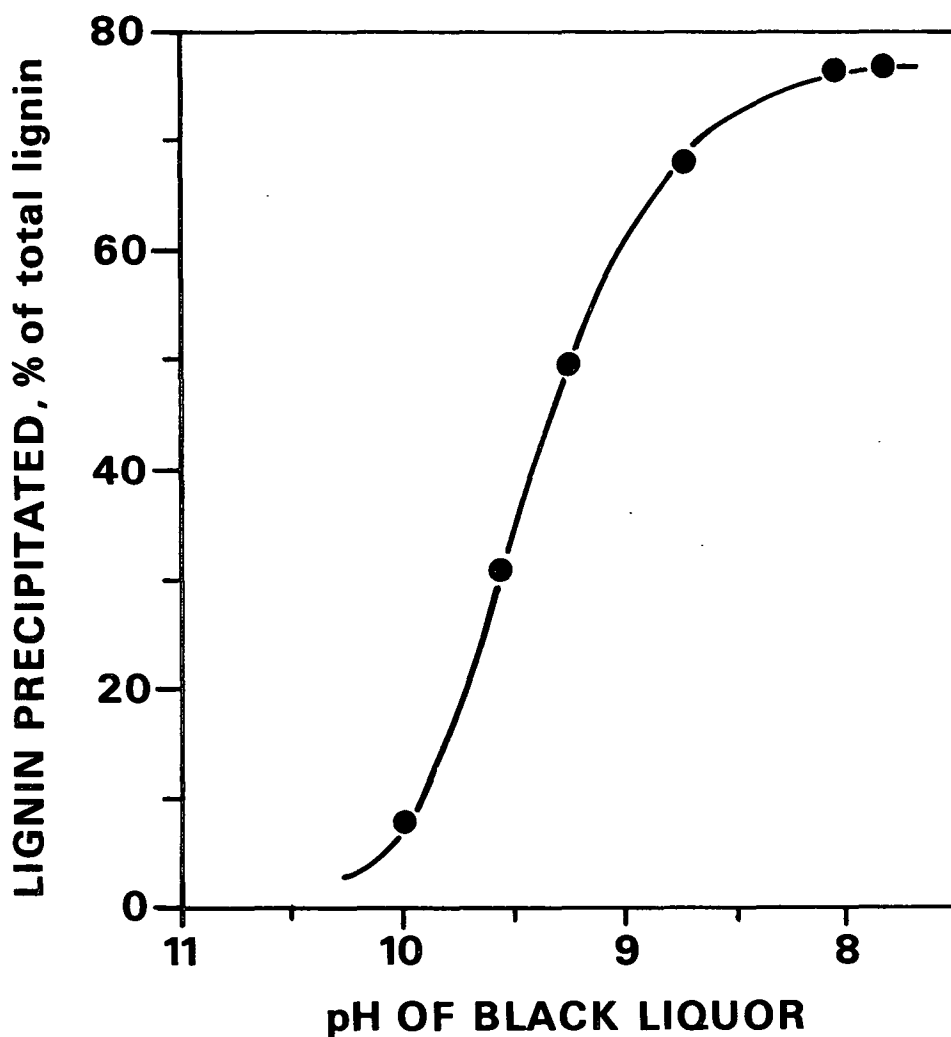
Figure 1. Relationship between black liquor pH and precipitated lignin yield (26.2% solids, 80°C, 1500 kPa).[13]

Table 4. The composition of sugar acids in a softwood black liquor.[14]

Acid	% by weight
Glycolic	7.2%
Lactic	17.6
2-Hydroxybutanoic	8.2
2-5 Dihydroxypentanoic	2.5
Xyloisosaccharinic	6.1
α-Glucoisosaccharinic	12.1
β-Glucoisosaccharinic	29.2
Miscellaneous acids	17.1

The composition of black liquor is complex. In simple terms one can consider black liquor to be composed of four groups of materials: alkali lignin, sugar acids, extractives, and inorganic substances.

DRYING OF BLACK LIQUOR

Evaporation of water is the first process to occur once black liquor particles are introduced into a recovery furnace. Liquor temperatures remain near the boiling point of liquor until the water evaporates.[15] This evaporation of water delays processes which occur at higher temperatures, such as pyrolysis, until the black liquor is dry. Large gradients of temperature can cause drying and pyrolysis within the same particle during heatup.

The behavior of sulfite liquor droplets (2 mm in diameter) was studied between 200-900°C.[16] The evaporation of water from these droplets was described as the initial stage of combustion. This initial behavior consisted of violent bubbling, characterized by rapid expansions and contractions of the liquor particle. The particle at the end of this boiling stage varied greatly in shape and was often found to be partially hollow. This behavior was independent of whether nitrogen or oxygen was present. The observations indicated evaporation occurred relatively free of oxidation; more detailed work is required to confirm these observations. Sulfate and sulfite liquors were found to behave similarly during the evaporation stage of combustion in air at 700°C.[17]

Little fundamental knowledge is available on the evaporation portion of black liquor combustion. The product of drying is the starting material for pyrolysis and thus is of importance in the combustion of black liquor.

PYROLYSIS OF ORGANIC MATERIALS

Pyrolysis is defined as the irreversible thermal decomposition of substances due solely to heat effects. Pyrolysis has also been referred to as devolatilization, carbonization, or thermal decomposition. It should not be confused with gasification or combustion, which requires the additional presence of oxygen. At high temperatures in an inert atmosphere, organic materials are partially cracked to smaller, unstable molecules. These fragments, mostly radicals, recombine to yield larger, relatively stable aromatic hydrocarbons.[18] The manner in which organic substances are heated has a large influence on the types and distribution of products.

The pyrolysis of simple compounds such as ethane involves a number of steps and involves a radical chain type of mechanism.[19] The pyrolysis of complex organics such as wood, coal, and black liquor proceeds through a complex series of ill-defined concurrent and consecutive reactions.[20] The kinetics of pyrolysis and chemical transformations of solid compounds are frequently characterized by three distinct regions:[19] an initially slow induction period, followed by an accelerated reaction period and finally by a falling off of the reaction rate. The pyrolysis of lignocellulosic materials and coal follows closely the kinetics of a first order reaction with respect to the unreacted material.[21,22] The temperature range for the pyrolysis activity of these materials can be characterized by determining the activation energies of the different materials.

The relative proportions of gases, tars, and char will vary widely according to the conditions of temperature, pressure, time, geometry, and environment under which pyrolysis occurs in organic materials. Rapid pyrolysis of carbonaceous

materials promotes the production of volatiles, while slow pyrolysis promotes char formation.[21,23]

The literature on the pyrolysis of organic materials will be reviewed beginning with materials of relatively uniform composition, such as cellulose, hemicellulose, and lignin. Pyrolysis of more complex materials (wood, coal, and black liquor) will then be discussed. The influence of inorganic species on char formation during pyrolysis and the char formation process will then be discussed as separate topics.

Cellulose Pyrolysis

Thermal degradation of cellulose to volatile products and char involves a series of highly complex reactions. These competing reactions are shown schematically in Fig. 2.
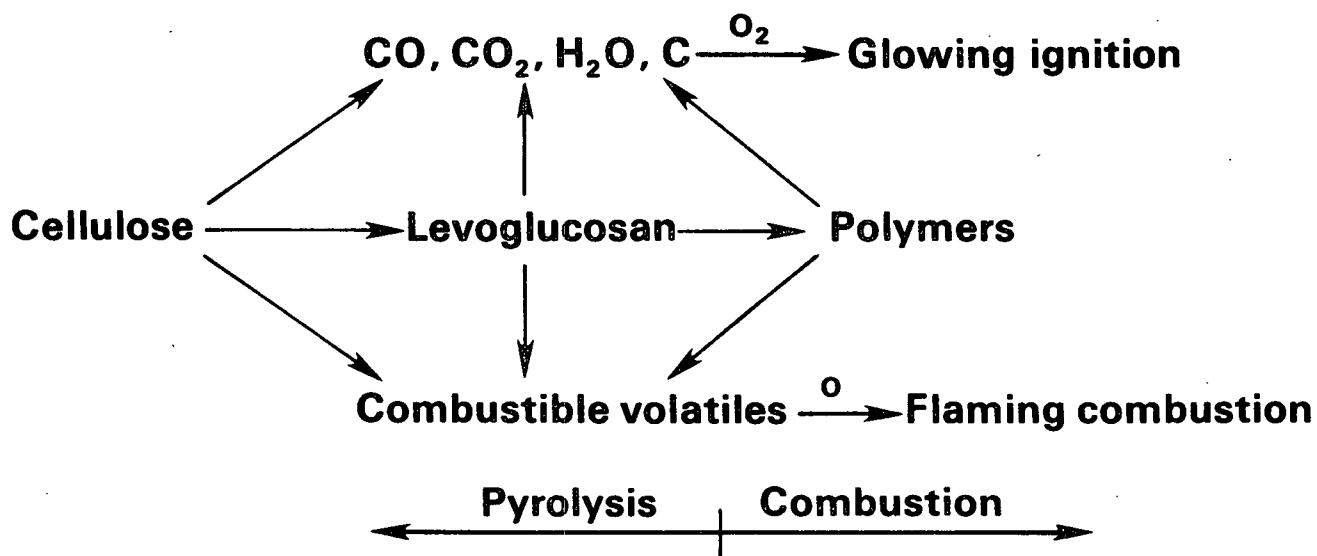

Figure 2. Competing reactions in the pyrolysis and combustion of cellulose.[24]

The reactions which take place both concurrently and consecutively may be classified in the following categories:[24,25] a) Depolymerization of cellulose by transglycosylation at about 300°C which provided a mixture of levoglucosan, other monosaccharide derivatives, and a variety of randomly linked oligosaccharides. This mixture was generally referred to as the tar fraction. b) The above reactions were accompanied by dehydration of sugar units in cellulose, which yields unsaturated compounds (i.e., 3-deoxy-glucosone, levoglucosone). c) At higher temperatures, fission of sugar units provides a variety of carbonyl compounds (acetaldehyde, glyoxal and acrolen). d) Condensation of the unsaturated products and cleavage of the side chains occurs through a free radical mechanism.

Mackay and Roberts[26] studied the effect of heating rate on char yield during pyrolysis of cellulose. Slower heating resulted in higher char yields. Table 5 shows that the heating rate exerted its major effect on cellulose char yield below 300°C. The lower heating rates were believed to increase the amount of dehydration reactions as these reactions occur at approximately 240°C. Dehydration was hypothesized to result in the formation of more thermally stable polymeric systems, which in turn lowered volatilization at higher temperatures.

Hemicellulose Pyrolysis

The thermal decomposition characteristics of hemicelluloses have been studied to a lesser extent than the other components of wood. Hemicelluloses begin to react at a lower temperature than cellulose or lignin, but are believed to go through the same basic types of reactions as cellulose.[21,24] Based on changes in the intrinsic viscosities of the degradation products, random chain cleavage was believed to be the initiating step in hemicellulose pyrolysis.[27]

Table 5. Effect of heating rate on char yield of cellulose.[26]

| Experiment | T^b | Temperature Ranges, °C[a] | | Char Yield, % |
		Low φ	Medium φ	
5a	500	20-500	--	28-29[c]
5b	500	--	20-500	20-21[c]
5c	500	20-350	350-500	28.7
5d	500	20-300	300-500	28.6
5e	500	20-250	250-500	21.0
5f	500	220-300	20-220, 300-500	27.2
7a	700	20-700	--	25-26[c]
7b	700	--	20-700	17-18[c]
7c	700	20-300	300-700	24.9

[a]Uncontrolled heating rate of the loaded furnace was approximately 20-25°C/min (medium φ). Through specific temperature ranges (noted in table) the heating rate was controlled to approximately 1°C/min (low φ).
[b]Final pyrolysis temperature; sample held at T for a soak time of 1 hour.
[c]Data from dissertation of Brunner[19] using equivalent analytical cellulose and pyrolysis reaction vessels.

Some work has been performed on the pyrolytic decomposition of different types of hemicelluloses.[28-30] The studies were performed by thermogravimetric analysis; the temperature at which the rate of weight loss reached a maximum (T_m) can be used to compare the thermal activities of materials. The T_m increased in the following order: xylans (250-260°C), galactoglucomannans (280-290°C), and arabinogalactans (300-310°C). The pyrolytic decomposition of hemicelluloses was essentially complete at 320°C.

Pyrolysis of Sugar Acids and Lactones

The thermal decomposition properties of 2-deoxy-D-arabino-hexonic acid and 2-deoxy-D-arabino-hexono-1,4-lactone were studied by Shafizadeh and Lai.[31] The

thermal analysis curves for these substances are shown in Fig. 3 and 4. The
negative differential thermal analysis (DTA) peak in Fig. 3 corresponds to the
melting point of the acid at 146°C. The differential thermogravimetric curve
(DTG) shows two peaks at 157 and 252°C which correspond to thermal decompositions.
The lactone in Fig. 4 shows the melting point occurs at 100°C with a decomposi-
tion taking place at 315°C. More char resulted from the pyrolysis of the acid
(35%) than the lactone (20%) at 400°C.[31]
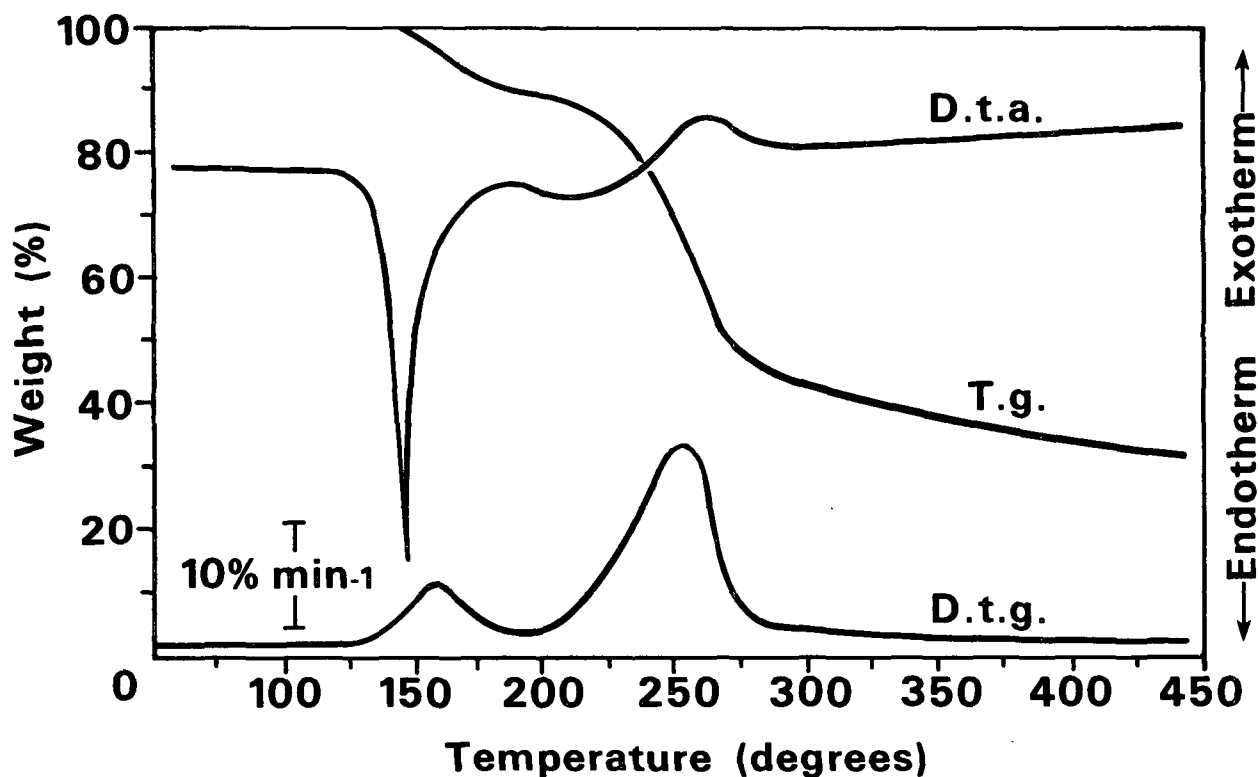

Figure 3. Thermal analysis curves of 2-deoxy-D-arabino-hexonic
acid at 400°C.[31]

Table 6 shows the gas-liquid chromatography (GLC) results of an investiga-
tion into the chemical transformation that occurred at 157°C for the acid. The
analysis indicated that melting of the acid was accompanied by the formation of
the corresponding 1,4- and 1,5-lactones. The presence of small proportions of

1-deoxy-D-arabinitol between 200-250°C indicated the occurrence of decarboxylation.
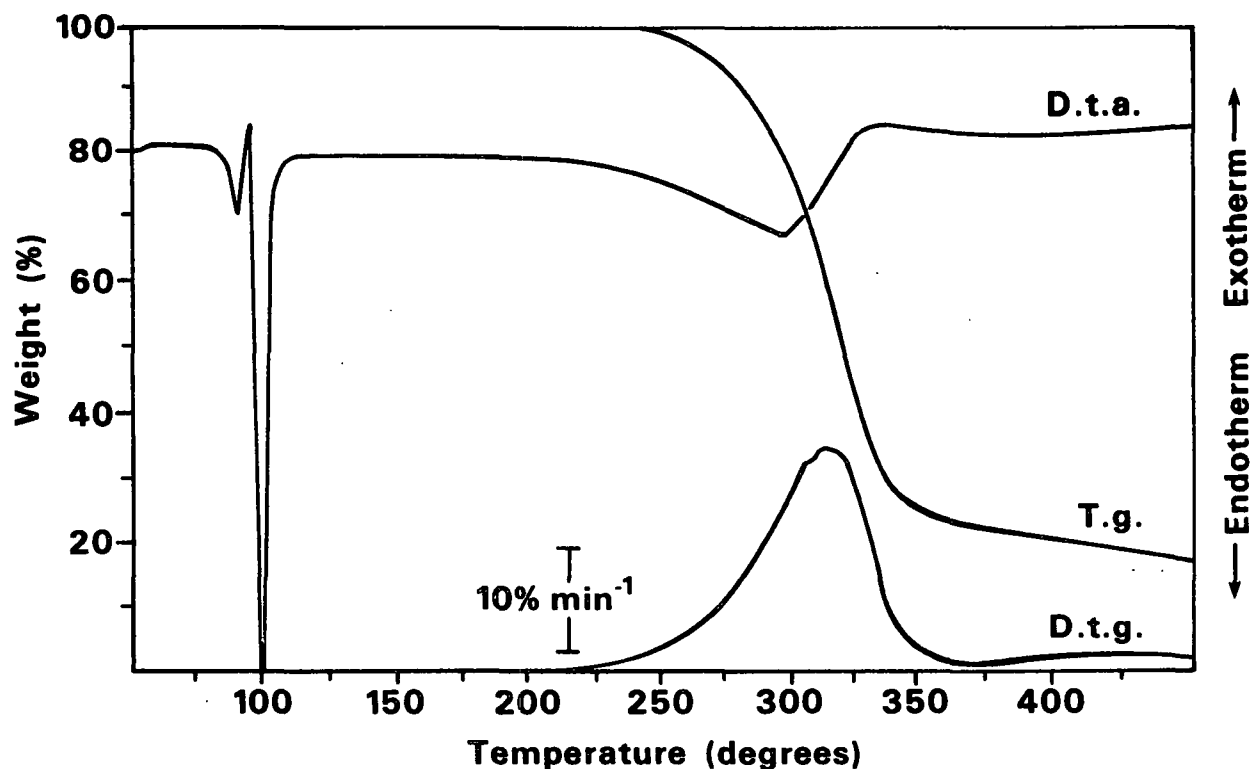

Figure 4. Thermal analysis curves of 2-deoxy-D-arabino-
           hexono-1,4-lactone at 400°C.[31]

Table 7 shows the pyrolysis products of the acid, the lactone, and the lactone with additional amounts of zinc chloride and sodium carbonate. The inorganic substances increased the yield of char. The pyrolysis of the acid and the lactone at 550°C resulted in many of the same pyrolysis products.

Lignin Pyrolysis

Thermal degradation of lignin occurs over a wider range of temperatures than cellulose and results in more char. Table 8 shows that the tree species from which lignin is isolated and the lignin isolation method, both influence the thermal behavior of lignins.

Table 6. GLC analysis of the pyrolysis residue.[31]

Sample Temperature, degrees	Acid, %[a]	Lactone, %	1-Deoxy-D-arabinitol, %
2-Deoxy-D-arabino-hexonic acid			
20	100.0	--	--
135	95.5	4.5	--
140	62.3	37.2	--
147	42.7	56.0	--
175	15.5	66.0	T[b]
200	9.1	50.3	5.2
250	T	29.8	6.5
2-Deoxy-D-arabino-hexono-1,4-lactone			
20	--	100.0	--
250	--	95.2	--
275	T	51.5	1.2
300	--	20.2	1.8

[a]The percentages are based on the original weight.
[b]T = trace amounts

The influence of heating rate on the char yield of lignin is shown in Fig. 5. The rate of heating during pyrolysis appeared to affect the char yield of lignin in a different manner than the char yield of cellulose. Heating rate affected cellulose pyrolysis below 300°C, while lignin pyrolysis was influenced at 360°C and above. Heating rate began to influence lignin pyrolysis at the same temperature where the formation of tars began. At higher heating rates, the pressure gradients driving the volatiles and tars out of the particle would be greater. This would decrease the contact time between the tars and the char and result in less tar reacting further to form char.[33]

Table 7.   Products of pyrolysis of 2-deoxy-D-arabino-hexonic acid and the
1,4-lactone at 550°C.[31]

Product	Acid	2-Deoxy, %		
		Lactone		
		Neat	+ ZnCl$_2$	+ Na$_2$CO$_3$
Acetaldehyde	0.5	1.8	0.9	1.1
Furan	T	0.2	T	T
Acetone	T	T	T	T
Acrylaldehyde	4.1	8.3	4.5	1.8
2-Methylfuran	T[a]	T	1.2	0.2
2,3-Butanedione	1.3	1.8	1.2	0.6
2-Butenal	1.0	0.6	0.4	0.8
1-Hydroxy-2-propanone ⎤ Glyoxal ⎬ Acetic acid ⎦	2.7	9.1	1.0	3.0
α-Angelicalactone	T	T	T	T
2-Furaldehyde	0.6	0.9	T	0.2
2-Furfuryl alcohol	0.2	0.3	0.1	T
β-Angelicalactone	T	T	T	T
5-(2-Hydroxyethylidene)-2(5H)furanone	10	14	4	3
Carbon monoxide	5.3	3.3	2.8	3.8
Carbon dioxide	12.6	8.4	12.5	19.0
Water	26.1	17.5	19.5	16.0
Char	18.2	9.4	29.3	32.8
Tar	16.5	25.1	17.1	10.0
2-Deoxy-lactone	(11.8)[b]	(34.5)	(1.0)	(0.7)
1-Deoxy-D-arabinitol	(2.0)	(1.1)	(0.4)	(0.5)

[a]T = trace amounts.
[b]Numbers in parentheses are percentages of the tar fraction.

Table 8. Thermal behavior of selected lignins during dynamic thermogravimetric analysis.[32]

Lignin and Cellulose Type (species sources)	Temp. at Maximum Rate of Wt. Loss	Maximum Rate of Wt. Loss[a]	Decomposition Temperature at 10% --weight loss-- °C	50% loss-- °C	Nonvolatile Residue at 550°C, wt.%
HCl lignin (oak)	335	7.1[a]	295	445	39.2
HCl lignin (mixed hardwoods)	330	6.7	295	460	39.7
HCl lignin (southern yellow pine)	400	3.3	300	527	45.1
Klason lignin (oak)	375	3.5	335	--	51.7
Klason lignin (mixed hardwoods)	375	3.1	330	--	50.2
Klason lignin (southern yellow pine)	400	3.3	370	--	50.4
Wet-oxidized lignin (oak)	315	7.0	265	515	44.6
Wet-oxidized lignin (mixed hardwoods)	370	6.3	235	435	37.8

[a]Maximum rate of weight loss was determined by measuring the maximum DTG peak height (mm) for each lignin and dividing it by the sample weight, mg.

The pyrolysis of kraft lignin has been described as a two stage process.[34] Initial decomposition occurred between 120-300°C as a result of fragmentation in the phenyl propane side chains, particularly at the terminal positions, yielding formic acid, formaldehyde, water, carbon dioxide, and sulfur dioxide. Major decomposition started at approximately 300°C and extended to 480°C, at which point 50% of the initial weight had been lost. Degradation in this region could be characterized by cleavage and fragmentation of principal linkages, releasing monomeric phenols into the vapor phase, followed by the onset of secondary degradation at higher temperatures.
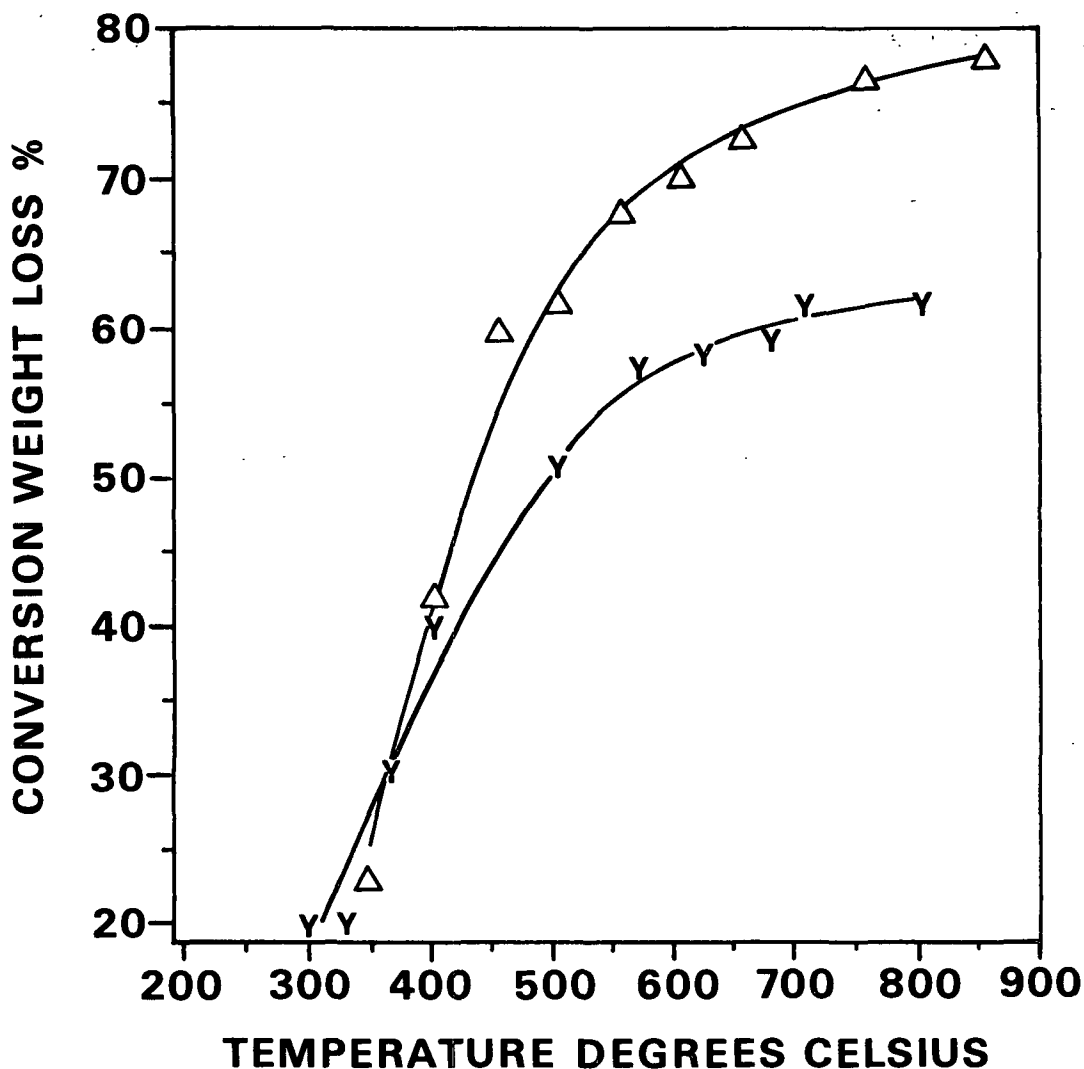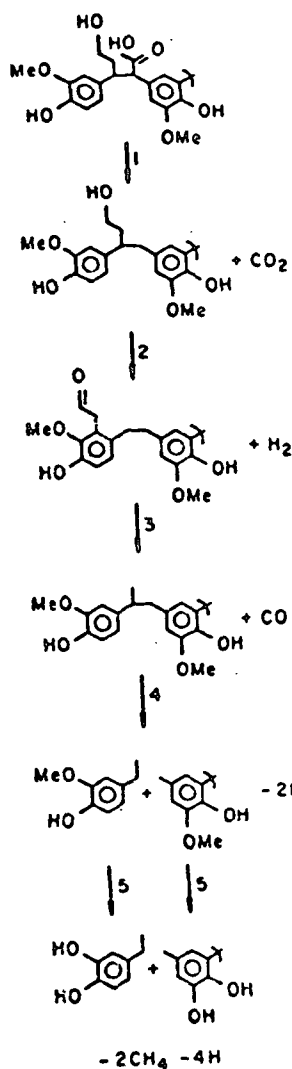
Figure 5. Pyrolysis of alkali lignin from steam exploded aspen, Δ-600°C/s, Y-10°C/min.[33]

The basic steps of lignin pyrolysis have been described in general terms. Pyrolysis models of native and kraft lignin have been developed by Klein et al.[38] Model compound pyrolysis reaction pathways and kinetics were used to simulate the primary and secondary reactions important in lignin pyrolysis. An example of the application of the model to a lignin macromolecule is shown in Fig. 6.[35]

The applicability of the model was limited to temperatures in the 300-500°C temperature range. The model was primarily useful for predicting the yields of

pyrolysis gases as the volatilization reactions were well represented; however, the condensation of the resulting smaller molecules to form char has not been modeled. The release of volatile products occurred over a relatively long time period (0-100 minutes) during the simulation runs. These factors tended to limit the application of this model.
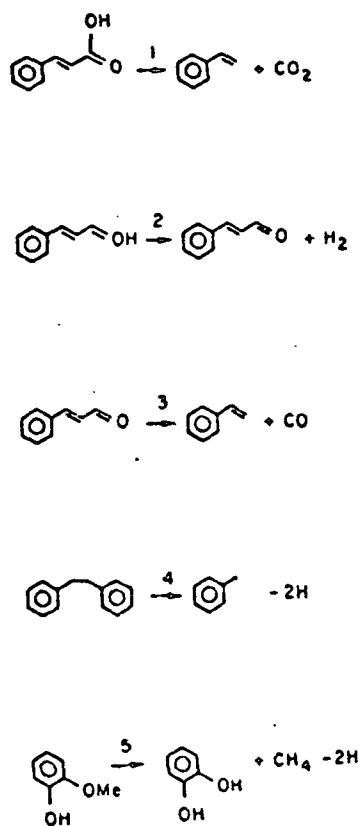

Figure 6. An example of the application of a lignin simulation model to the pyrolysis of kraft lignin.[35]

Wood Pyrolysis

The pyrolysis of wood represents a combination of the thermal decomposition properties of its components: hemicellulose, cellulose, and lignin. Hemicellulose is the most reactive component, decomposing between 200-325°C, yielding mostly volatile products. Cellulose decomposes between 240-360°C, also yielding mostly volatile products. Lignin decomposes between 280-500°C, yielding predominantly char.[26,39]

The thermogravimetric traces of wood and its major components are shown in Fig. 7. Figure 7 suggests that an interaction between cellulose and lignin occurred during pyrolysis, which resulted in a lower char yield for wood. However, Sekiguchi et al.[40] found the weight loss upon wood pyrolysis to be the sum of the weight loss upon the pyrolysis of the wood components within the experimental error of the equipment, concluding that there was no synergistic effect between cellulose and lignin on char yield during pyrolysis of wood. Figure 7 illustrates the narrow temperature range of cellulose and hemicellulose thermal degradation compared to the relatively wide temperature range of lignin pyrolysis.

The pyrolysis of wood has been divided into three zones:[21] 1) Up to 200°C, the wood became dehydrated and evolved traces of carbon dioxide, formic, and acetic acids. 2) Between 200-280°C, pyrolysis was a relatively slow endothermic process, yielding gaseous products which were largely noncombustible. 3) From 280 to 500°C, pyrolysis was exothermic with combustible gases (CO, CH_4, H_2) and tars being formed. Primary pyrolysis products reacted further during pyrolysis; these secondary reactions could be catalyzed by charcoal. The volatilization process was essentially complete at 500°C with only 4-10% additional volatilization occurring between 500-900°C.[26]
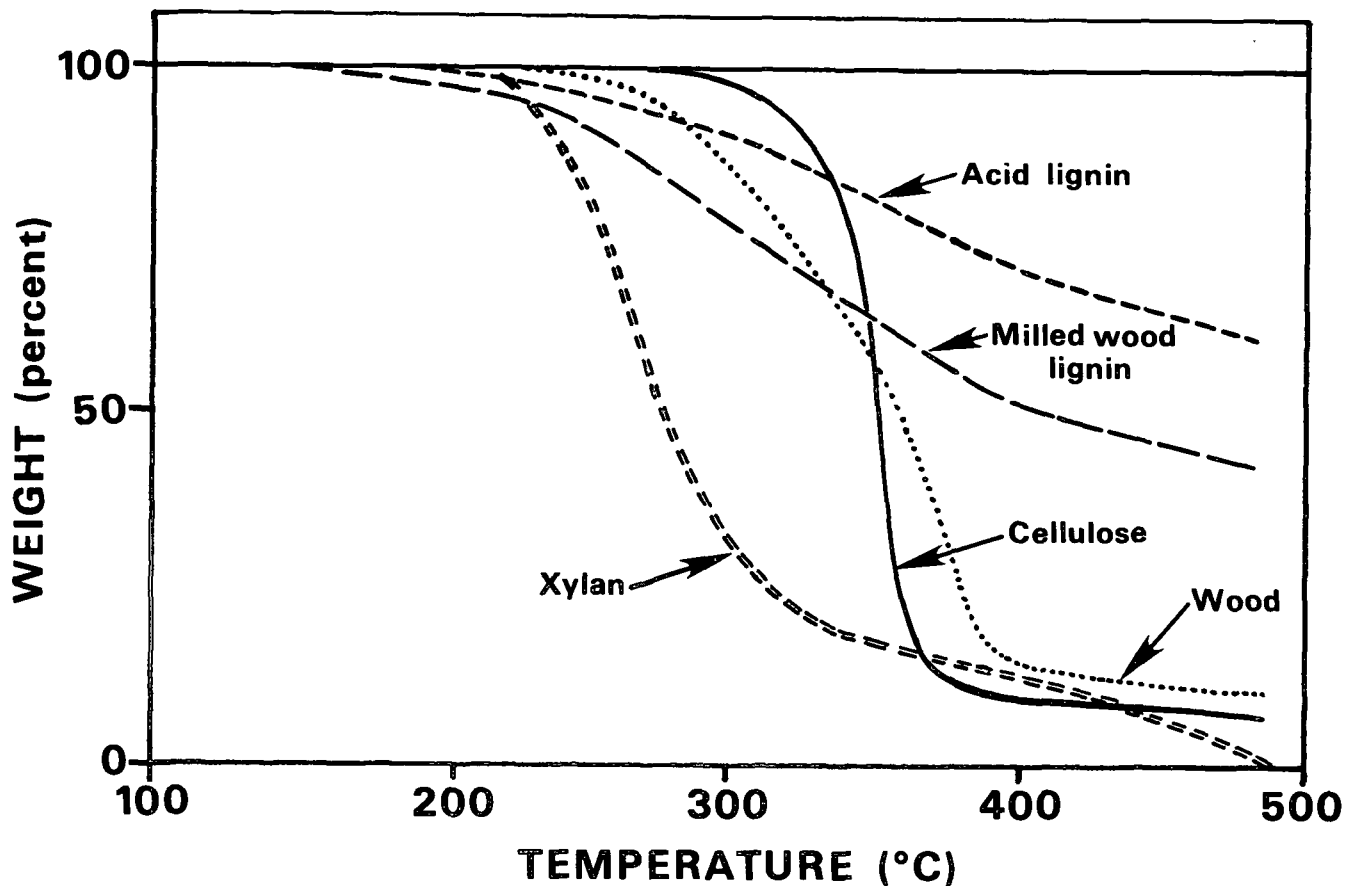
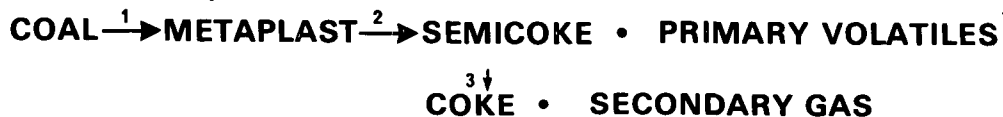Figure 7. Thermogravimetry of wood and its components.[24]

Coal Pyrolysis

Heated at a moderate rate, coal begins to decompose between 350 and 400°C into a carbon rich residue and hydrogen rich volatile fraction.[22] The decomposition continues until a temperature (typically around 950°C) is reached which, if maintained for an extended time, results in a residue of nearly pure carbon possessing a structure approaching that of graphite. The accumulated volatiles are comprised of various gases and liquids, the relative proportions of which depend on the coal type and the manner of heating. Rapid heating techniques for coal permit substantially more volatiles to be evolved than traditional slow heating methods. The liquid or tar fraction appeared most strongly influenced during rapid heatup.

Many investigators have approximated coal pyrolysis as a first-order decomposition occurring uniformly throughout the particle. Figure 8 shows other coal pyrolysis models which have been proposed. A problem with the more complex models was the large number of parameters which were adjusted to fit decomposition data of coal (i.e., 15 rate and stoichimetric parameters for model D in Fig. 8). A simple model has been proposed which describes the decomposition of coal as an infinite number of competing first order reactions described by a Gaussian distribution of activation energies.[41] This analysis permitted correlation of coal decomposition data by using four parameters, which was only one more than was required in the simple single step model represented as model A in Fig. 8.

A. Simple Single - Step Unidirectional Decomposition
$$\text{COAL} \xrightarrow{1} \text{RESIDUE} \bullet \text{VOLATILES}$$

B. Series Decomposition
$$\text{COAL} \xrightarrow{1} \text{METAPLAST} \xrightarrow{2} \text{SEMICOKE} \bullet \text{PRIMARY VOLATILES}$$
$$\downarrow^{3}$$
$$\text{COKE} \bullet \text{SECONDARY GAS}$$

C. Two Competing Unidirectional Decompositions
$$\text{COAL} \underset{2}{\overset{1}{\Longleftrightarrow}} \begin{array}{l} \text{RESIDUE}_1 \bullet \text{VOLATILES}_1 \\ \text{RESIDUE}_2 \bullet \text{VOLATILES}_2 \end{array}$$

D. Multi-Step Series - Composition Model

INTERMEDIATE RESIDUE$_2$ • PRIMARY GAS$_2$

RESIDUE$_4$ • PRIMARY GAS$_4$

$$\text{COAL} \xrightarrow{1} \text{ACTIVATED COAL}$$

RESIDUE$_5$ • PRIMARY GAS$_5$

RESIDUE$_6$ • SECONDARY GAS

INTERMEDIATE RESIDUE$_3$ • PRIMARY TAR
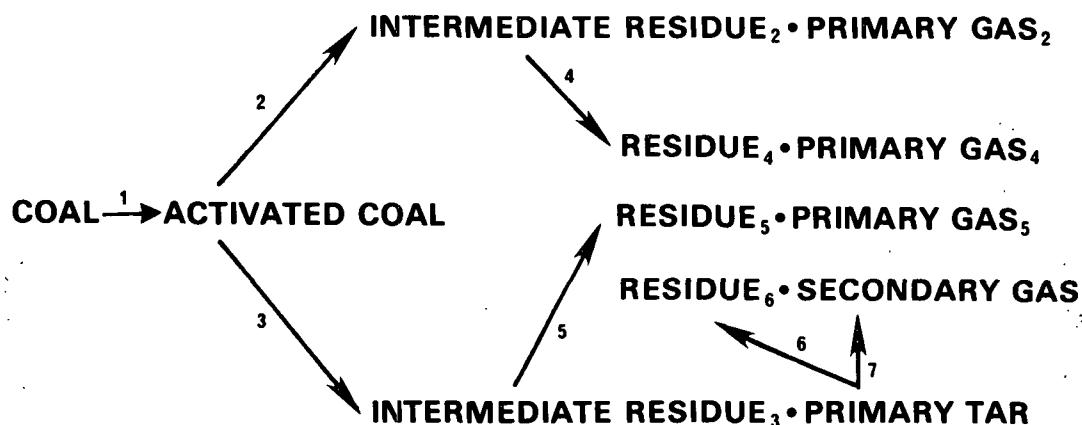
Figure 8. Coal pyrolysis models.[22]

The effect of pressure, particle size, and heating rate on volatile yields was investigated by Anthony et al.[41] The pressure (0.01-100 atm) was found to be significant in determining volatile yields, while particle size (50-1000 microns) was of some importance and heating rate (650-10,000°C/s) had no effect. Heating rate had an effect on char yields when comparing the relatively low heating rates (< 20°C/min) of proximate and thermogravimetric analysis with tests conducted at higher heating rates. The yield of char was higher at the lower heating rates.

Pressure was believed to influence char yield by changing the rate of secondary reactions. Elevated pressures retarded the escape of reactive species and increased the rate of secondary reactions. Tarry species appeared to be the most affected as increased pressures were found to suppress the formation of tarry materials.[41]

The sample size has sometimes been misconstrued as a heating rate effect, since the time required to attain the final temperature usually increases with increasing size. The effect of particle size has been attributed to differences in the extent of secondary reactions which are strongly influenced by the residue times and the concentration of reactive species in contact with hot surfaces.[22]

Coal type was found to be important as bituminuous coals exhibited higher yields of char at higher pressures, while pressure had no effect on the yield of char decomposed from anthracite.[41] Bituminous coals form tarry species and swell (2-22 times their original volume)[42] during pyrolysis, while anthracite coals do not form tarry species and do not swell upon pyrolysis.

Black Liquor Pyrolysis

Many of the same trends occur in black liquor pyrolysis as the pyrolysis of other carbonaceous materials. Rapid heating (> 1000°C/s) of black liquor resulted in less char.[43] The effect of particle size on char yield becomes observable for 50-100 micron particles, which is similar to coal.[43]

The pyrolysis of black liquor between 300 and 1000°C was investigated by Feuerstein et al.[44] Figure 9 shows the gas yields as a function of temperature. The concentrated solids (65%) were tested at slow heating rates as equilibrium temperatures were reached after approximately two hours. The slow heating resulted in char residues between 60 and 70% for the range of temperatures studied.

Black liquor pyrolysis was studied under steady state conditions by Brink et al.[45] Concentrated black liquor was injected at a constant flow rate into the reactor. Figure 10 shows the dry gas production for the steady state and batch experiments.

The increase in gas evolution for the steady state process was suggested to be due to the additional presence of water vapor which reacted with carbon to yield carbon dioxide, carbon monoxide, and hydrogen. The moles of the major pyrolysis gases produced as a function of temperature are shown in Fig. 11. The much higher heating rate at the steady state conditions was a more likely explanation for the increased volumes of gases produced, with secondary reactions possibly playing an important role in the differences observed.

The pyrolysis of black liquor has been studied with Beckwith et al.[46] using thermogravimetric analysis (TGA) techniques. Figure 12 shows a typical weight loss profile for black liquor. All the black liquors tested produced similar

TGA curves. The main pyrolysis activity of black liquor (decomposition of organic materials) occurred between 200-500°C. Figure 13 shows data which lend support to a hypothesis that black liquor pyrolysis occurs by a series of reactions dependent on temperature.
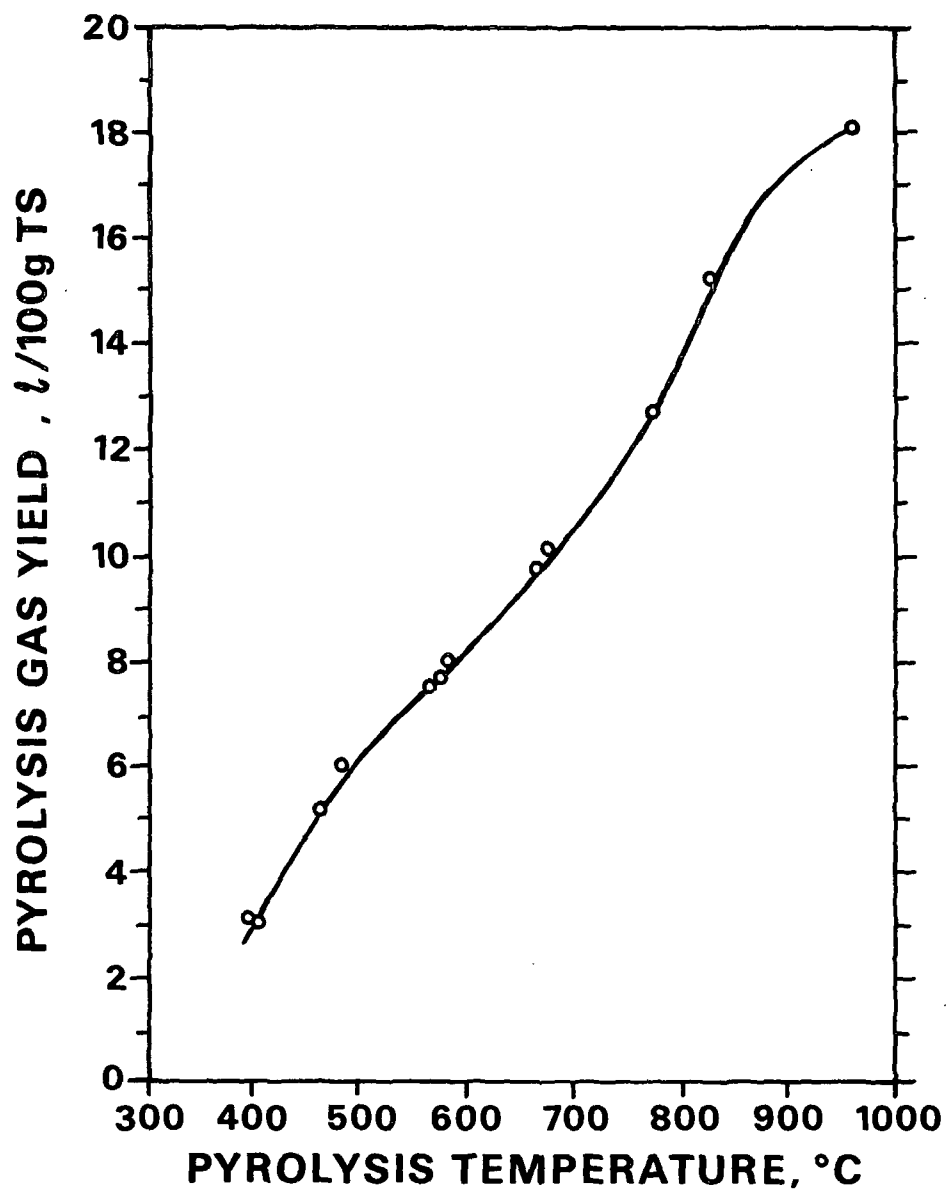

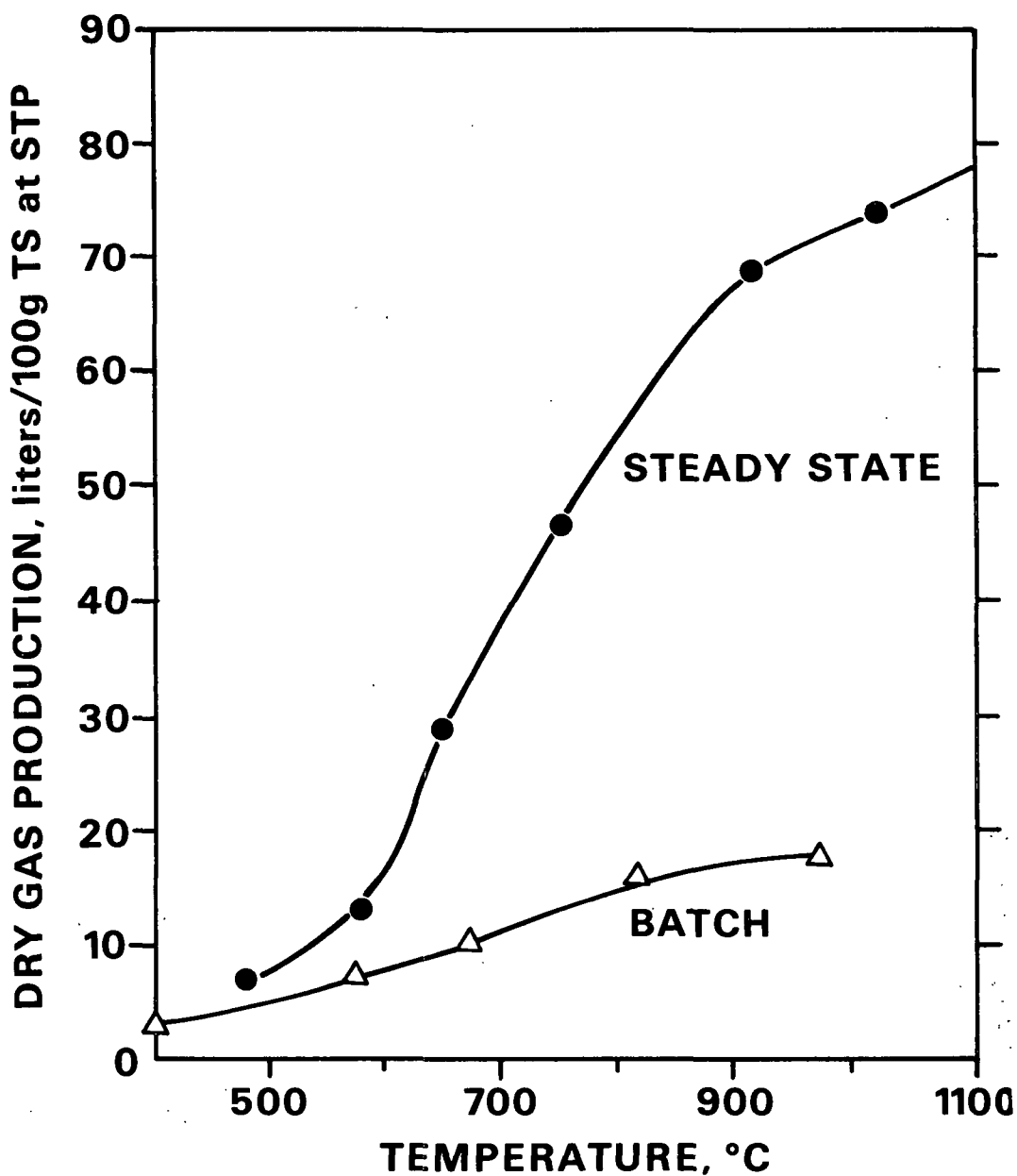Figure 9. Gross volumetric pyrolysis gas yields.[44]

Figure 10. Volumetric gas production as a function of temperature.[45]

The pyrolysis of black liquor has not been studied thoroughly relative to wood or coal. Investigations to date indicate basic similarities exist between the pyrolysis of wood, coal, and black liquor. More work needs to be done to fully characterize the pyrolysis of black liquor.
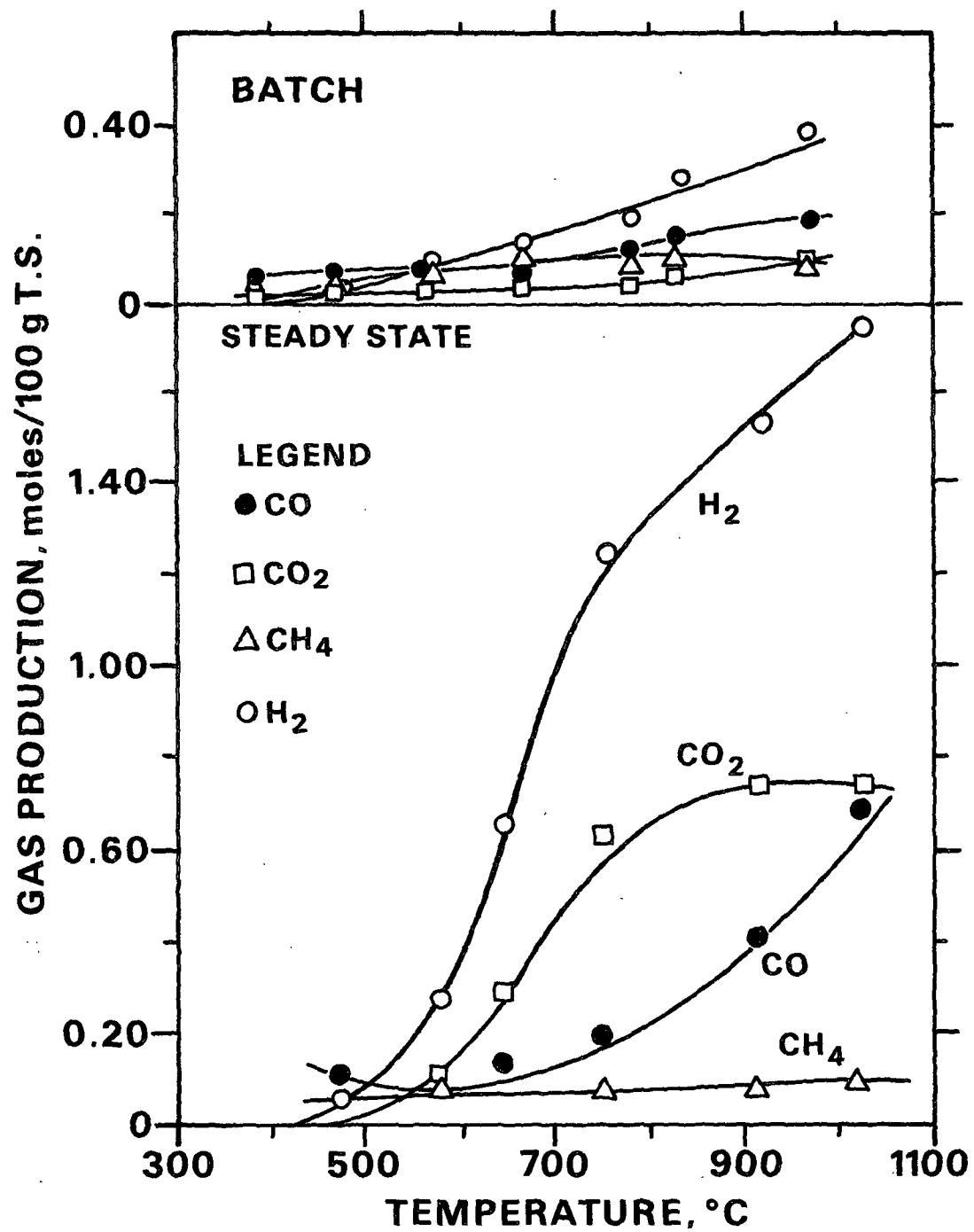
Figure 11. Moles of major gases produced as a function of temperature.[45]
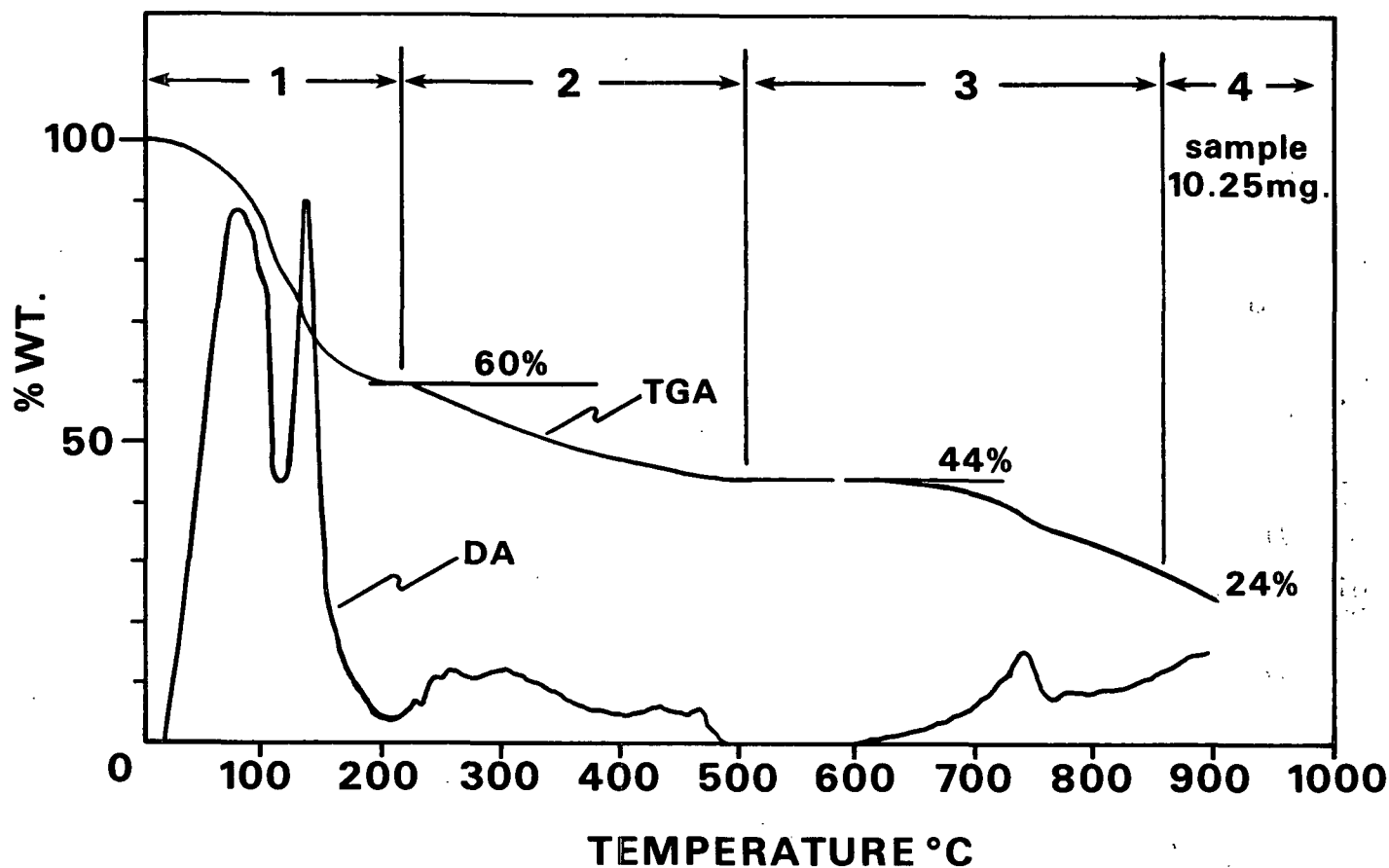
Figure 12. Thermogravimetric analysis of black liquor with derivative curve.[46]

INFLUENCE OF INORGANIC SALTS ON THE PYROLYSIS OF ORGANIC MATERIALS

The influence of inorganic impurities on the kinetics of the pyrolysis of carbonaceous materials has been studied. Very small concentrations of salts of the alkali and transition metals have exerted profound catalytic effects on various reactions which occurred during pyrolysis.[48] Figures 14 and 15[49] show that the tested inorganic materials influenced cellulose pyrolysis more than lignin pyrolysis by increasing the rate of char forming reactions.[26,50,51]
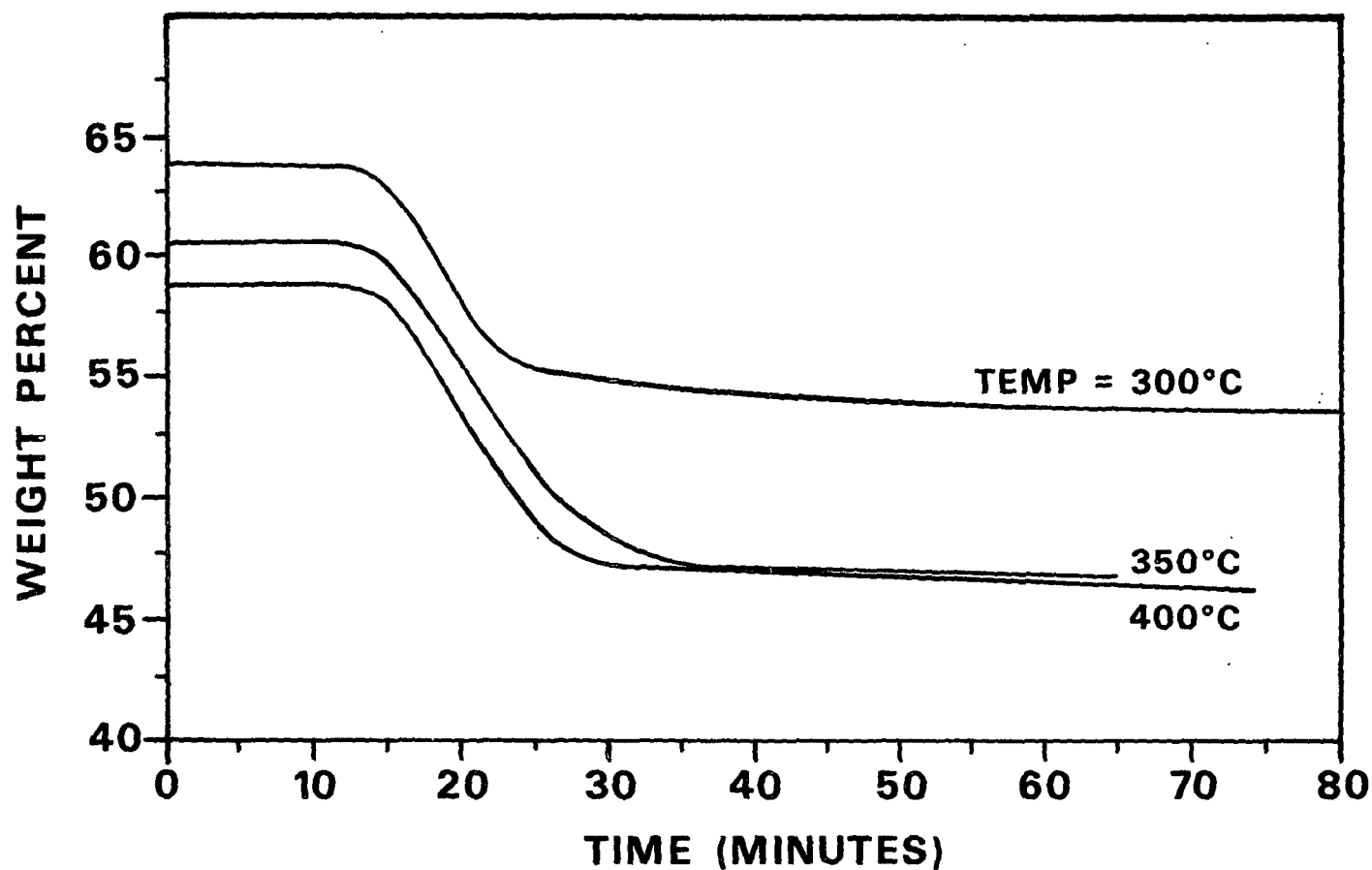
Figure 13. Thermogravimetric analysis of black liquor at different endpoint temperatures.[47]

The pyrolysis of 2-deoxy-D-arabino-hexano-1,4-lactone was studied at 550°C.[31] When catalysts ($ZnCl_2$, Na_2CO_3) were added, decomposition took place at lower temperatures with evolution of water and carbon dioxide. Analysis of the products revealed that the catalyst promoted decarboxylation, dehydration, and condensation of the products to nonvolatile molecules of higher molecular weight, which resulted in char on further heating.

Figure 14. Thermogravimetric traces of alpha-cellulose with and without inorganic salts (3°C/min).[47]

Figure 15. Thermogravimetric traces of lignin with and without inorganic salts (3°C/min).[47]

LIGNIN WITH:

——— NO TREATMENT

------- 2% $No_2B_4O_T \cdot OH_2O$

·········· 2% NaCl

—·— 2% $KHCO_3$
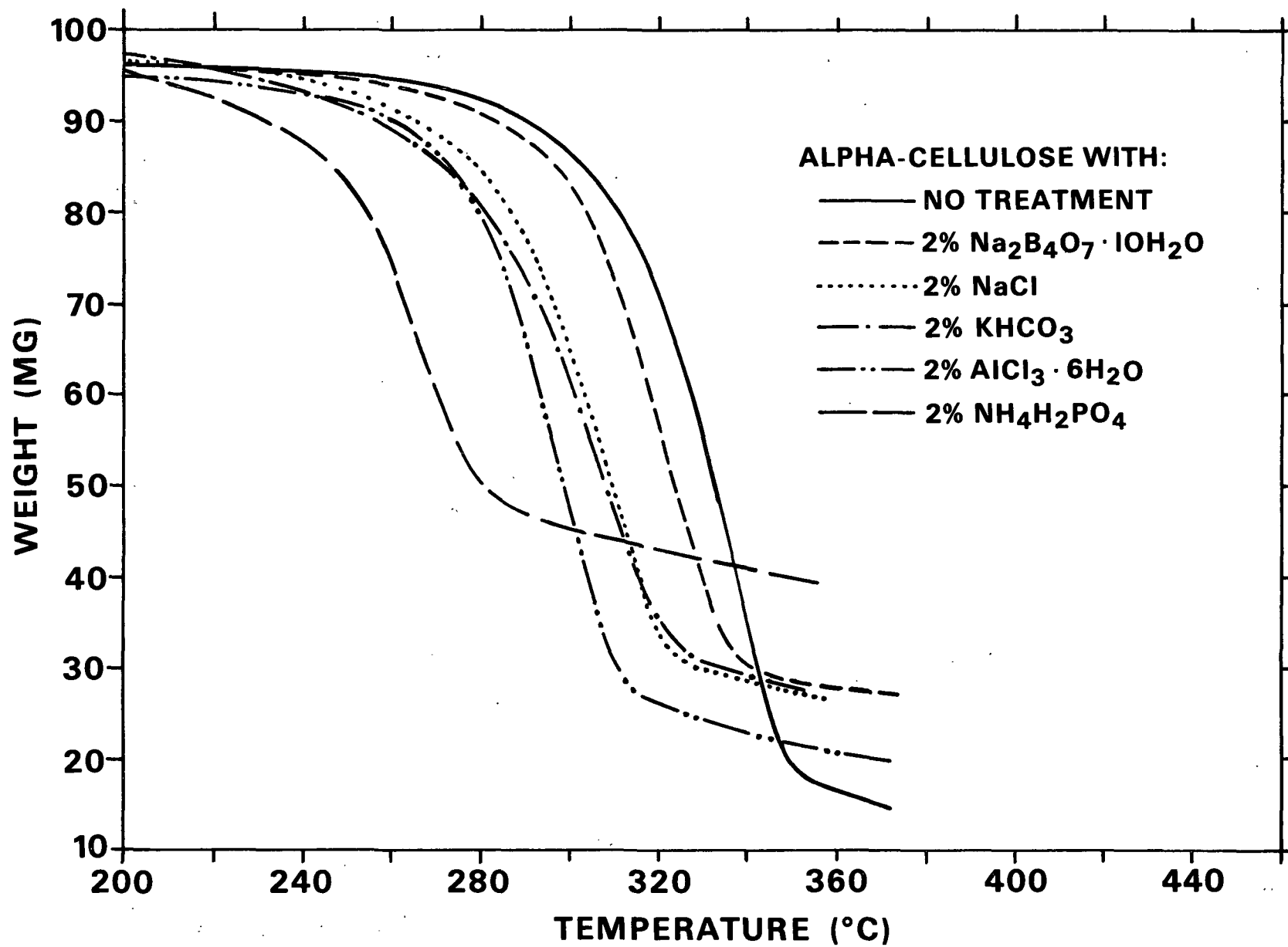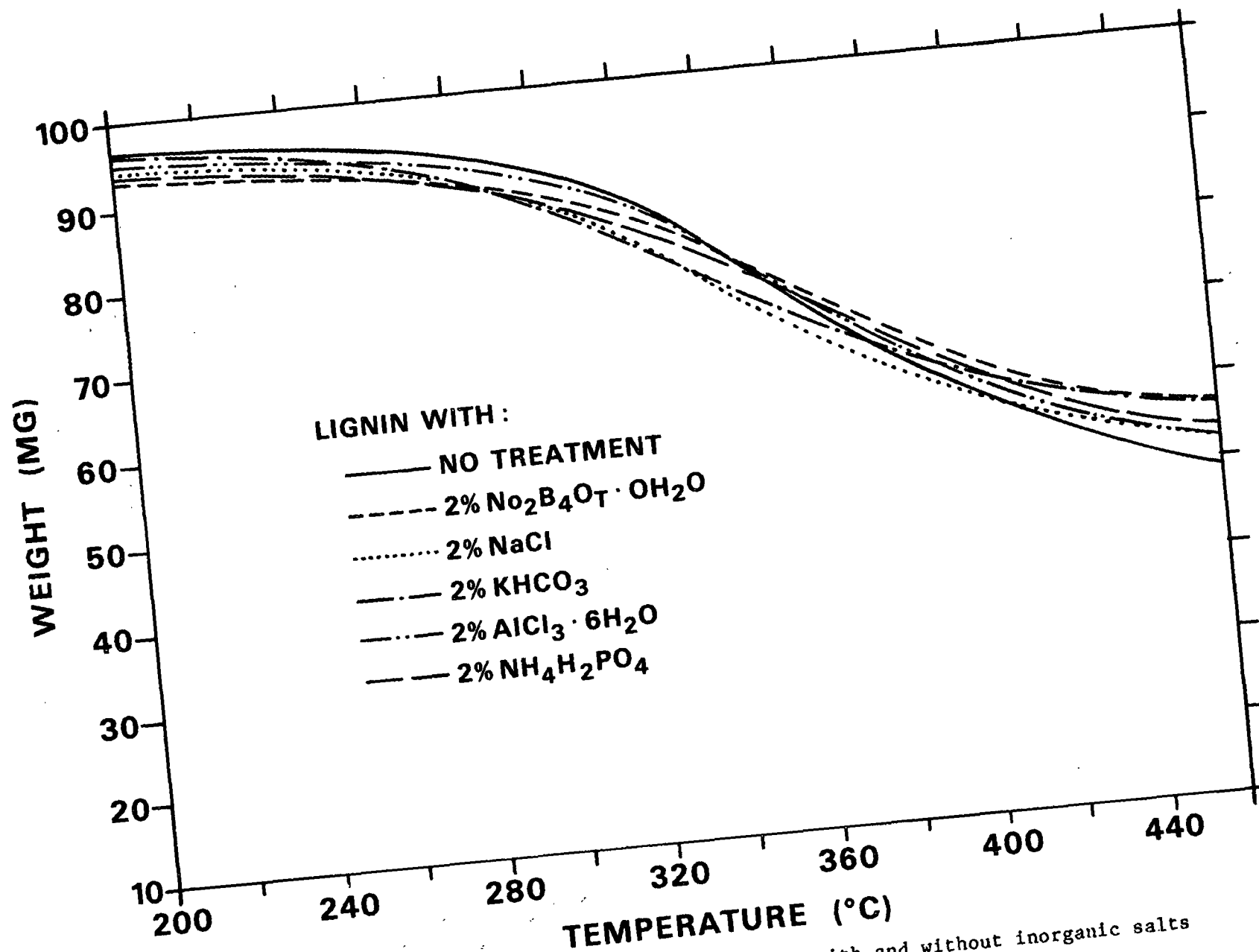
—··— 2% $AlCl_3 \cdot 6H_2O$

——— 2% $NH_4H_2PO_4$

The main effect of inorganics on cellulose pyrolysis was the suppression of levoglucosan formation.[50,52] The relatively simple mass spectrum of products from cellulose pyrolysis was replaced by a much more complicated spectrum upon the addition of 5% potassium carbonate to cellulose as shown in Fig. 16. There was a noticeable absence of levoglucosan in the treated sample. The masses associated with furan compounds predominated in the spectra of the treated sample. This treatment increased the yield of char significantly while reducing the yield of tars.[50]

A hypothesis put forth to explain the effect of potassium carbonate on cellulose pyrolysis was given by Evans et al.[50] The alkali material was believed to catalyze the cross-linking between cellulose chains and to prevent the steric rearrangements necessary for transglycosylation. This allowed the simple fission reactions to occur which resulted in more char formation.

Shafizadeh and Sekiguchi[51] studied the pyrolysis products of cellulose (400°C). Diammonium phosphate increased char formation by 14%, while sodium chloride increased char by 2%. The chars were subjected to permanganate oxidation. The formed benzene polycarboxylic acids were analyzed. Chars pyrolyzed from cellulose with the inorganic salts added had a larger amount of the highly substituted benzene carboxylic acids than the other chars. The results indicated that the pyrolysis of cellulose with inorganics resulted in chars exhibiting more condensation or cross-linking.

Pyrolysis of cellulosic materials resulted in char yields between 2-17%.[31,40] Lignin pyrolysis resulted in char yields ranging from 50-70%.[40,49] Inorganics presumably can promote dehydration reactions during the pyrolysis of lignin in
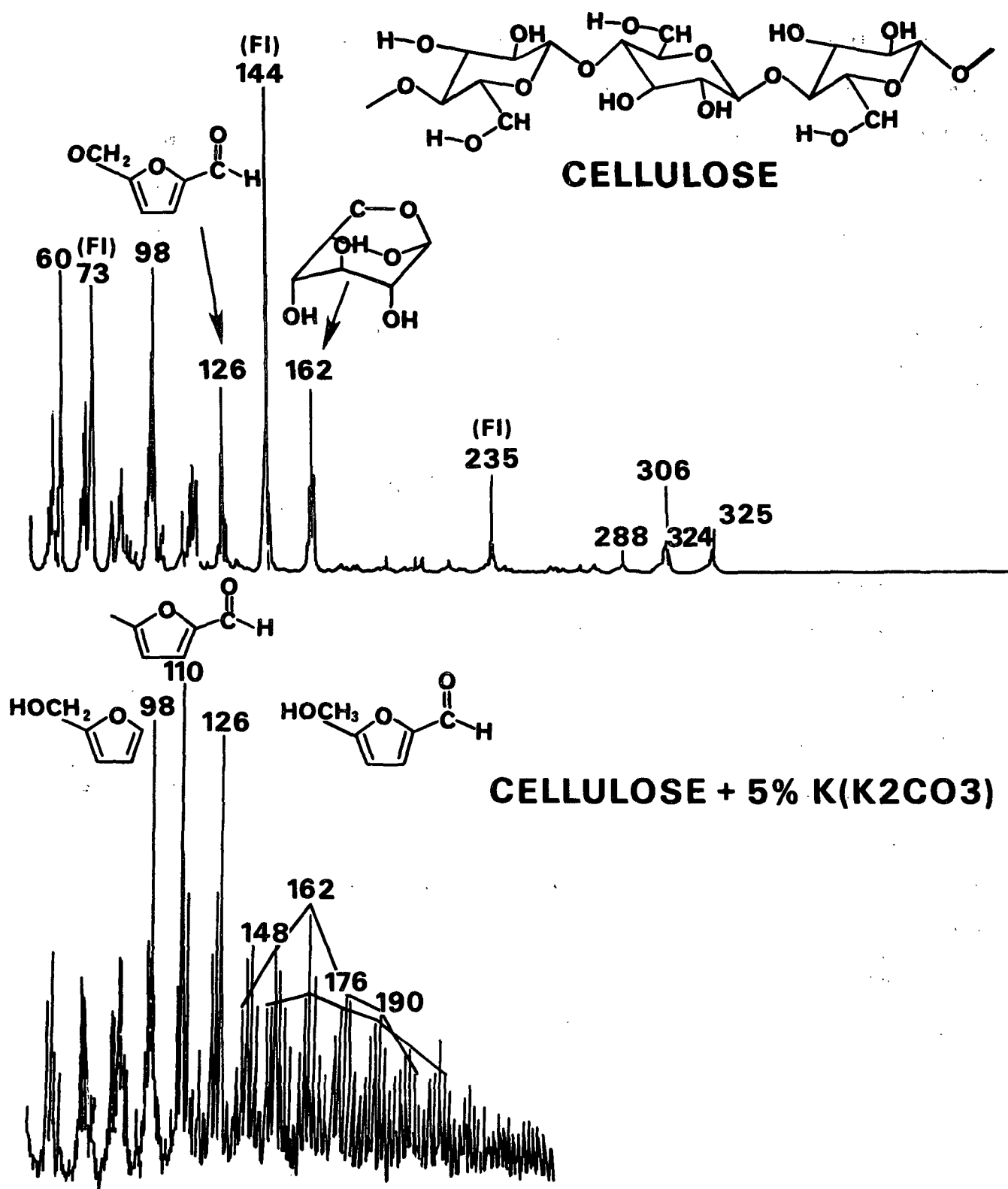
Figure 16. Spectra of the primary pyrolysis products of cellulose (top) and cellulose treated with 5% potassium carbonate (bottom). Conditions: 900°C, 5-10 ms contact time, 25 mg.[50]

the same manner as during the pyrolysis of cellulose.[26] The presence of more thermally stable aromatic groups in lignin apparently diminishes the effect of increasing the rate of dehydration reactions. The effect of some inorganics on the thermal characteristics of lignin pyrolysis is shown in Table 9.

Table 9. The effect of inorganic salts on the thermal behavior of HCl lignin (oak) and kraft lignin.[32]

| Lignin Type | Salt | Temp. at Maximum Rate of Wt. Loss °C | Decomp. Temp. at | | Nonvolatile Residue at 550°C, wt. % |
			10% —wt. °C	50% loss— °C	
HCl lignin	(control)	335	295	445	39.2
HCl lignin	ZnCl$_2$	380	275	515	40.7
HCl lignin	NaCl	330	305	425	38.5
HCl lignin	SiO$_2$	340	300	460	38.1
HCl lignin	Na$_2$CO$_3$	330	305	470	37.1
Kraft lignin	(control)	380	285	545	49.7
Kraft lignin	ZnCl$_2$	400	305	--	53.8
Kraft lignin	NaCl	375	285	--	53.0
Kraft lignin	SiO$_2$	390	295	--	51.0
Kraft lignin	Na$_2$CO$_3$	390	310	--	51.0

FORMATION OF CHARS DURING PYROLYSIS OF LIGNOCELLULOSIC MATERIALS

In comparison to the low molecular weight volatile products, little attention has been focused on the secondary reactions involved in the transformation and carbonization of the solid phase of lignocellulosic materials during pyrolysis, the chemical composition of the char, and its reactions.[51]

Earl[53] used solid state ^{13}C NMR to study the pyrolysis characteristics of spruce and oak wood samples between 280-390°C. The pyrolysis of saccharides occurred before lignin. Significant portions of the polysaccharide component remained at 340°C. The breadth of the aromatic resonance of chars from wood pyrolyzed at 390°C indicated the char was composed of a variety of condensed ring components. Spruce wood was found to be more resistant to thermal degradation than oak. It could not be determined whether the differences observed were due to differences in the heat transfer properties or the chemical composition of the wood.

Many materials which undergo pyrolysis contain differing amounts of holocellulose and lignin; thus, the yield and the composition of chars from these materials would be of interest. Cellulose theoretically contains 44.4% carbon ($C_6H_{10}O_5$) and lignin has been reported to have carbon contents between 60-63%.[54] Table 10 shows that pyrolysis of cellulose results in an increasingly carbon rich char as the temperature of pyrolysis is increased.

Table 10. Residual char yield of cellulose and its elemental analysis.[51]

Condition	Char Yield, wt. %	Composition			Formula (Ref. to C_6)	H/C
		C	H	D(diff.)		
Untreated		42.8	6.5	50.7	$C_6H_{10}O_5$[a]	1.7
300°C for 5 min	89.43	44.0	6.4	49.6	$C_6H_{10.4}O_{5.0}$	1.7
325°C for 5 min	63.3	47.9	6.0	46.1	$C_6H_{9.0}O_{4.3}$	1.5
350°C for 5 min	31.8	59.9	5.2	34.9	$C_6H_{6.2}O_{2.6}$	1.0
400°C for 5 min	16.6	76.5	4.7	18.8	$C_6H_{4.4}O_{1.1}$	0.7
450°C for 5 min	10.5	78.8	4.3	16.9	$C_6H_{3.9}O_{1.0}$	0.6
500°C for 5 min	8.7	80.4	3.6	16.0	$C_6H_{3.2}O_{0.9}$	0.5

[a]Theoretical value.

Mackay and Roberts[54] studied the pyrolysis of 22 cellulosic and lignocellulo-
sic materials representing a wide range of compositions: 0-70% lignin, 15-100%
holocellulose, and 0-13% extractives. Samples were heated at 15°C/min up to
500°C. The objective was to determine the final char yield by knowing the amount
of lignin, holocellulose, extractives, and ash in the sample. A model was formed
assuming each component pyrolyzed independently of the other and each component
had a characteristic carbon yield (carbon content of the char/carbon content of
the original material) upon pyrolysis. A regressional model, which fit the data
very well, gave the total mass yields of the components with 95% confidence
intervals: holocellulose - 18.6 ± 1.1%, lignin - 53.1 ± 2.6%, extractives -
48.2 ± 12.6%. The holocellulose and lignin values are in good agreement with
experimental data presented by Tang[49] in Fig. 14 and 15. The carbon yields were
also determined: holocellulose - 39.6 ± 3.7%, lignin - 76.0 ± 6.7%, extrac-
tives - 53.0 ± 32.3%.

A conceptual mechanism of char formation in lignin pyrolysis is shown in
Fig. 17. The expected carbon yield based on this mechanism would be approxi-
mately 69%, which is in good agreement with the results. The actual process is
much more complicated, but the figure gives a good conceptualization of pyrolysis,
where larger molecules split up into smaller fragments and then recombine to
form a graphitelike structure.

Theoretically, at very low heating four out of six carbon atoms (67% carbon
yield) in each glucose monomer could be retained in the char during cellulose
pyrolysis. Actual carbon yields of cellulose pyrolysis are lower. Higher
heating rates result in higher volatilization. Mackay and Roberts[54] found a
carbon yield of 40% at a heating rate of 15°C/min. Shafizadeh and Sekiguchi[51]

(a) schematic structure of lignin

(b) common subunit of lignin structure

(c) conceptual geometry for formation of graphite-like layer from subunit residues produced during pyrolysis of lignin
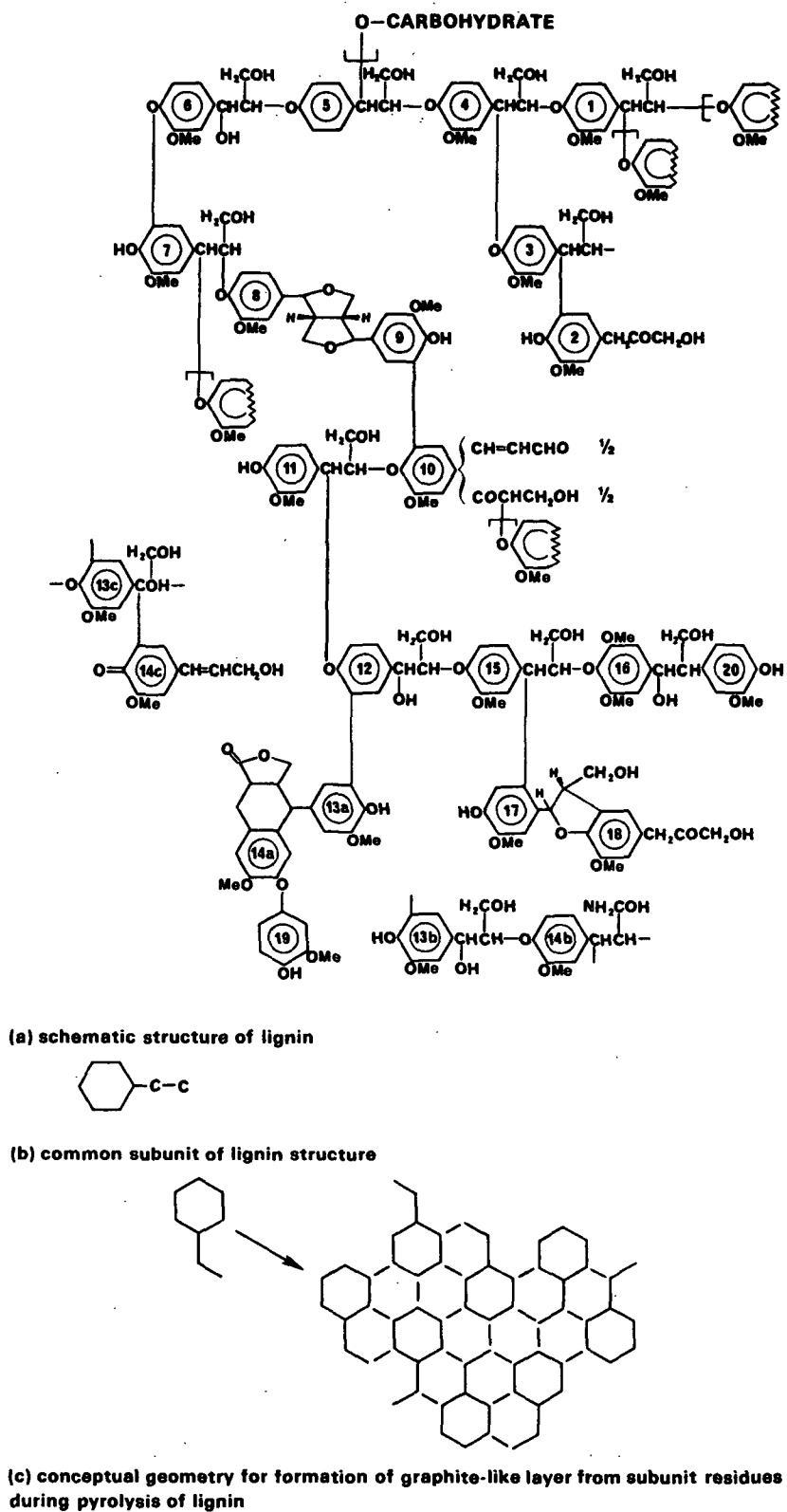
Figure 17. Conceptual mechanism of char formation in liquor pyrolysis.[54]

immersed 450 mg of cellulose in a hot flowing nitrogen gas stream and found a carbon yield of 16.3% (Table 10). Both experiments were carried out at 500°C.

The formation and structure of chars produced on heating of cellulose, lignin, and wood to 400°C has been studied by Shafizadeh et al.[40] The chars were investigated by FTIR and CP/MAS ^{13}C NMR and the results discussed in conjunction with parallel permanganate oxidation studies.[51] The aromatic groups in the chars of wood, lignin and cellulose were considerably substituted or cross-linked. Park and Lee[55] found lignin and cellulose formed the same types of polycyclic aromatic compounds. The percent of aromatic carbons in char from cellulose (69%), wood (70%), and lignin (66%) were similar.[40] This indicated the preexisting aromatic groups in lignin did not increase the aromatic concentration of the char, although lignin provided more char than cellulose.

Figure 18 shows the concentration of different carbon species in char formed during pyrolysis of cellulose between 325-500°C.[40] Figure 19 shows the same carbon species based on the original carbon content. The figures show the rapid decrease of the glycosidic bonds between 325-400°C. The concentration of carboxyl and carbonyl groups reached a maximum at 350°C. The aromatic components began to form at 325°C. The aromatic concentration of the chars continued to increase with increasing temperature, and at 500°C the aromatic carbon species represented 88% of the char.

The literature indicated lignin and cellulose pyrolyze independently in lignocellulosic materials. Lignin forms much more char than cellulose; however, the composition of these chars pyrolyzed were very similar.
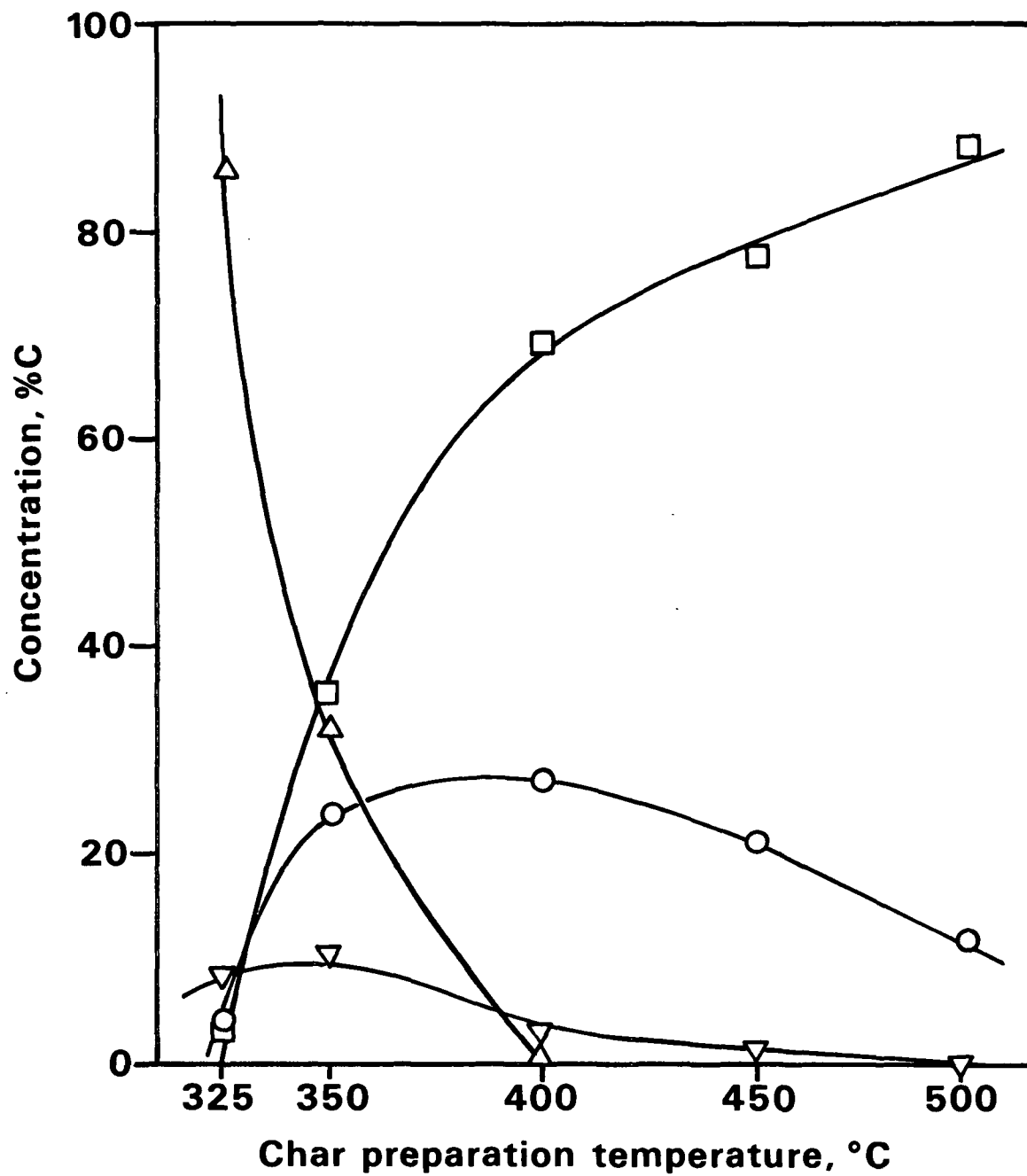
Figure 18. Concentration of different carbon species in char prepared
at 325-500°C: Δ – glycosidic; – aromatic; o – paraffinic;
∇ – carboxyl and carbonyl.[40]
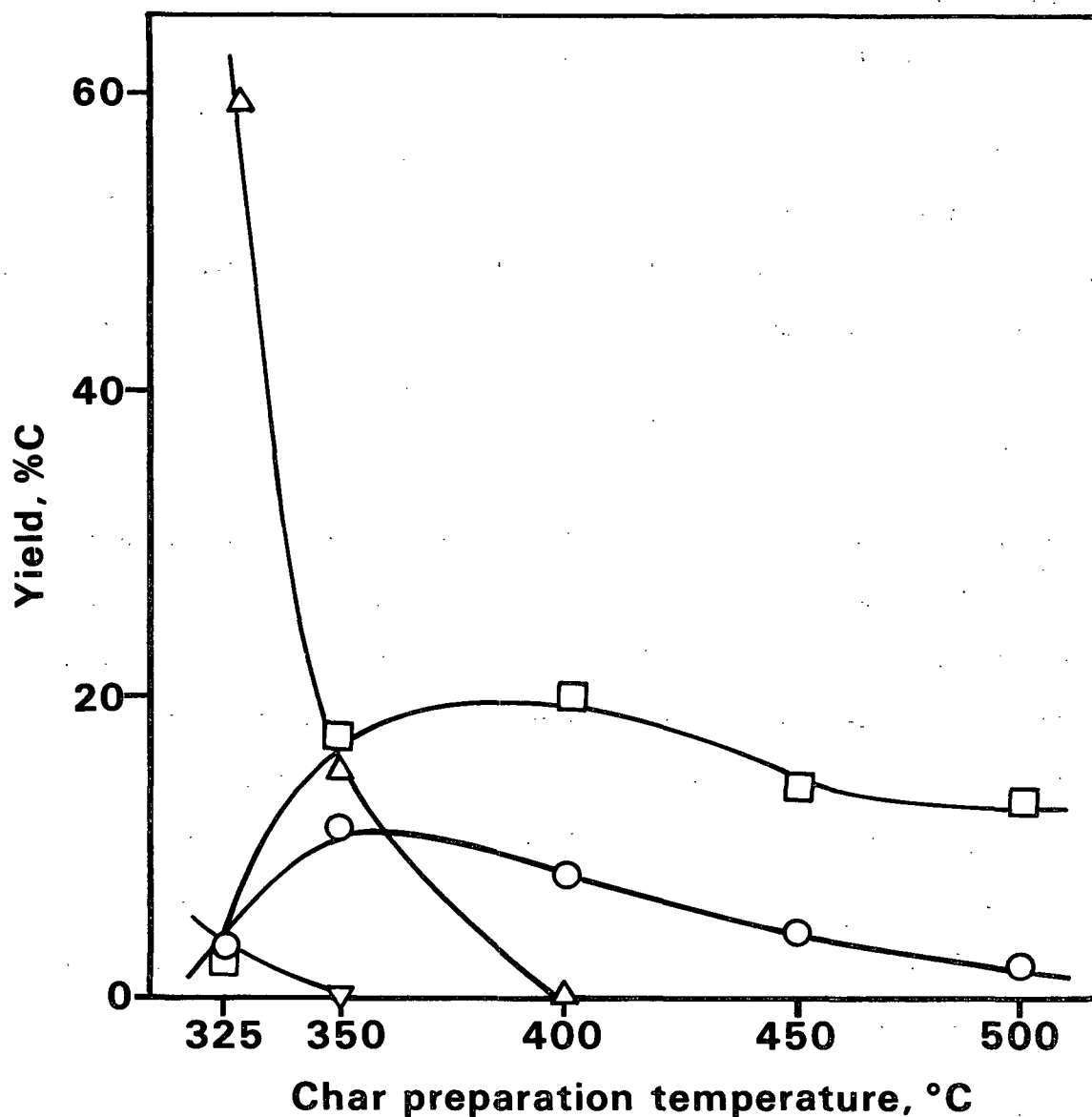
Figure 19. Yield of different carbon species based on the carbon content
of cellulose: Δ - glycosidic; - aromatic; o - paraffinic;
V - carboxyl and carbonyl.[40]

SWELLING OF COAL AND BLACK LIQUOR

Coal and kraft black liquors are both carbonaceous materials which upon
pyrolysis swell and form chars. Similarities between the swelling of the two
materials may be expected. The information available on black liquor swelling

is of a more qualitative nature or performed at relatively low temperatures com-
pared to data available on the swelling of coal.

Coal Swelling

The swelling of coals is generally limited to bituminous coals, which upon
heating soften into a deformable material. The temperature limits and time dura-
tion of plasticity depend on heating rate and other factors. Nominally the swol-
len volumes of pyrolyzed particles attain up to a 30-fold increase in volume,[42,56]
although values up to 1100 times the original volume have been reported.[57]

Coal starts out as a porous solid and when heated begins to soften between
300-400°C.[58] The formation of a substance known as "metaplast" was believed to
be responsible for this softening.[59] Initial decomposition of coal generates
gases, char and metaplast within the coal particle. Metaplast is an inter-
mediate product that has been characterized as a tar.[60] Metaplast further
decomposes or polymerizes during pyrolysis to form more stable and more aromatic
materials as well as light gaseous components. These secondary reactions
appear to be related to plasticity. The solidification process begins between
450-500°C, becoming complete at 550°C.

The volatile transport in nonplastic coals occurs by diffusion and hydrody-
namic flow through pores; for plastic coals the expansion of bubbles originating
from pores was believed to be the main mechanism.[59] The bubble transport mecha-
nism was supported by the formation of jets observed in high speed photography
of pyrolyzing particles. The pores in coal tended to disappear at the higher
swell factors (final diameter/original diameter of the particle).[22] Highly
swollen particles consisted of a thin outer shell "surrounded by a cellular
structure of membranelike walls, much like foam."[59]

Plasticity of coal is necessary for proper coking of coal. Two instruments have been used in the past to measure the plastic or viscous properties of coal: the Arnu dilatometer and the Gieseler plastometer. The main function of these instruments is to test coals for their suitability for coking. Figure 20 shows a typical curve for coal tested in an Arnu dilatometer. The dilatometer measures the percent contraction or the percent dilation of a standard pencil made of finely ground coal (60-70 microns). The initial indication of plasticity for coal is a contraction as the pores within the softened solid collapse.

A black liquor sample (dry solids) was sent to the BCR national laboratory at the University of Pittsburgh to be tested with an Arnu dilatometer. The standard procedure is to raise the temperature of the device to 300°C, at which time a 3°C/min. heating rate is begun. The test continues until the coal becomes a rigid char (usually 500°C). When tested, black liquor exceeded the capability of the device to measure dilation before a temperature of 300°C was reached. Also, the black liquor solids did not contract before swelling as coals do during this test.

Figure 21 shows the plasticity curve for a typical swelling coal in a Giesler plastometer. A reference material can be used to obtain a viscosity. Coal, when it becomes fluid in the Gieseler plastometer, creates a foam generating erroneously low viscosity values.[58] Another problem with these instruments is the slow heating rate, usually 3°C/min. or lower.

Recently, an instrument has been developed which can measure the viscous or plastic properties of coal at high heating rates (up to 800°C/s) and high temperatures (up to 1,000°C).[61] Figure 22 shows a typical curve for the experimental plastometer.
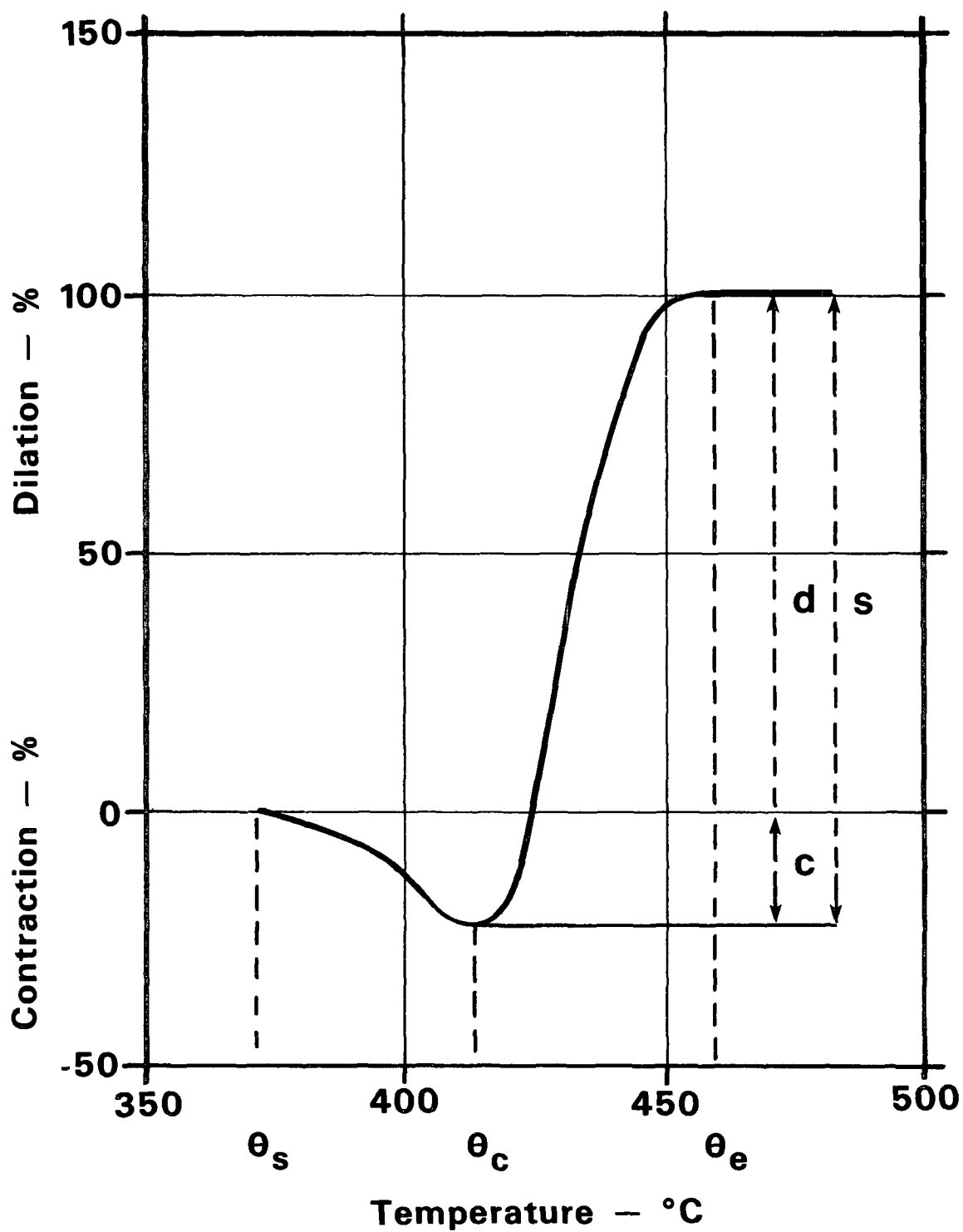
Figure 20. Plasticity curve for coal in an Audibert-Arnu
dilatometer (2°C/min).[58]
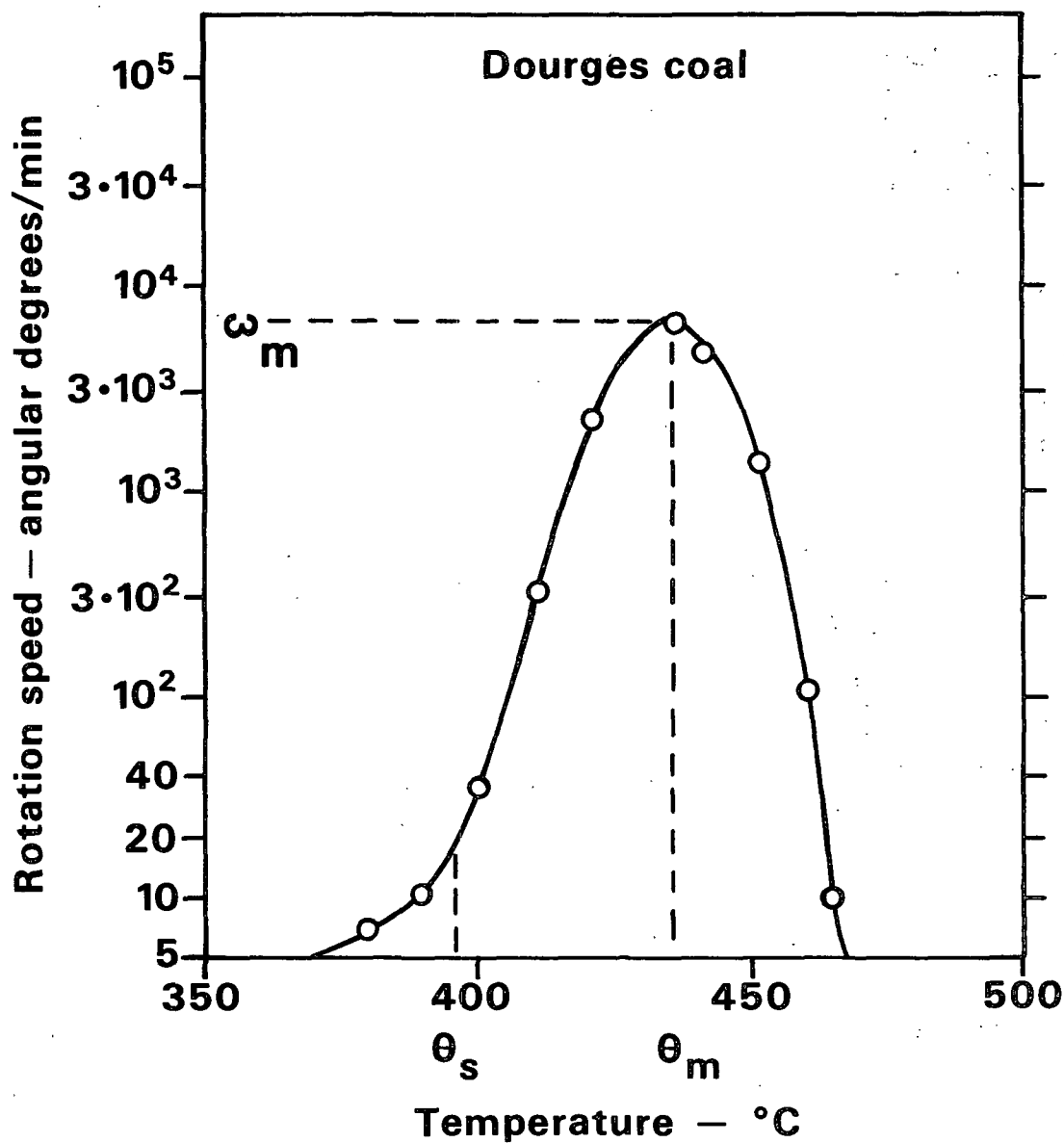
Figure 21. Plasticity curve of coal in a Gieseler plastometer.[58]

A plastic period was arbitrarily defined as the interval during which the torque was less than 0.014 Nm, which corresponded to a viscosity of 36,000 PaS. Figure 23 shows the plastic period as a function of temperature for 100 mg samples of coal. This period was modelled by the sequential reactions of coal into metaplast and metaplast into char. A direct correlation between plasticity and metaplast content was assumed in this model.

RUN 019 0.1 MP2 HELIUM
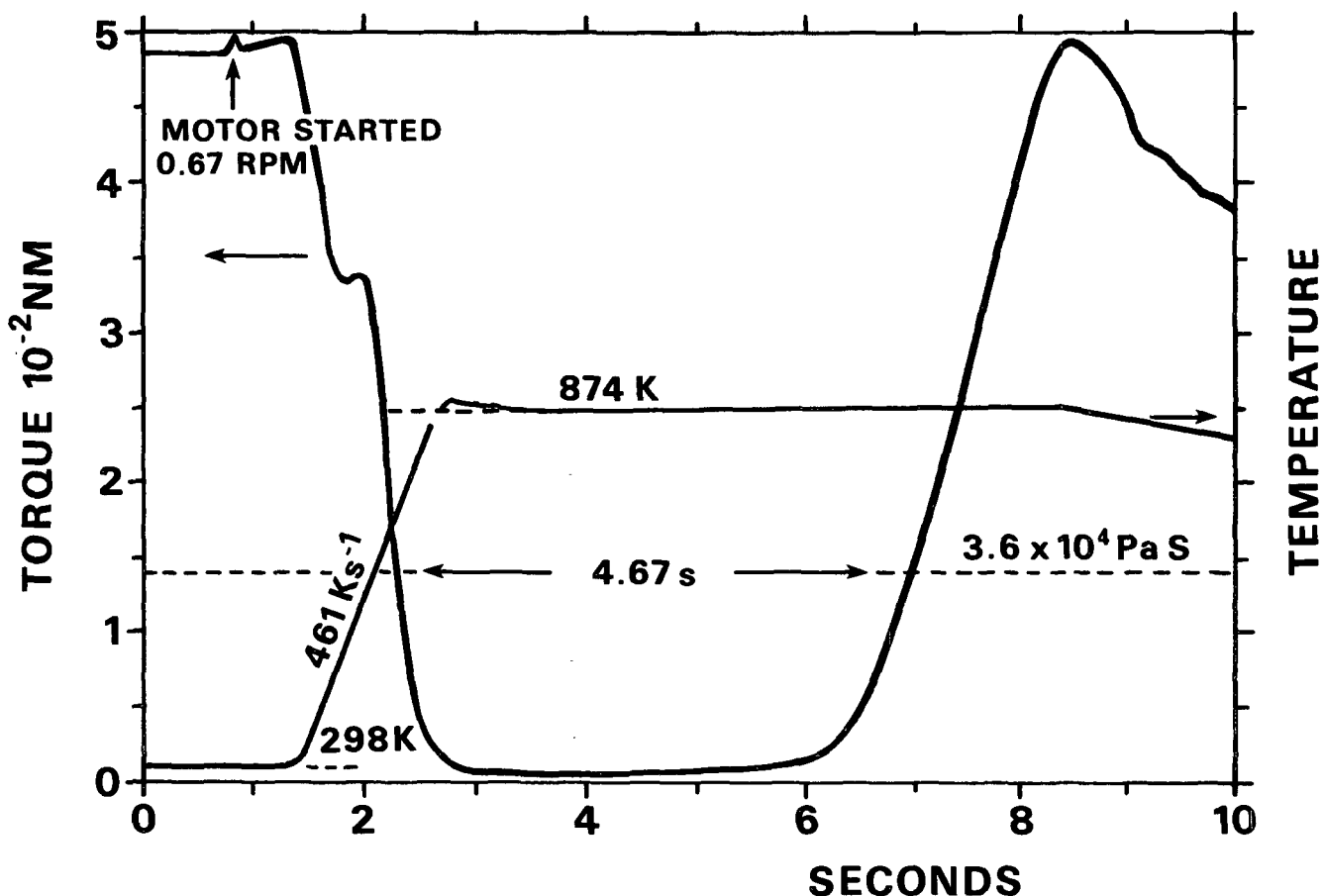
Figure 22. Typical raw data from a plastometer.[61]

The main factor influencing plasticity is the coal type. Plasticity is generally minimal to negligible for coals of subbituminous rank or lower and for coals of anthracite rank. Coals of bituminous rank exhibit a range of plastic behavior which is related to the volatile matter. Plasticity is evident for coals with 35-40% volatile matter, plasticity is a maximum between 25-28%, and plasticity does not exist at a 15-18% volatiles range.[58]

Higher heating rates generally increased the swelling of coal.[56] A higher heating rate changed the softening temperature little but increased the resolidification temperature, hence the duration of the plastic regime increased.

Brookes[62] found a higher heating rate resulted in less swelling. The coals in his investigation exhibited relatively poor swelling (volume increases less than four times the original). Comparisons in this area were difficult due to the various investigations using different coals, various particle sizes, and various apparatuses for testing coal. The heating rate was usually not defined well in quantitative terms.

RUNS IN I ATM HELIUM
HEATING RATE = 450K/S
PITTSBURGH NO.8 COAL

SINGLE RXN MODEL

$$P \xrightarrow{K_1} M \xrightarrow{K_2} C$$

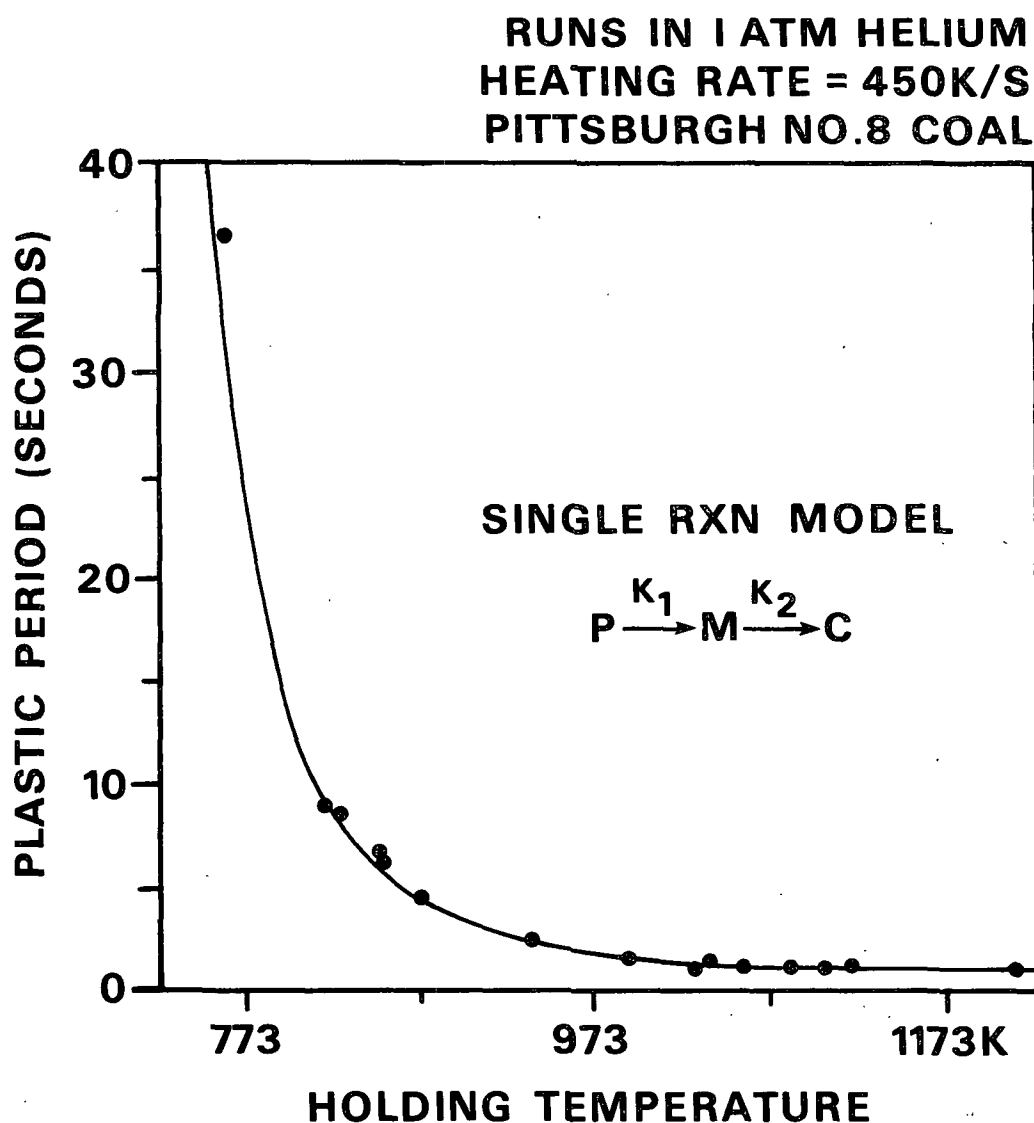Figure 23. Duration of coal plastic period, comparison of observed data points and predicted values (represented by the curve). Plastic period is shown as 4.67 s in Fig. 22.[61]

The swelling was greater in an inert atmosphere than in an oxidizing atmosphere.[58,63] The swell factor (final diameter/original diameter) increased 1.33 times in air and 3.87 times in nitrogen (500-950°C, 20-100 microns).[63] Particle size had no influence on swelling under the conditions tested. Mackowsky and Wolff[64,65] found the particle size did have an effect, with larger particles producing larger volumes. Swell factors were between one and three for particles in the 0.06-2.34 mm diameter range. A large amount of scatter in the swelling data was found for the same coals tested under the same conditions.[66,67]

Figure 24 presents the essential elements of a coal model formulated by Melia and Bowman.[42] A few basic assumptions were made in formulating the model: 1) the gases escaped via the pores, 2) the pores enlarged as a result of swelling, 3) there was a zero temperature gradient within the particle, 4) the pyrolysis heat of reaction was neglected, 5) the surface tension was neglected, and 6) a distributed activation energy kinetic model was used. The viscosity profile was modeled as a step change with the softening (577°C) and hardening (777°C) temperatures determined by a best fit of the data. The model fit the data reasonably well.

Oh[59] has attempted to model the swelling of coal. The model successfully predicted the decrease in volatile yields resulting from an increase in atmospheric pressure. This was accomplished by modeling bubble transport and the impact of residence time on secondary reactions. However, more analysis was required to adequately fit the model to available coal swelling data.

The formation of tars during coal pyrolysis was responsible for coal transforming into a viscous, deformable material. Initially, softening of coal resulted in shrinking as the pores found in coal collapsed or closed. The

swelling resulted from bubble growth as the volatilization of pyrolysis gases

proceeded within the coal particle. The type of coal and the duration of the

deformable regime determined the extent of swelling.
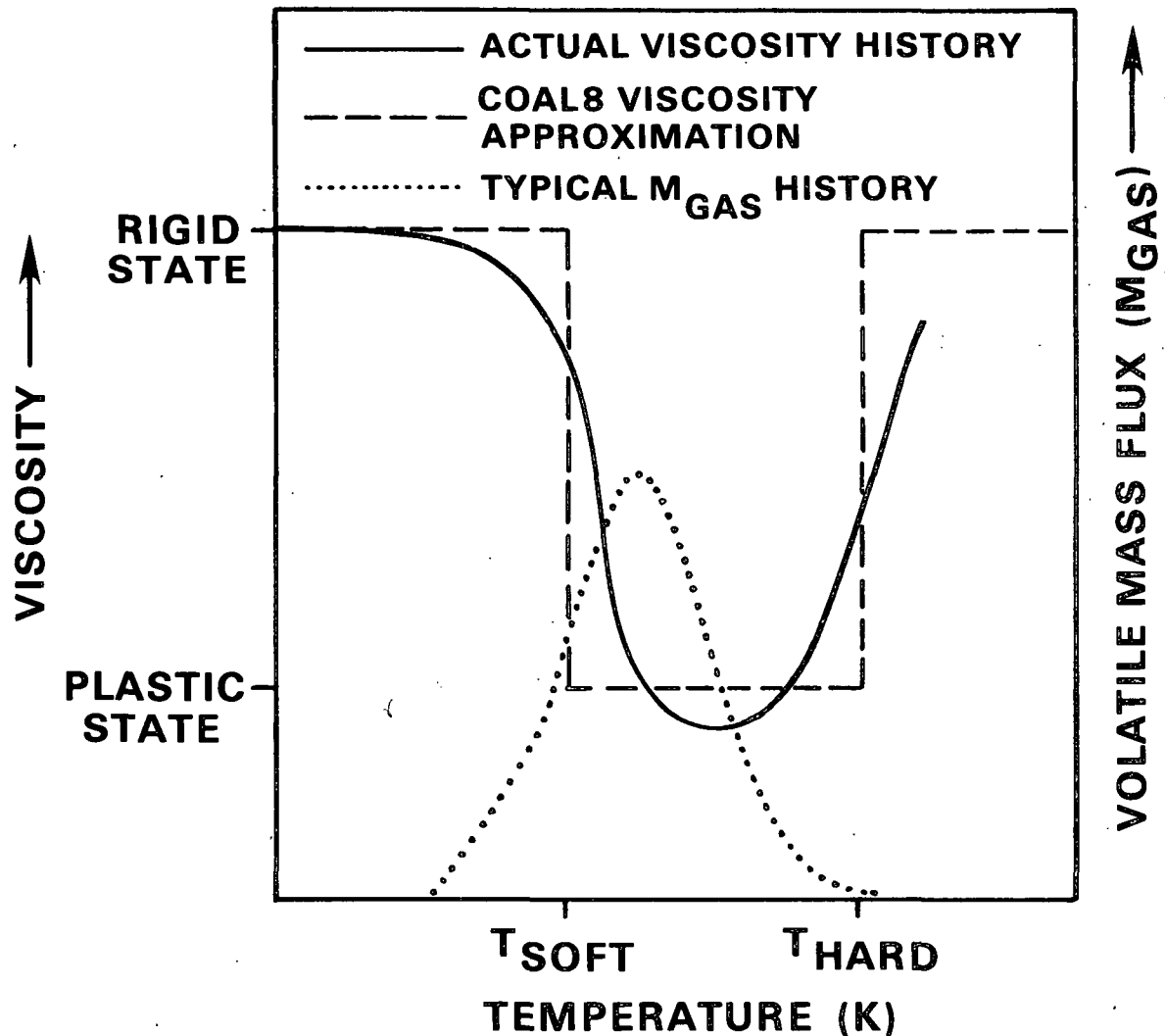

Figure 24. A coal viscosity model.[42]

Black Liquor Swelling

Black liquor is normally combusted at relatively high temperatures (1100°C).

Black liquor is usually sprayed into a recovery furnace between 65-75% solids.

Significant swelling occurs during the combustion of black liquor particles.

The swelling has been primarily related to the pyrolysis of black liquor.[68] The

literature pertaining to the swelling of black liquor will be presented in chronological order: studies performed first will be presented first.

The pulping of some eucalyptus trees had a deleterious effect on the operation of the recovery area of a pulp mill.[3] The difficulties with eucalyptus black liquor evaporation and burning had been attributed to the extractives in the original wood, particularly ellagic and gallic acids. The presence of ellagic and gallic acids was found to be associated with relatively high black liquor viscosities and increased tendencies of black liquor to precipitate during evaporation.

The swelling of black liquor was tested by placing dried solids in a muffle furnace at 420°C.[3] The swelling was judged by two criteria: 1) the extent of swelling and 2) the textural appearence of the char surface. A correlation existed between these two criteria as those liquors which swelled extensively also had a homogeneous appearance and those liquors that swelled to a lesser extent had a heterogeneous appearance.

Ellagic acid added to wood before high temperature cooks had relatively little effect on liquor swelling compared to the large effect when added to wood cooked at low temperatures or when added to black liquor. Although the extractives significantly decreased the swelling of black liquor, other factors were involved as extractives could not alone explain the very poor swelling of some eucalyptus black liquors.[3]

Oye et al.[4] conducted swelling tests of black liquor in air between 300-500°C in a muffle furnace. The swelling was determined after 75 seconds (the time required to reach maximum swelling for the 0.3 gram samples tested).

The particle volumes were determined by a photographic method. The results from these tests are shown in Fig. 25-27.
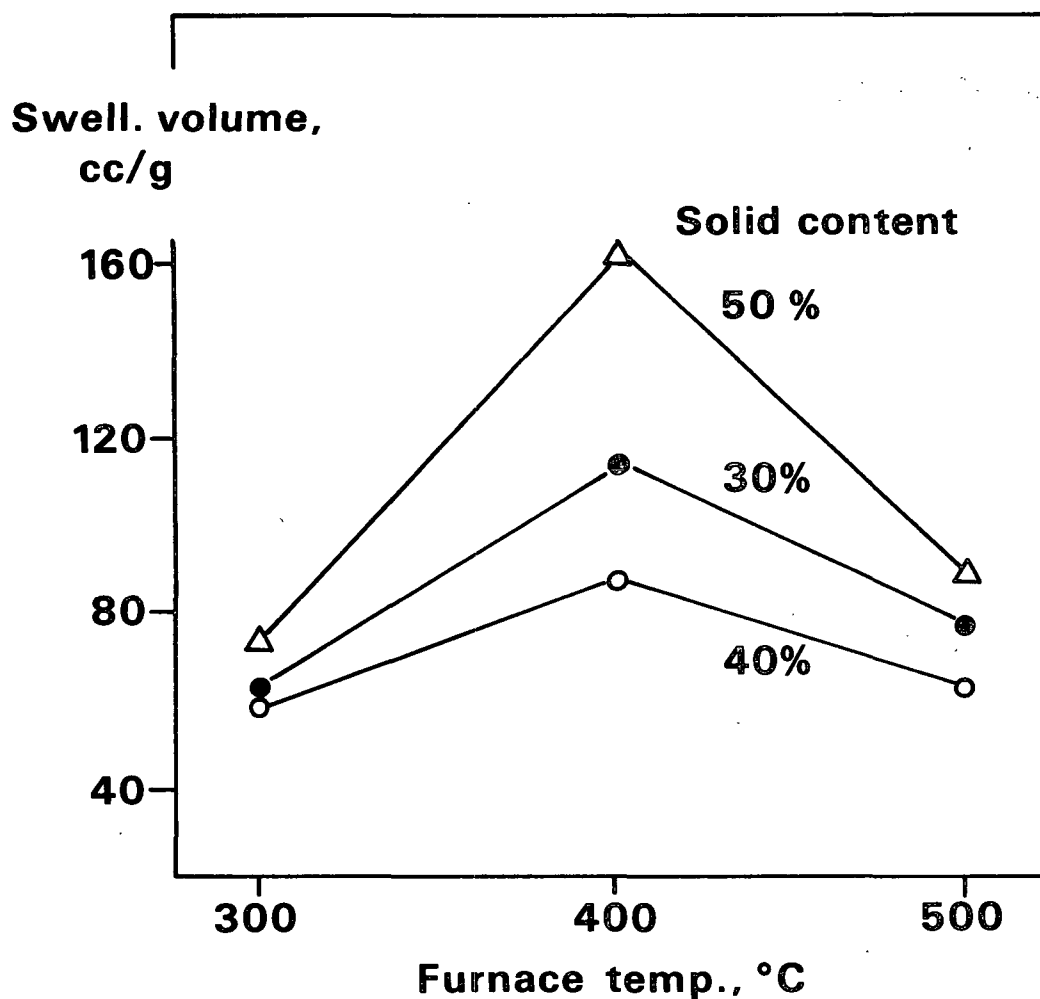
Figure 25. Swelling volume of hardwood sulfate black liquor at various solid contents vs. furnace temperature.

The most important effect appeared to be temperature, with the effects of particle size and solids content unclear as the confidence intervals for the data were not given. A temperature of 400°C produced higher swollen volumes than either 300 or 500°C under the conditions tested. Combustion studies were also performed at higher temperatures with specifics of the experimental procedure

not given. Combustibility could be estimated only generally from the swelling
of different types of black liquor.
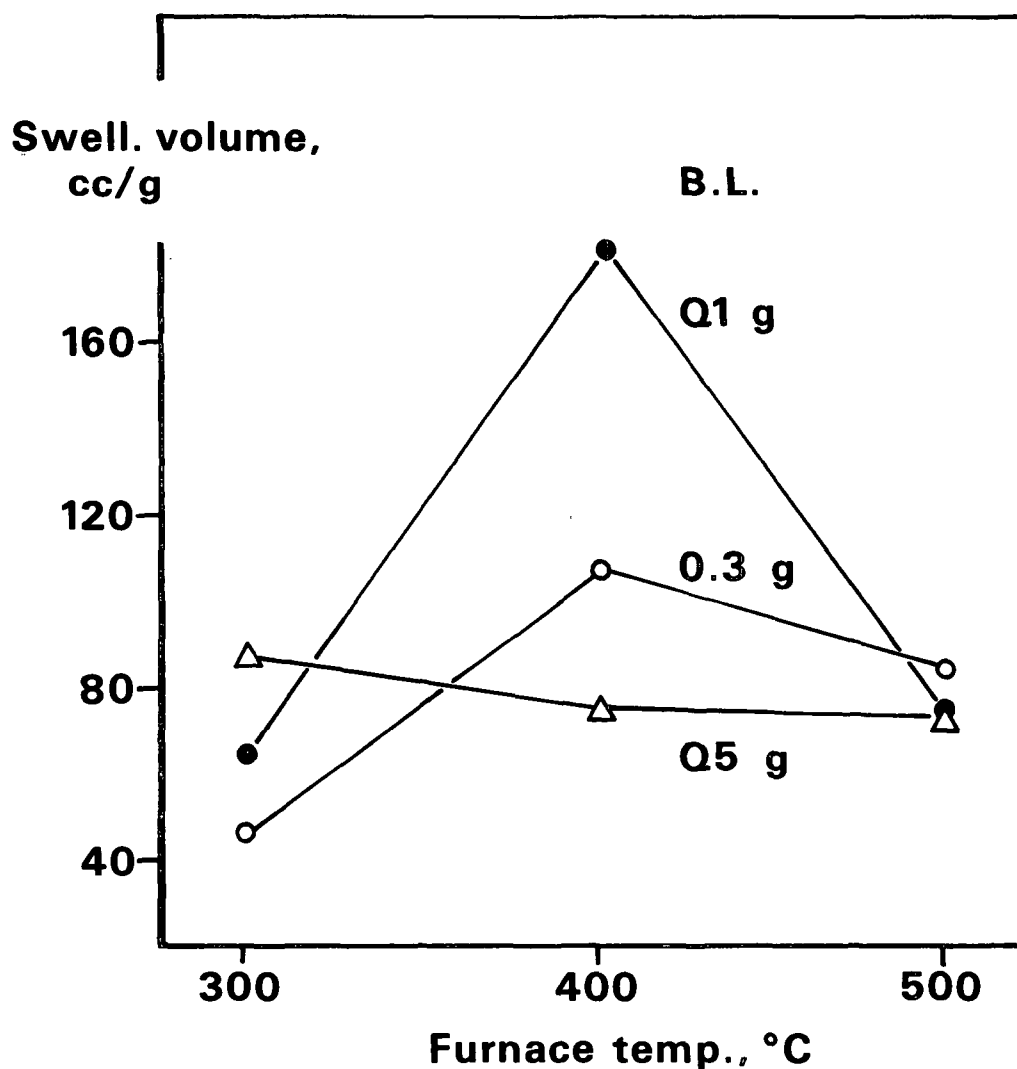
Figure 26. Swelling volume at various amounts of specimen vs.
furnace temperature.

Further studies of the swelling of eucalyptus black liquor were performed in
a muffle furnace at 400°C after 2 minutes.[5] Char volumes were measured by the
volume of sand displaced by the char particles. Figure 27 shows the relation-
ship between the viscosity of various black liquors (measured at 40°C and 40%
solids) and their swelling volume. Figure 28 shows a higher viscosity was
generally associated with a lower swelling volume. Of the inorganic components

studied (total ash, CaO, MgO, SiO$_2$, and Fe), none had an appreciable effect on the viscosity or swelling volume. The presence of phenolic compounds increased viscosity and decreased the swelling volume.
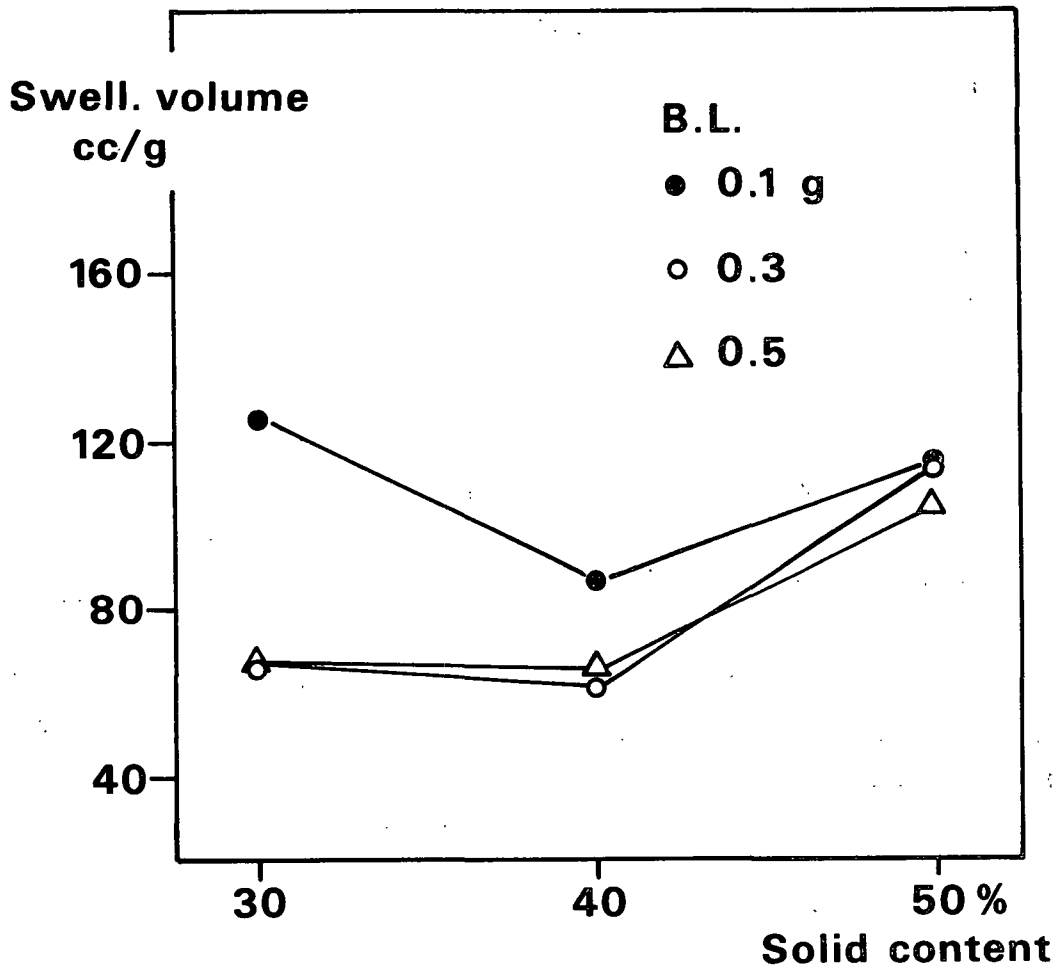
Figure 27. Swelling volume at various amounts of specimen vs. solid content.

Oye et al.[5] were the only investigators to comment on the variability of the swelling data. Replicates of two black liquor samples were given: 1) 40, 36, 36, 33, 32, 31, 29, 31, 30, 32 mL /g - 33 ± 3.4 (± 1 std. dev.) and 2) 6, 6, 10, 5, 15, 7, 11, 10, 8, 5 mL/g - 8.3 ± 3.2. These two samples represented the extremes of the swelling observed with different tree species.
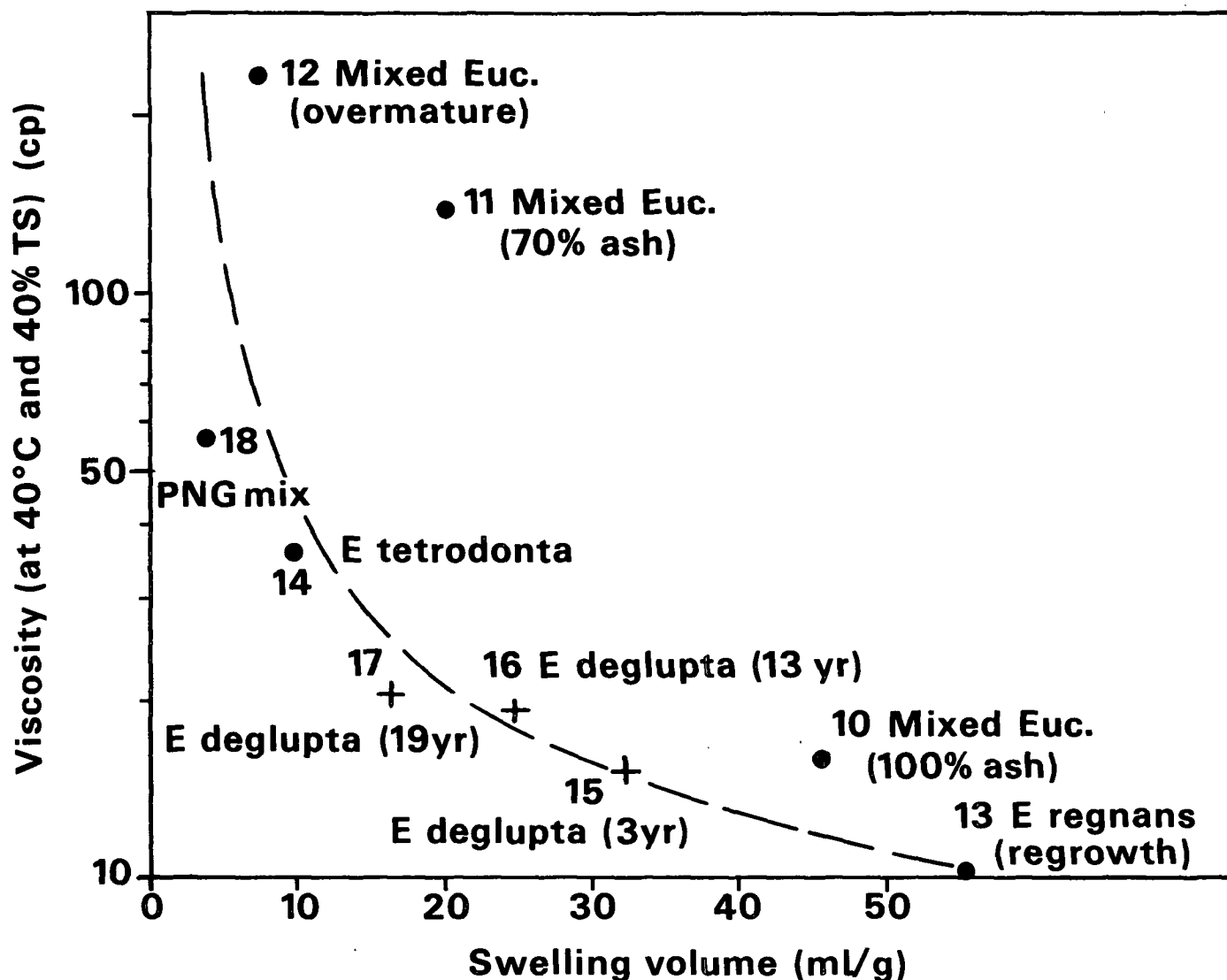
Figure 28. Relationship between swelling volume and viscosity.[5]

Kubes et al.[6] also found the extractives of red cedar to significantly inhibit swelling as shown in Fig. 29. A correlation was found between the swollen volume and a pseudoactivation energy determined by differential thermal analysis (DTA). DTA was used in an attempt to determine differences in the combustibility of black liquors.[2,69] Unfortunately, this has not led to an understanding of the combustibility of black liquor.

WESTERN HEMLOCK   RED CEDAR
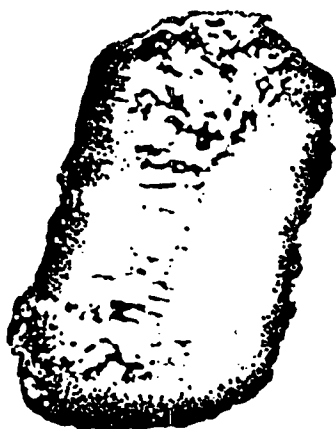
+5%   +10%
RED CEDAR RESINS   2 cm

Figure 29. The effect of wood species and resins on swollen volume.[6]

The Indian pulp and paper industry faces problems in evaporation and combustion of black liquor when the amount of hardwoods (including eucalyptus species) is increased above about 20% of the total wood processed. The viscosity, precipitation point, and swelling volume of a wide range of black liquors were studied.[70]

The precipitation point of black liquor was taken as an indication of colloidal stability. The precipitated material had ash contents between 30-50%. Problem black liquors generally contained more polyphenolic compounds, precipitated at lower solids contents, and had higher viscosities than "normal" black liquor. The addition of caustic was used to increase residual alkali and lower viscosity; the additional alkali had no effect on precipitation point or swelling

volume.[70] There was a wide range of values exhibited for swelling, precipitation, and viscosity. There was no correlation found between any two of these properties.

Kulkarni and Pant[71] continued to work with Indian hardwoods to determine which factors were responsible for colloidal instability. Colloidally unstable liquors had higher molecular weight fractions and increased amounts of sugar acids. The sugar acids were found in the precipitated material along with lignin. Table 11 shows some of the data obtained for different tree species. The swelling volume did not correlate with viscosity, but appeared to be related more closely to the precipitation point black liquor.

Table 11. Properties of hardwood kraft spent liquors.[71]

Species	T. tomentosa	M. Latifolia	E. tereticornis	Mixed Hardwood
Total solids, % w/w	20.3	19.8	18.2	20.9
Residual alkali as Na$_2$O, g/L	5.8	6.6	8.6	9.1
Swelling volume ratio, mL/g	8	17	23	13
Inorganics as NaOH, %	28.0	28.2	33.1	31.6
Viscosity, cp at 80°C at 55% solids	145	79	370	123
Precipitation point at % solids	28	No precipitation	No precipitation	37

Black liquor combustion and pyrolysis of single black liquor particles immersed in a flowing gas stream at 700 and 900°C were studied.[68] The maximum swelling during air oxidation was found to be one third to one half of the volumes attained during pyrolysis. This follows the trend observed in the swelling of coal.

The combustion of small black liquor droplets (0.5-2.5 mm in diameter) between 600-900°C in a radiation furnace was studied by Hupa et al.[15] The combustion process was divided into four stages: 1) drying, 2) pyrolysis and combustion of volatile components, 3) char residue combustion, and 4) reactions of the inorganic residue. Significant swelling of the particle took place during the second (pyrolysis) stage. The volume was determined by measuring two particle diameters from photographs, taking the geometric average and then, assuming a spherical shape, calculating a volume. Swollen volumes of up to 20-30 times the original volume were found.

In general, char residues of heavily swelling liquor droplets burned more rapidly than less swelling ones.[15] The results indicated that other factors were also involved. The differences in black liquor combustion behavior (analyzed from the length of burn times) did not have a simple relationship with any of the known liquor properties: liquor heat value, organic/inorganic ratio, and percent of the volatiles evolved.

The effect on swollen volume of adding foreign substances to black liquor was determined and is shown in Fig. 30 and 31. The effect of sodium sulfate addition on swelling was explained by a simple dilution effect. The addition of tall oil reduced the relative swelling significantly greater than would be expected by a dilution effect. Figure 32 shows the change in swelling with the change in pH for acidified kraft black liquor.

Kraft liquors swelled much more than sulfite based liquors. The sulfite liquors also took significantly longer to burn. Figure 33 shows the swelling behavior and char residue burn time vs. the percentage of sulfite black liquor for kraft/sulfite mixtures.
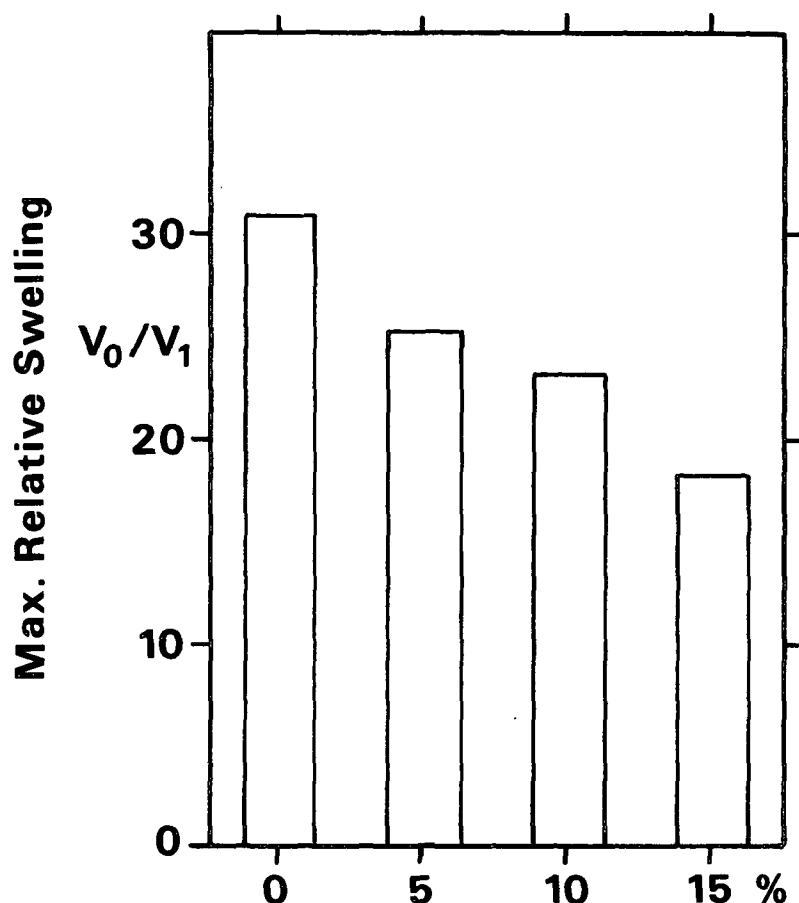
Figure 30. Influence of sodium sulfate on black liquor swelling (800°C, 60% solids).[15]

The effect of the main components of black liquor on swelling were tested with various materials at 400°C for 5 minutes by Milanova et al.[72] Indulin C and sucrose were used to represent kraft lignin and sugar acids in one set of experiments. Precipitated kraft lignin and spent liquor solids from a holocellulose cook were also tested. The degradation products of a holocellulose cook are mainly the sodium salts of sugar acids.

Figure 34 shows the swollen volumes found for Indulin C, sucrose, and a mixture of the two components in a 1:2 (lignin:carbohydrate) ratio. The mixture

of the carbohydrate and the lignin resulted in a higher swollen volume than either of the two components tested separately.
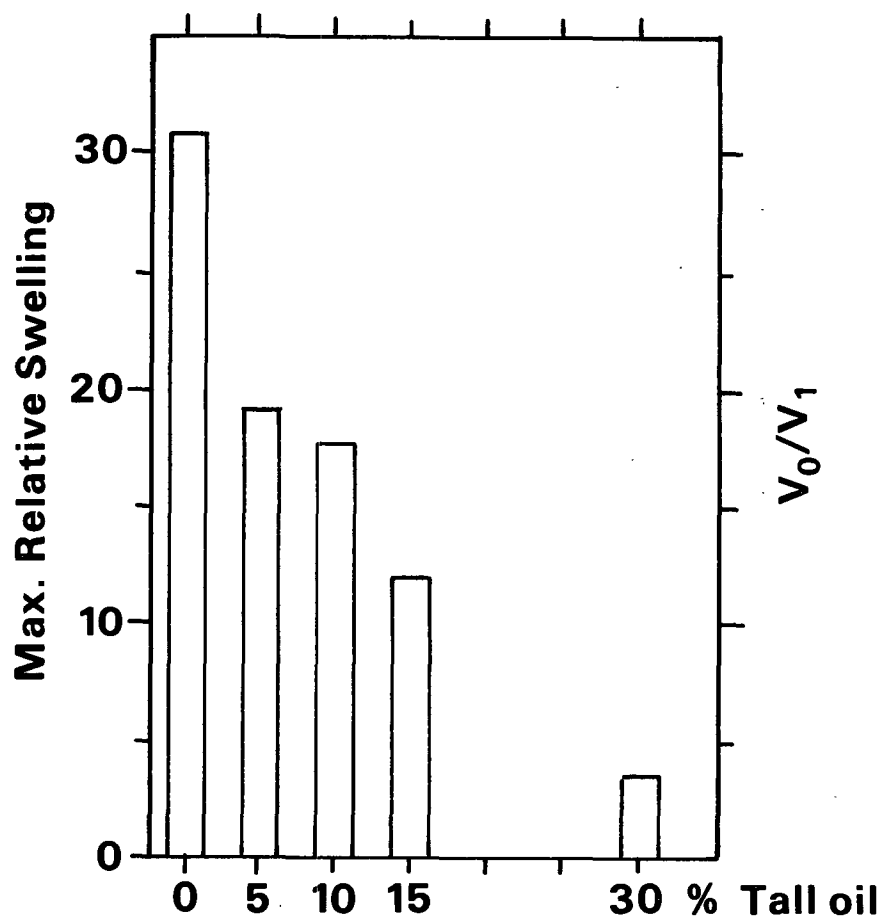
Figure 31. Influence of tall oil on black liquor swelling (800°C, 60% solids).[15]

Table 12 shows the swollen volume results of the spent liquor from holocellulose, precipitated kraft lignin, and a 1:1 mixture of the two components pyrolyzed at 400°C. The spent liquor from holocellulose produced the highest swollen volume under the conditions tested. Table 12 and Fig. 34 showed lignin did not swell significantly relative to the other mixtures tested. It was difficult to ascertain the importance of the swelling behavior of lignin/sugar acid mixtures because no other ratios of the components were presented.
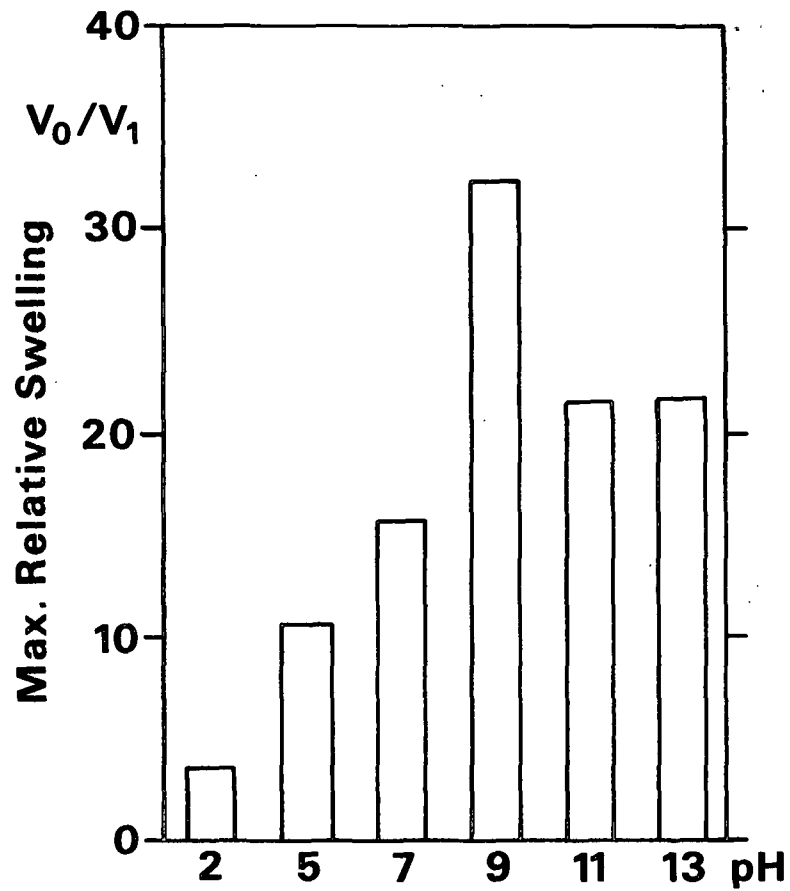
Figure 32. Influence of pH on black liquor swelling (800°C, 60% solids).[15]
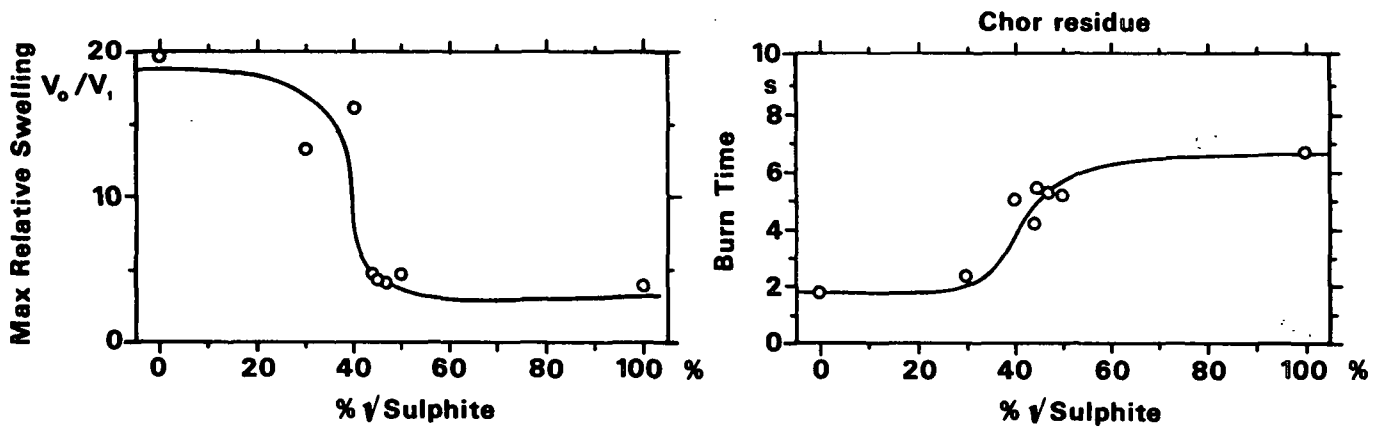
Figure 33. Burn time and swelling of kraft/sulfite mixtures.[15]

SUCROSE

SUCROSE + INDULIN C (2:1 MIXTURE)

INDULIN C
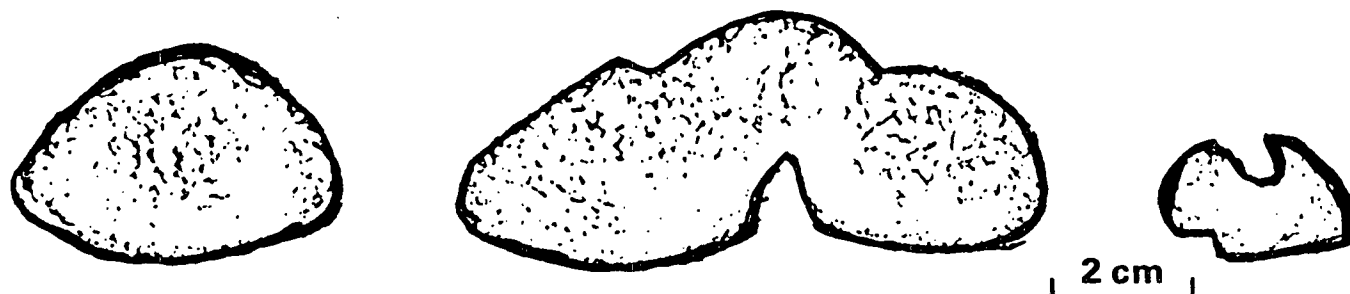
Figure 34. Swelling of sucrose, Indulin C, and a combination of the two substances heated at 400°C for 5 minutes.[72]

Table 12. Thermal properties of kraft liquors and their components.[72]

Tested Material	Activation Energy, E_a kJ/mol	Swollen Volume, V_{sw} cm^3/g
Kraft lignin	50	4
Alkalyzed kraft lignin	214	--
Kraft spent liquor solids from holocellulose	63	47
Mixture of liquor solids from holocellulose and alkalyzed kraft lignin (1:)	96	30
Kraft spent liquor solids	75	30

The main similarity between the swelling of black liquor and coal during pyrolysis was that the composition appeared to be the most important factor in determining the extent of swelling. The main difference between the swelling

behavior of the two materials was the temperature at which swelling was initiated. Dilatometer tests showed coal started to swell at approximately 420°C, while black liquor started to swell below 300°C. In dilatometer tests black liquor did not exhibit an initial contraction as coal did during heatup. More information is required on the swelling of both coal and black liquor to make more meaningful comparisons.

ANALYSIS OF PROBLEM

The swelling of kraft black liquor occurs to some extent before combustion commences and has been associated primarily with the pyrolysis phase of black liquor combustion. The pyrolysis of black liquor has not been as thoroughly studied as the pyrolysis of other complex organic materials.

Pyrolysis studies performed with organic materials such as wood, coal, lignin, and cellulose show many of the same characteristics. An increase in heating rate can decrease the char yield at relatively low heating rates (1-50°C/min). At heating rates between 270-10,000°C/s,[41,60] the heating rate did not have an effect on char yield. A decrease in the extent of secondary reactions was believed to be responsible for lower char yields at particle sizes below 100 microns. An increase in pyrolysis temperature results in lower char yields. The pyrolysis of black liquors should be affected by process conditions in a similar manner.

The pyrolysis of the organic components of black liquor occurs between 200-550°C. Both cellulosic and lignin materials yield chars which are predominantly polycyclic aromatic structures at 500°C. Black liquor would be expected to produce similar chars upon pyrolysis. The literature indicates that the components of lignocellulosic materials pyrolyze independently of one another. The components of black liquor would also be expected to pyrolyze independently of one another.

Some types of inorganic species can influence the pyrolysis of cellulosic materials significantly with respect to char yield but have a smaller effect on lignin pyrolysis. The sugar acids in black liquor are present in the form of

sodium salts. Only small amounts of salts, including sodium salts, were required to catalyze dehydration reactions which are largely responsible for the increased char yields upon pyrolysis of cellulosic materials. Due to the high concentration of inorganic materials initially present in black liquor, the addition of more sodium salts would not be expected to change the char yield upon pyrolysis.

Past studies of kraft black liquor swelling have predominantly been studied at 400°C and placed in muffle furnaces for periods ranging from 1.5-5.0 minutes. Under these conditions pyrolysis of the organic substances found in black liquor was not complete. The heating rates and the final temperatures were low compared to conditions found in a commercial recovery furnace. The pyrolysis literature of organic substances indicated that higher heating rates would yield different pyrolysis products. By studying the swelling process at higher heat fluxes and higher temperatures, the results could be applied toward understanding events occurring in a recovery furnace.

Some studies have focused on the particularly adverse effects on swelling of certain extractives associated with black liquors derived from selected tree species. These extractives, when added in small quantities, had rather large effects on the rheological properties of black liquors. Unfortunately the change in rheological properties measured at room temperature could not be correlated with the changes in swollen volume of black liquor chars upon pyrolysis. The literature suggested reduced swelling of black liquor resulted in black liquor exhibiting poor combustion characteristics.

The degree of black liquor particle swelling within a recovery furnace would also affect the flight paths of the particles. Black liquor chars which swell

excessively during combustion have a greater tendency to become entrained in air and deposit on the heat exchangers at the top of the recovery furnace. An excessive amount of carryover can lead to increased downtime. The potential exists for an optimum amount of black liquor swelling for the efficient operation of a recovery furnace. The swelling characteristics likely depend on both the liquor characteristics and the operating conditions of the recovery furnace. More information is required on black liquor swelling to determine the controlling factors of this phenomenon.

THESIS OBJECTIVES

A fundamental understanding of the factors which determine the extent of swelling in black liquor particles during pyrolysis does not exist. The objective of this thesis study was to investigate the swelling of kraft black liquor. Specifically, this study was to determine the key factors which are responsible for swelling under heating conditions that would approximate those of a commercial recovery furnace. The swelling of black liquor has been closely associated with pyrolysis; thus, the study of black liquor swelling was performed in a nitrogen environment.

The types of products which result from pyrolysis of black liquor particles probably have a large influence on the swelling behavior of black liquor particles. The pyrolysis products of black liquor are primarily determined by the manner of heating and by the black liquor composition. The manner of heating can be studied by changing the pyrolysis temperature and the heating rate of particles. The study of moisture content and particle size of black liquor can influence the heating rate of the particles and was included in the investigation. These variables were termed the process variables. The compositional variables to be studied were kraft lignin, sugar acids, extractives, and inorganic salts.

An additional objective of this study was to continuously monitor the pyrolysis gases evolving from black liquor particles. This should lead to a better understanding of the swelling process. Indirect volume measurements will also be required to monitor the temporal variations of black liquor swelling.

EXPERIMENTAL

The reactor used for this study allowed one to view the swelling of black liquor particles during evaporation and pyrolysis. The reactor is shown in Fig. 35. Details of the experimental apparatus, the experimental procedures, and the material preparation can be found in Appendix I. Black liquor particles were attached to a wire, which was connected to a microbalance. The particles were heated by flowing a hot nitrogen gas stream past a particle. Heat transfer occurred primarily by convection, with some radiative heat transmitted 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.

An optical port was available for viewing and taking photographs of the black liquor particles. Particle volume could be inferred from the projected area of the particle measured from photographs. The measured volumes of the particles were divided by the original dry weight of the particle. Char particles differing in particle size, moisture content, and pyrolysis temperature could be compared on the same basis. Gas samples were withdrawn continuously by a gas sampling line below the particle. Carbon dioxide, carbon monoxide, and water vapor were detected using infrared instrumentation. Data acquisition was performed by a microcomputer through analog/digital interface.

The process variables studied were the gas temperature, the heating rate, the initial solids content of the particle, and the particle size. The gas temperature was varied from 300-900°C. The heating rate was varied by changing the flow rate of the gas stream in the reactor while keeping the gas temperature constant. The heat flux to the particle could be approximately doubled by tripling the gas

flow rate. The initial solids content of black liquor was studied at five levels ranging from 65-100% solids. The particle weight was studied from 2-80 mg (1.36-4.65 mm in diameter).
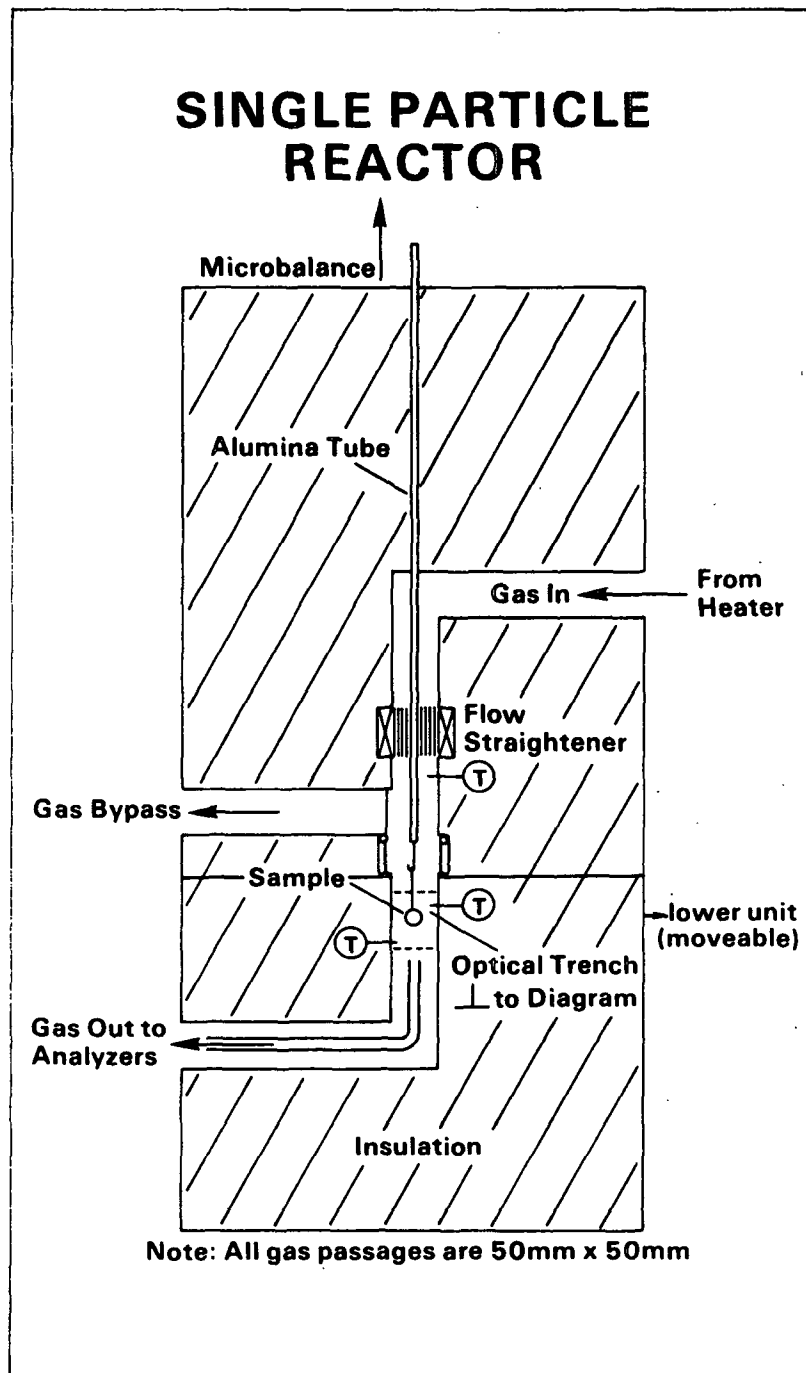
Figure 35. Schematic of single particle reactor.

The compositional variables studied were alkali lignin, sugar acids, inorganic salts, and extractives. The alkali lignin and sugar acids were isolated from the loblolly pine black liquor used during the study of the process variables. The isolation procedures resulted in acidic samples. Caustic was added to kraft lignin and sugar acids until a pH of 12 was reached. Sodium sulfate was the inorganic salt used in the experiments.

Extractives were obtained from loblolly pine chips by successive extractions using a benzene/ethyl alcohol mixture, ethyl alcohol, and water. Black liquor from cooks of extractive-free wood were also analyzed. Small bombs (60-80 g OD) were used to obtain black liquor for this portion of the study. Extractives were also added back to liquors derived from extractives-free wood.

Statistical analysis of the data can be found in Appendix II. All statistics given are at the 95% confidence level, unless specified otherwise.

RESULTS AND DISCUSSION

The process variables were studied first and will be discussed first. Black liquor obtained from a laboratory loblolly pine kraft cook was used for all the experiments involving the process variables. After the study of the process variables had been completed, the work was begun with the compositional variables. Most of the compositional work was performed at the process conditions which produced the highest swollen volume for black liquor. The swollen volume of black liquor particles should be the most sensitive to the effects of black liquor composition at these conditions.

PROCESS VARIABLES

Heating Rate

A change in gas flow rate (at constant gas temperature) was used to change the heat flux to the particle. In this way the heating rate of the black liquor particles could be changed qualitatively. The heat fluxes at various reactor conditions were measured by evaporating water from a small metal cup (6.3 mm in diameter) and recording the mass loss rate. The heat flux could be calculated from the mass loss rate. Details of the procedure and calculations can be found in Appendix I.

Table 13 shows the heat fluxes measured in the reactor at different gas temperatures and gas flow rates. The gas velocities were calculated at the center of the channel. Calculations revealed a laminar gas flow was present under the reactor conditions used in this investigation. The heat fluxes in a commercial recovery furnace varied from 90-160 kW/m^2, depending on the location at which measurements were taken.[73,74]

Table 13. Heat flux at various reactor conditions.

Gas Flow Rate, °C	833 cm³/s		2500 cm³/s	
	Heat Flux, kW/m²	Gas Vel., m/s	Heat Flux, kW/m²	Gas Vel., m/s
500	18	1.7	33	5.0
700	42	2.1	68	6.3
900	67	2.5	106	7.6

Tables 14 and 15 show the results of a factorial experiment with three variables tested at two levels. The gas flow rate, the gas temperature, and the initial black liquor solids content were the independent variables, and the maximum particle volume and the time required to reach maximum particle volume were the dependent variables. For all the tests, 40-45 mg (3.2 mm in diam.) particles were used.

Table 14. Effect of gas flow rate on swollen volume.

Gas Flow Rate % Solids	Swollen Volume (cm³/g initial solids)			
	833 cm³/s		2500 cm³/s	
	65%	100%	65%	100%
400°C	72	46	76	38
500°C	200	56	194	52

- Swollen volume ± 5 cm³/g (± 1 std. dev.).

The particle sizes found in a commercial recovery furnace vary over a wide range of diameters: 1-15 mm with an average size of between 3-4 mm; thus the particle sizes studied represent an average particle in a recovery furnace. The data represent an average of two replicates. Details of the statistical analysis of the data can be found in Appendix II.

Table 15. Effect of gas flow rate on time to maximum volume.

| Gas Flow Rate | Time, s | | | |
| | 833 cm³/s | | 2500 cm³/s | |
% Solids	65%	100%	65%	100%
400°C	65	48	48	32
500°C	38	29	28	22

- Time ± 1 s (± 1 std. dev.).

The three variables affected the time to reach the maximum swollen volume at the 95% confidence level. Temperature, moisture content, and the interaction of these two variables affected the final swollen volume (99% confidence); heating rate did not have a significant effect on the final swollen volume attained. The other variables were not significant. The gas flow rate (heating rate) had the effect of changing the time to maximum volume but not the maximum volume attained (effectively changing the swelling rate). This behavior was found to occur throughout the range of conditions attainable on the reactor (833-2500 cm³/s, 300-800°C).

Particle Size

The effect of particle size on the swollen volume is shown in Table 16. The mean and standard deviation of 9 tests performed at a standard size of 40 mg are also given. The particle size did not have a major influence on the swollen volume of the particle.

One effect of decreasing the particle size is to increase the heat flux to the particle. The heat flux has already been shown not to have an effect on the maximum particle volume. The results from analyzing differences in particle size and heating rate indicated the rate at which the volatiles were leaving the particle did not influence the extent of swelling at the tested conditions.

Table 16. Effect of particle size on the normalized swollen volume.

Black Liquor		Time to Max. Vol., s	Vol., cm^3/g
wt., mg	diam., mm		
2	1.36	2.5	92
2	1.36	3.0	61
4	1.71	4.5	88
5	1.85	4.0	64
8	2.16	6.5	69
11	2.41	6.5	85
13	2.54	--	71
20	2.93	8.0	48
21	2.98	8.0	63
40	3.69	13.0 ± 1.3[a]	68 ± 20[a]
48	3.92	14.5	61

[a]Average ± 1 standard deviation.
Conditions: 65% solids, 700°C, 1666 cm^3/s gas flow rate.

Temperature

The effects of pyrolysis temperature and black liquor solids content are shown in Fig. 36. For a given solids content, maximum swelling occurred at approximately 500°C. The pyrolyzing black liquor appeared to be most fluid at 500°C. Figure 37 depicts the apparent fluidity changes of black liquor pellets during pyrolysis. Dry black liquor was tested in the form of pellets. At 300°C, the pellets swelled but retained their original cylindrical shape, indicating the material was not very deformable. When pyrolyzed at 500°C, the pellets were transformed into spheres, which indicated a more deformable material. Tars begin to form at approximately 360°C; the formation of tars could explain the

increase in deformability of the pyrolyzing black liquor between 300-500°C. The
pellet forming process was found to lower the swollen volumes of black liquor
chars, thus pellets were not used in subsequent experiments.
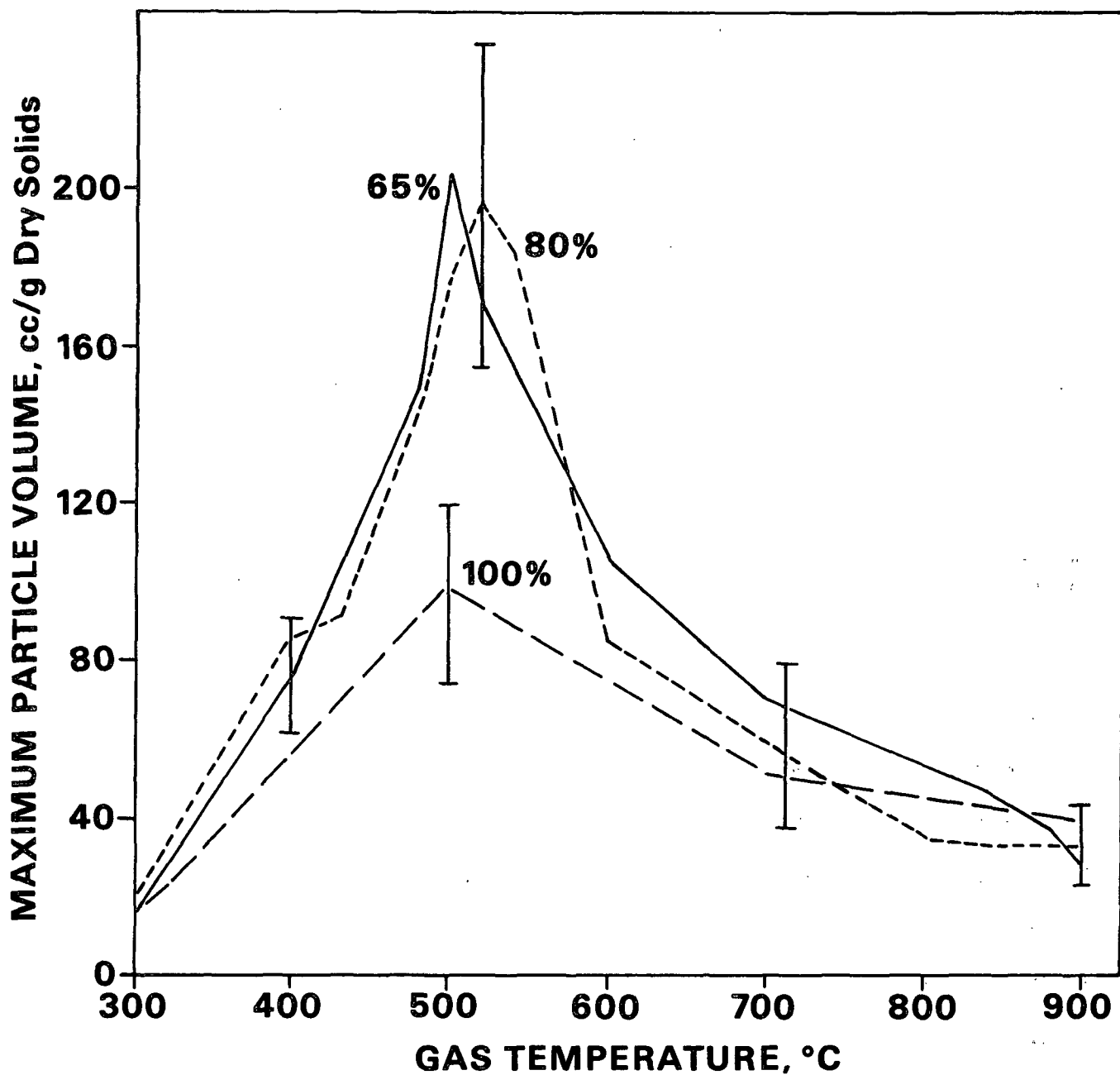
Figure 36. Maximum particle volume vs. gas temperature for 65, 80, 100%
           solids black liquor. Brackets indicate ± 1 std. deviation.

300°C   500°C

Scale: |————————|
                1 cm
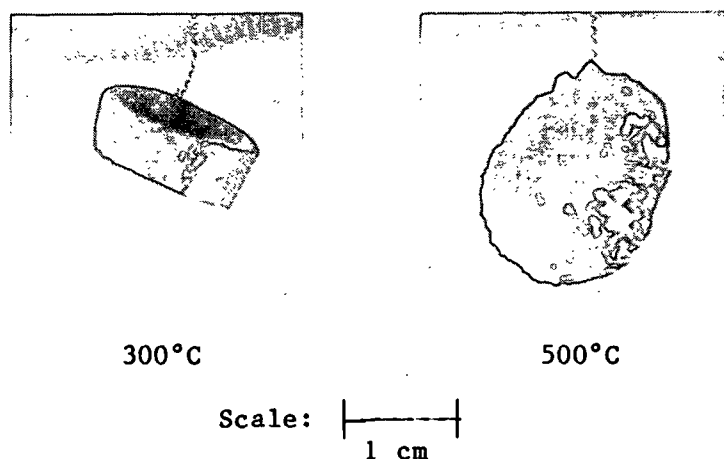
Figure 37. Photographs of black liquor pellets (40 mg) pyrolyzed at
            300 and 500°C.

The changes in volume with respect to time are shown in Fig. 38 at three

different temperatures for black liquor at 80% solids. The evolution of carbon

dioxide with time for three particles at different temperatures is shown in Fig.

39. The evolution of carbon dioxide is a good indicator of pyrolysis activity.

The evolution of carbon monoxide was also monitored and traced a curve similar

to that of carbon dioxide. The carbon monoxide curves were found in smaller

quantities and for clarity were omitted from Fig. 39. The region at which rela-

tively large swelling rates (> 1 cm^3/s) were found is indicated by the shaded

areas below the curves in Fig. 39.

Figures 38 and 39 reveal certain features of the swelling process. Figure

39 reveals that the evolution of pyrolysis gases determines the duration of the

swelling process. The swelling began and ended approximately at the same time

the pyrolysis gases began and ceased to evolve. Thus, the black liquor char was

deformable throughout the pyrolysis of black liquor. These same trends occurred

independent of the pyrolysis temperature (500-900°C).
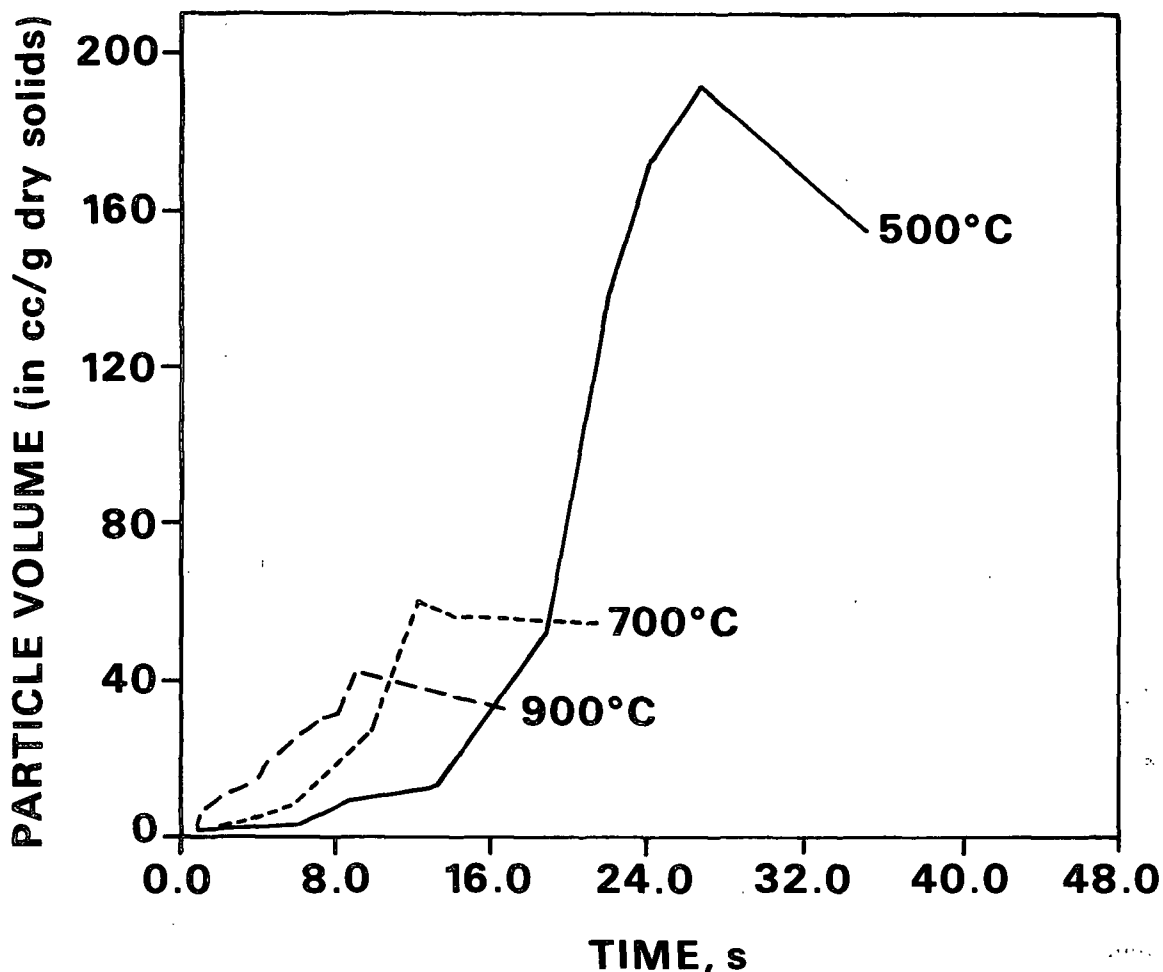
Figure 38. Particle volume vs. time at different temperatures
(80% solids, 40 mg).

Figure 38 shows that the swelling rate during pyrolysis decreased as the tem-
perature was increased between 500 and 900°C; this occurred despite the increased
volume of pyrolysis gases evolved at higher temperatures. The rate at which pyrol-
ysis gases evolved from black liquor particles was shown earlier not to have an
effect on the maximum particle volume. The heat flux at 700°C and a high flow
rate was similar to the heat flux at 900°C and a low flow rate (Table 13), but
the swollen volumes of the black liquor chars were different. These observations
indicated the pyrolysis temperature was more important in black liquor swelling

than the rate of heat transfer to the particle. Changes in the deformable properties of black liquor appeared to be responsible for the different swollen volumes measured. Very little is known about the changes in char structure resulting from the pyrolysis of lignocellulosic materials above 500°C. Although only a small amount of volatiles are formed between 500 and 900°C, significant changes in the char structure occur which could influence the deformable properties of the char.
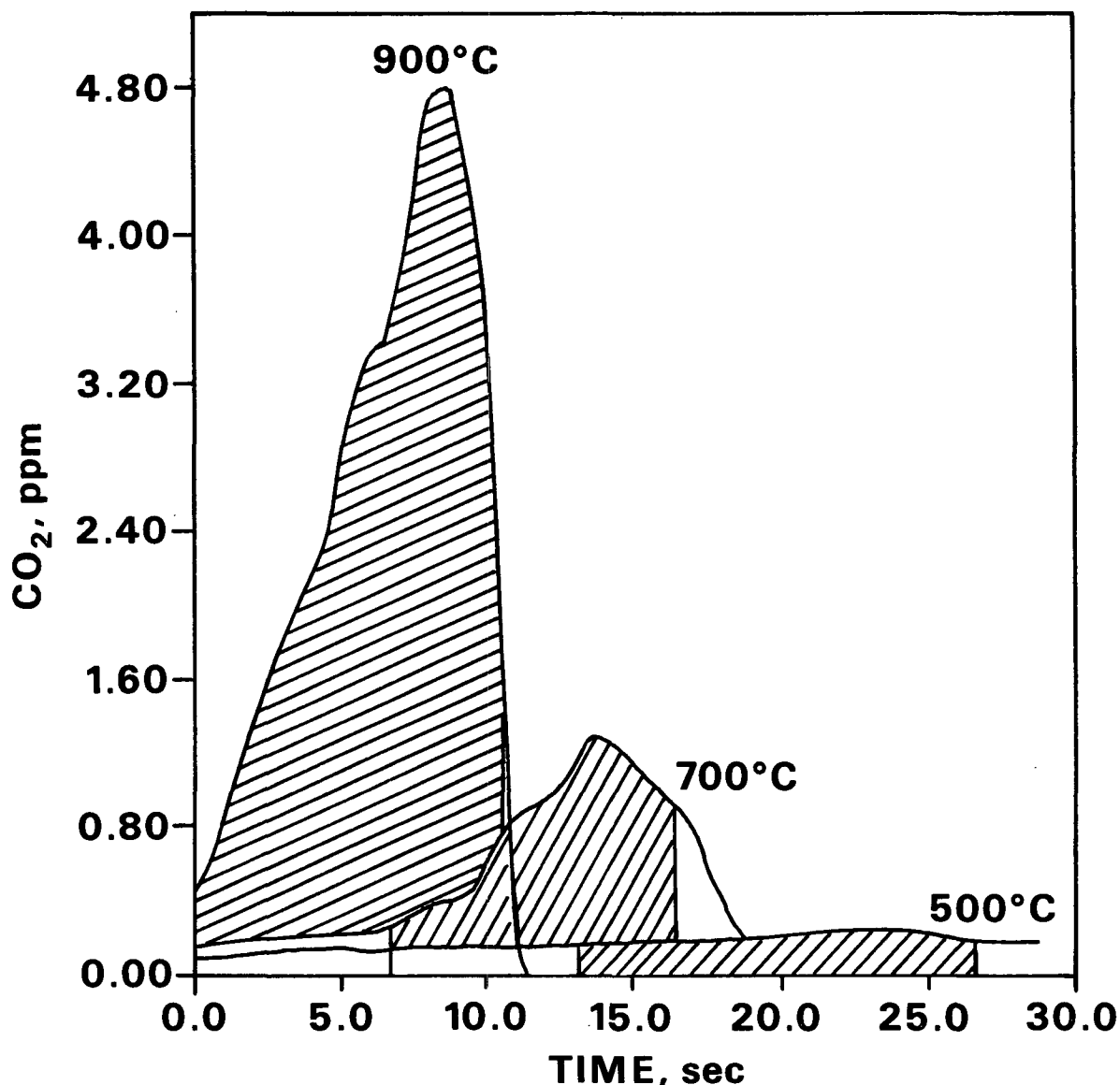
Figure 39. Carbon dioxide concentration of gas stream below the particle as a function of time (80% solids, 40 mg). The shaded portion indicates swelling rates greater than 1 cm^3/g-s.

Moisture

The moisture content is an important variable in the combustion of black liquor. Efforts are being made to increase the percent solids going to the recovery furnace. A higher percent solids would decrease the energy consumption in a recovery furnace. Black liquor was studied in this investigation from 65% to 100% solids content.

At the beginning of this study, dry black liquor was ground with mortar and pestle and formed into small pellets (6.35 mm in diam.) with a pellet press. Dry samples of black liquor were obtained by placing liquor samples in an oven at 140°C under nitrogen. A test was run to determine to what extent these factors affected the black liquor swelling during pyrolysis.

Table 17 shows the results of four samples (all near 100% solids) pyrolyzed at 500°C. The particle sizes ranged between 2.9-3.9 mm in diameter (20-50 mg). The "ground" samples refer to samples ground with mortar and pestle. The single particles were broken off a large piece of dried black liquor.

Table 17. The swollen volume of four different 100% solid samples (average of 4 replicates).

| Physical State | Drying Temperature | | | |
| | 140°C | 100°C | | |
	Ground	Ground	Single Particle	Pressed Pellet
Vol., cm^3/g	72	103	103	69

Least significant difference (LSD) - 26 cm^3/g (averages differing by 26 or more are significantly different).

The results showed that the black liquor should be dried at 100°C under nitrogen. The pellet making process should not be used in studies involving the swollen volume of black liquor particles. An explanation of the least significant

difference (LSD) statistic with a sample calculation is given in Appendix II. The replicate test results and the analysis of variance tables are also presented in Appendix II.

The black liquor samples in Table 17 were pyrolyzed in small metal cups. The use of metal cups became necessary for the pyrolysis of the different fractions of black liquor. The metal cups restricted the swelling somewhat by forcing the swelling to occur against the flowing nitrogen gas stream; this tended to reduce the amount of swelling. A number of samples were run with and without the metal cups. The cups appeared to affect all the samples in the same manner. An example is presented in Table 18. The variability of the swelling data appeared to be reduced by pyrolyzing black liquor in the metal cups.

Table 18. The influence of specimen holders on swollen volume
(average of three replicates).

% Moisture	Swollen Volume cm^3/g Dry Solids			
	86%	73%	65%	
Pyrolysis in cups	68	113	121	LSD-17 cm^3/g
Pyrolysis w/o cups	85	124	142	LSD-43 cm^3/g

Preliminary results for the effect of solids content on swollen volume were shown in Fig. 36. The 80% solids mixture was a combination of the 65 and 100% black liquor samples. Figure 36 shows that moisture influences swelling between 80 and 100% solids, but not between 65 and 80% solids. The moisture had a significant effect on swelling between 400 and 700°C. The effect of moisture content was more critically analyzed when an infrared water vapor meter became available later in the study.

During the study of the black liquor composition it became evident that the extractives, including soaps, significantly lowered the swollen volume of black

liquor. The removal of soaps by skimming of black liquor was a rather imprecise method of soap removal. The samples tested in Fig. 36 did not come from the same batch of skimmed black liquor; therefore, differences in soap content may have existed. The black liquor samples in Tables 19 and 20 came from the same batch of skimmed black liquor; therefore, the soap contents of the black liquor samples were presumed to be identical.

A large sample of black liquor was evaporated at 100°C under nitrogen and 95 kPa vacuum. Small samples were taken out periodically to obtain samples at different solid contents (65, 73, 86, and 96% solids). The remaining sample was dried overnight to obtain a 100% solids black liquor. The samples took on three distinct rheological characteristics. The 65 and 73% liquors were a very viscous liquid. The 86% liquor was a hard tarry substance. The 96 and 100% solids were a porous solid, having lost any tarry characteristics.

The five black liquor samples differing in initial solids content were pyrolyzed at 500°C with the results shown in Table 19. The results indicated that the 65 and 73% black liquors swelled more than the 96 and 100% black liquors which swelled more than the 86% black liquor.

Table 19. The effect of initial solids content on swollen volume. Pyrolysis at 500°C in small metal cups (average of 3 replicates).

% Solids	65%	73%	86%	96%	100%
Vol., cm^3/g	121	113	68	95	87

LSD, 17 cm^3/g

Least significant difference (LSD) - 26 cm^3/g (averages differing by 26 or more are significantly different).

Subsequent results which are shown in Table 20 indicated that there were no significant differences in the swollen volumes of the 86 and 100% solids black liquors. The 65% solids black liquor was significantly different from the 86 and 100% samples at 500°C and 700°C at the 99% confidence level based on a t test between means. The hypothesis that the three samples in Table 20 gave the same swollen volumes at 900°C could not be rejected at 90% confidence.

Table 20. The effect of initial solids content and temperature on swollen volume (average of 3-5 replicates).

| % Solids | Swollen Volume, cm^3/g | | |
Temperature	65%	86%	100%
500°C	196 ± 33	114 ± 14	90 ± 24
700°C	97 ± 19	50 ± 13	52 ± 10
900°C	48 ± 12	35 ± 7	40 ± 8

± one standard deviation

Steam was added to the nitrogen gas stream to determine if steam could promote swelling in dry black liquor solids pyrolyzed at 500°C. The steam/nitrogen mixture was in a 1:1 ratio on a volume basis. The particles pyrolyzed in nitrogen gave a mean maximum particle volume of 46 ± 7 cm^3/g (± one standard deviation) and the steam/nitrogen mixture gave a maximum particle volume of 53 ± 4 cm^3/g. The addition of steam to the nitrogen gas, used to pyrolyze black liquor particles, did not produce a significant effect on the maximum volume attained for black liquor during pyrolysis.

The analysis of water vapor evolution from pyrolyzing black liquor particles revealed changes in pyrolysis activity between black liquor samples differing in initial solids content. The profiles of carbon dioxide and water vapor evolution

during pyrolysis of three black liquor particles differing in initial solids
content are shown in Fig. 40.
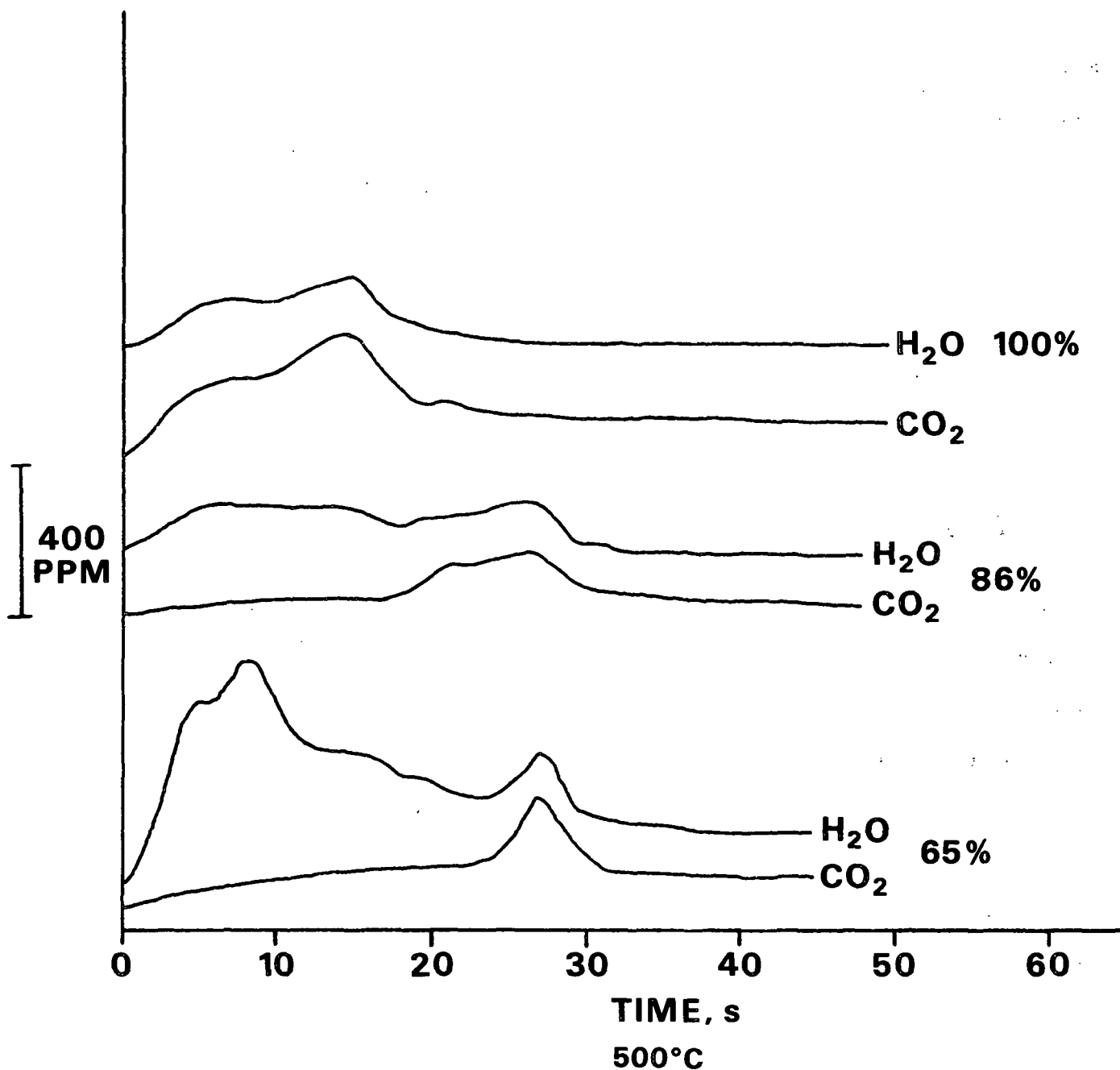
Figure 40. The water vapor and carbon dioxide evolution curves of
black liquor particles at 65, 86, and 100% initial
solids (500°C, 30-35 mg).

Viscous black liquors (< 80% solids) went through a rapid evaporation phase before the occurrence of significant swelling during pyrolysis. The evaporation phase consisted of rapid swelling (< 2 times the original volume) and contractions of black liquor droplets. During this evaporation period a relatively large amount of water was evolved, which was indicated by the large water vapor peak (in the absence of pyrolysis gases) early in the process for the 65% black liquor droplets. The 86% solids black liquor particles did not go through a dynamic evaporation stage; instead, the water vapor was given off more slowly, which was indicated by the broad water vapor peak. These differences in evaporation behavior occurred at 500 and 700°C; at 900°C, evaporation and pyrolysis occurred simultaneously and there appeared to be no differences in the evaporation behavior of black liquor particles differing in initial solids content.

Figure 40 indicated the pyrolysis of black liquor at 86% solids was slower than black liquor at 65% solids. The broad water vapor peak for the 86% solids curve shows some moisture may have been retained as the particle began to pyrolyze. This would result in a lower internal temperature and a slowing of the pyrolysis rate. Cantrell[75] studied the sulfur dioxide release during black liquor pyrolysis and also found differences in the pyrolysis activity of black liquor differing in initial solids content. A minimum for the first order reaction rate constant of sulfur dioxide release from black liquor during pyrolysis was found between 60 and 100% solids at about an 84% initial solids content.

Figure 41 shows the particle volume versus time for four particles differing in initial percent solids. Shrinking of the chars from black liquor at 65 and 80% solids content can be seen in Fig. 41; shrinking also occurred for chars of black liquor at the 86 and 100% initial solids content, but the behavior was not

documented. The chars from 86 and 100% solid black liquor did not attain the high swelling rates of the chars from 65 and 80% black liquors. The results indicated that mildly drying black liquor to solids contents above 80% influenced the drying and pyrolysis behavior of black liquor when heated between 400 and 700°C.
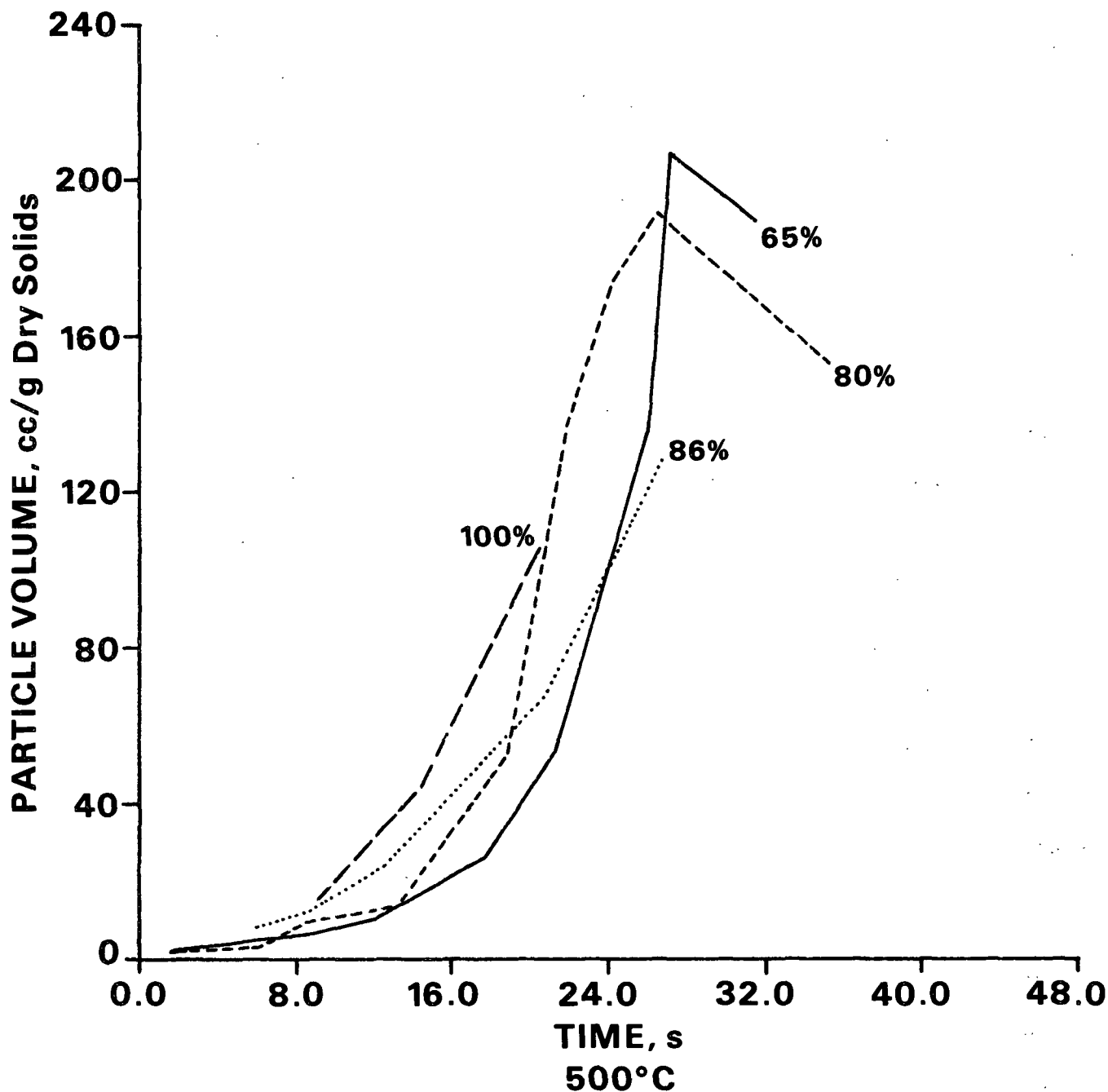
Figure 41. Particle volume vs. time for black liquors varying in initial solids content (500°C, 30-40 mg).

The chars formed from the pyrolysis of black liquors differing in initial solids content were investigated further with a CP/MAS ^{13}C NMR spectrometer in an attempt to determine whether any structural characteristics of the chars would correlate with the swollen volumes of the chars. Table 21 shows the corrected intensities of the major structural groups present in the chars. X1 and X2 represent two different tests at different ranges of the spectrometer (X1, 300 to -100 ppm; X2, 220 to -30 ppm). Details of the procedure and sample calculations can be found in Appendix I. For the discussion, 86C will be used to designate char pyrolyzed from an 86% solids black liquor particle.

Table 15. Structural intensities calculated from CP/MAS ^{13}C NMR spectra of chars resulting from black liquor pyrolyzed at 500°C.

% Solids	65%		73%		86%		100%	
Vol., cm3/g	121		113		68		87	
Corr. Int.	X1	X2	X1	X2	X1	X2	X1	X2
Carboxyl	10.2	10.2	11.3	11.3	8.5	7.8	8.8	8.4
Aromatic	59.4	63.3	57.7	63.2	62.1	68.4	58.4	63.7
Aliphatic	29.9	31.2	30.3	30.3	29.0	29.5	32.1	32.6

The aliphatic content did not vary significantly between the chars. The aromatic content was higher for the 86C than the other chars. The 86% solid black liquor pyrolyzed more slowly during pyrolysis than the other black liquors. A slower pyrolysis implies a lower internal particle temperature or a lower heating rate, either of which would produce more char and could be responsible for the higher aromatic content of the 86C. Analysis of the chars as they progress through evaporation and pyrolysis may provide more detailed explanations for the observed behavior.

The carboxyl content of the chars correlated with the swelling of the chars. The higher swelling chars (65C and 73C) had higher carboxyl contents 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 mainly to the sugar acids in black liquor. The carboxyl groups thermally decompose at relatively low temperatures and would not be expected to be present in chars pyrolyzed at 500°C. The chars obtained for the analysis with NMR were quenched with nitrogen at room temperature immediately after attaining maximum volume; the pyrolysis of the organic materials was not complete at this point. The pyrolysis runs were also conducted without preheating the surrounding reactor walls, which facilitated the quenching.

During the evaporation of black liquors to higher solids contents, subtle changes may have occurred in black liquor which resulted in lower evaporation rates of high solid black liquors (86%). The lower evaporation rates in turn may have influenced pyrolysis at relatively low temperatures (400-700°C). At higher temperatures (> 700°C) the evaporation and the pyrolysis of black liquor occurred at the same time. The result was no difference in the swelling behavior of black liquor differing in initial solids contents.

The influence of the initial percent solids on the swelling behavior of black liquor during pyrolysis was relatively small. From a practical standpoint, the slower evaporation and pyrolysis at initial solids contents around 85% may be of more concern than any differences in swelling.

The Relationship Between Pyrolysis Gas Evolution and Swelling

The pyrolysis gases have been shown (Fig. 39) to evolve during the approximate period of swelling for all the conditions tested. One of the main goals of

this thesis was to better define the relationship between the evolution of pyrolysis gases and the swelling of pyrolyzing black liquor particles.

Figure 42 shows the carbon dioxide profile with time for a pyrolyzing black liquor particle. The time at which photographs were taken during the swelling process is indicated in the figure by vertical dashed lines with the swollen volume indicated above them. The area under the curve between photographs represents the amount of carbon dioxide evolved during this time period. Data obtained from a number of particles were analyzed to determine whether a relationship existed between the amount of gases evolved and the change in particle volume. Figure 42 shows that this relationship could be tested during the pyrolysis of a single particle. Figure 43 shows that there was no correlation found between the amount of gas given off and the increase in swollen volume for a number of particles analyzed at 500°C. There was also no correlation at 700°C or 900°C. A plot of this relationship for 500, 700, and 900°C is shown in Fig. 44.

The plot shows that the temperature has a more important effect on particle swelling than the amount of pyrolysis gases evolved from the particle. The relationships are opposite from what would be expected if swelling was controlled by the amount of pyrolysis gases evolved.

There was a high degree of variability in the swollen volume for a given set of experimental conditions. This variability could not be explained by the gas evolution profiles, as there was no correlation between swollen volume and either the duration of the pyrolysis or the area under the significant swelling portion of the carbon dioxide curve. Figure 45 shows that the variability occurs near the end of the swelling process. A cross section of a black liquor particle pyrolyzed at 700°C is shown in Fig. 46. The variability occurred near the end

of the pyrolysis most likely as a result of nonuniformities in the developing char structure during pyrolysis.
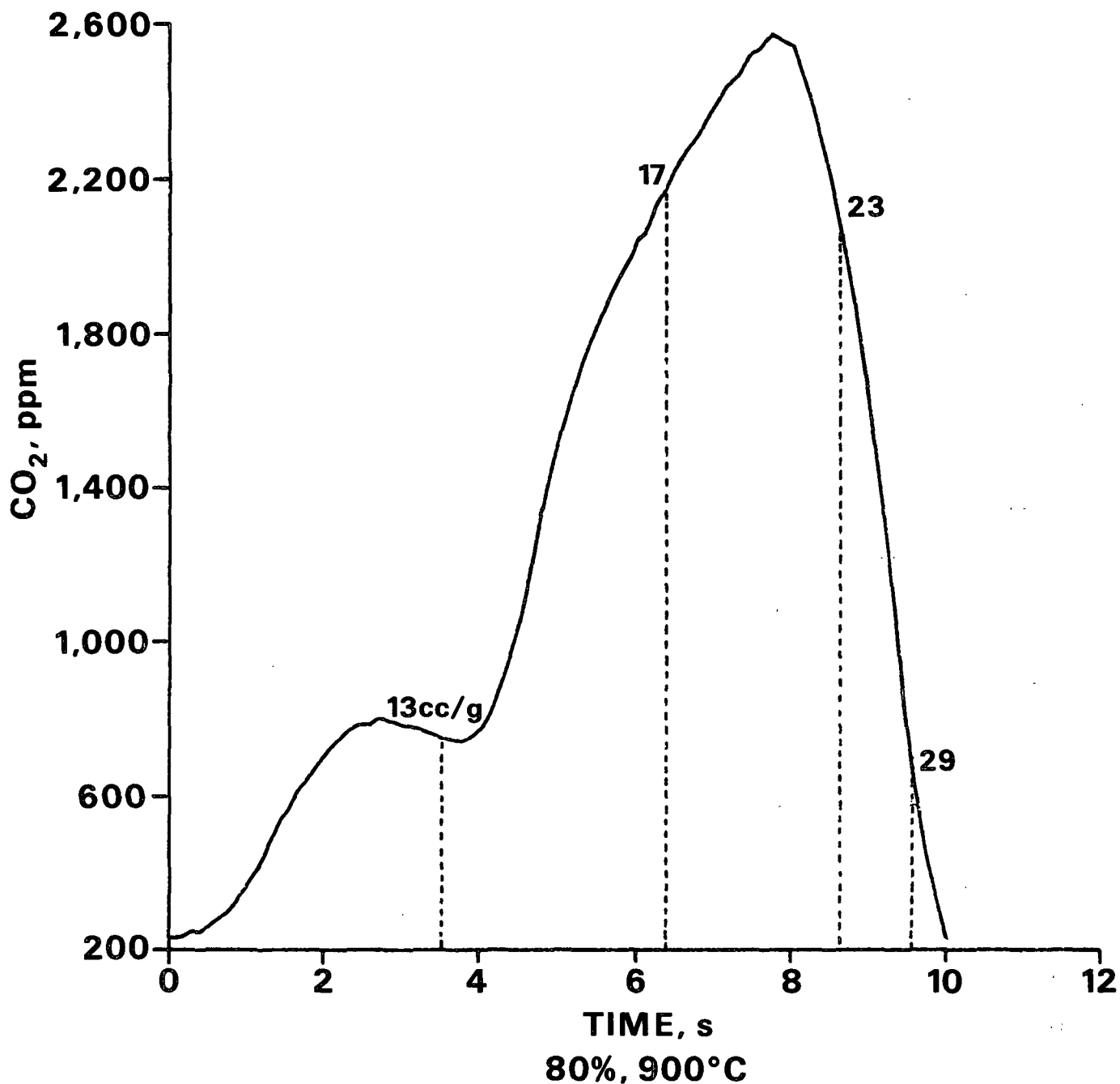
Figure 42. Carbon dioxide profile of a black liquor particle with photographs indicated by dashed lines. The volume of the particle, at the time the photograph was taken, is indicated above the dashed lines (80%, 900°C).
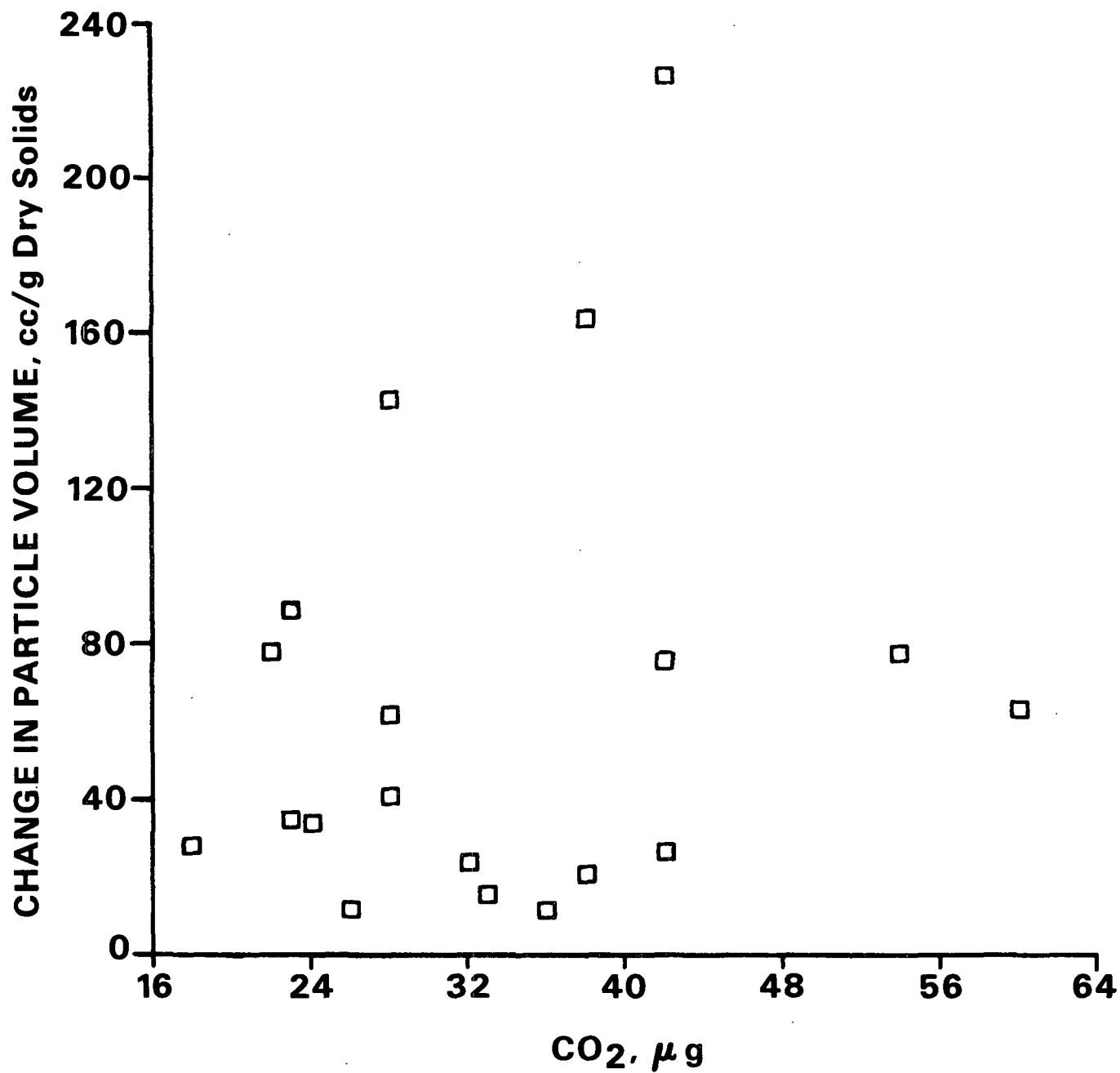
Figure 43. Change in particle volume vs. amount of carbon dioxide evolved at 500°C.
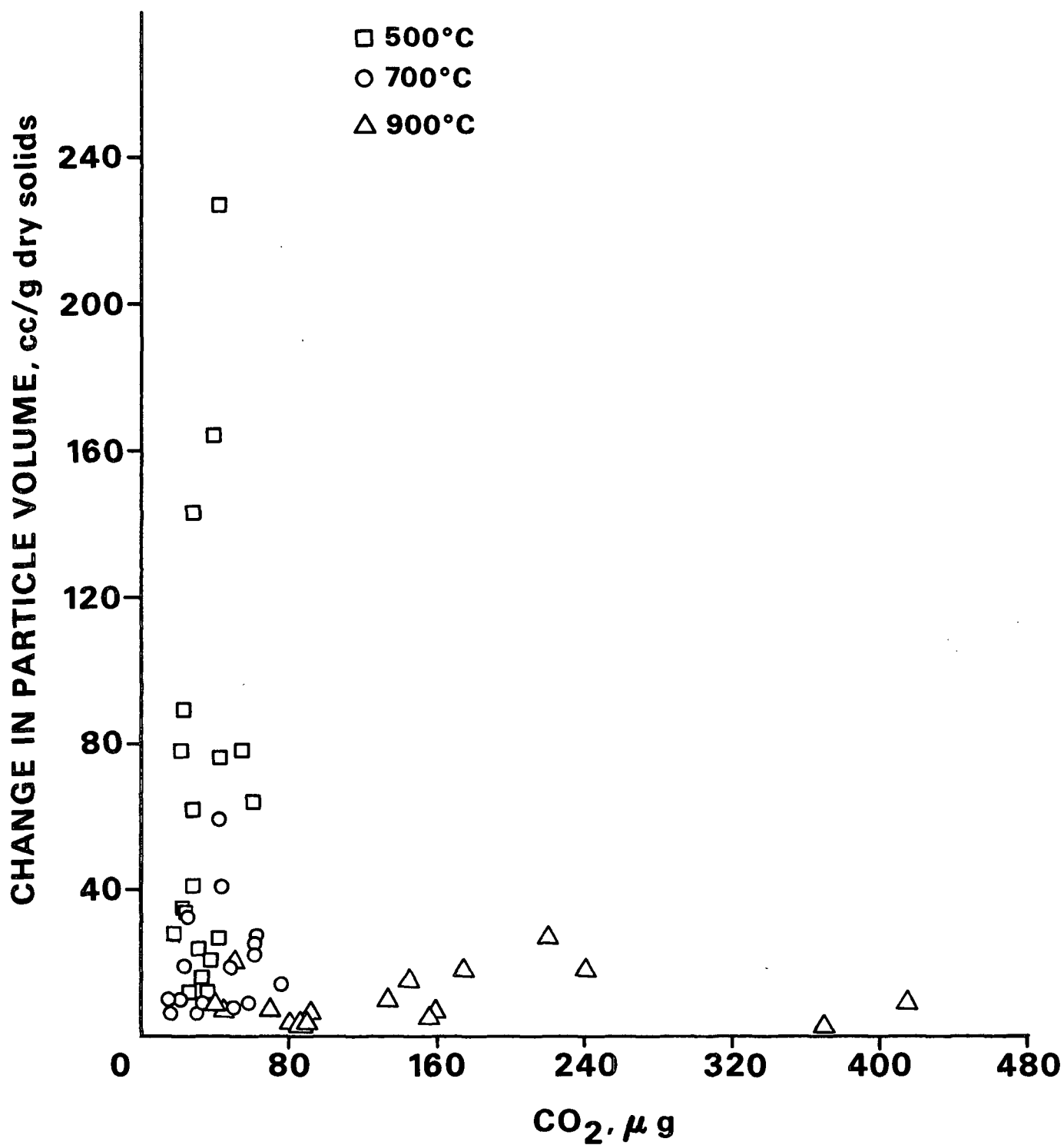
Figure 44. Change in particle volume vs. amount of carbon dioxide
evolved at 500, 700, and 900°C.
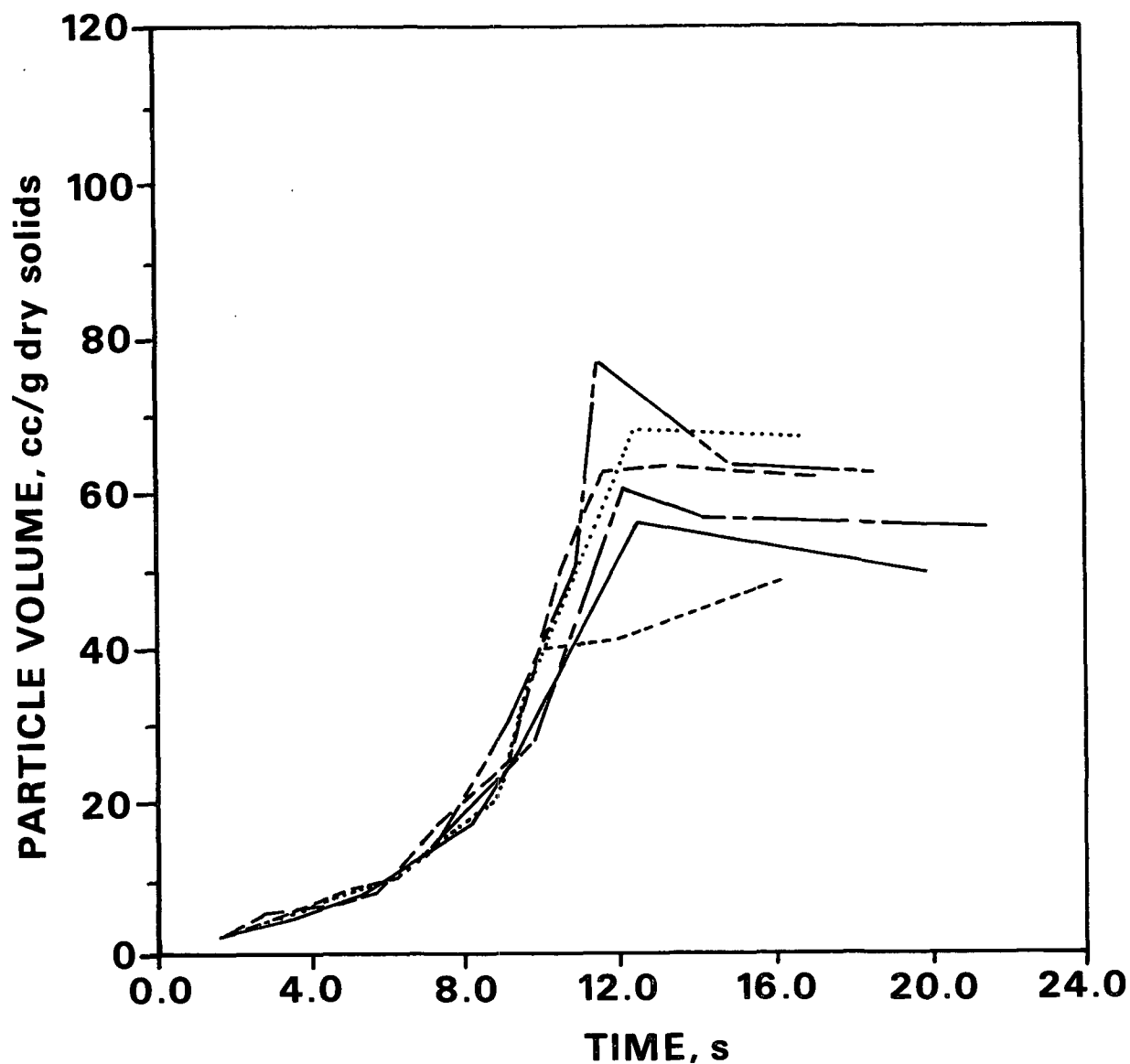
Figure 45. Particle volume vs. time (80%, 700°C, 40-45 mg).

The results indicated that swelling occurred primarily during pyrolysis;

however, the amount of pyrolysis gases did not determine the extent of swelling.

The data indicated the deformable characteristics of the pyrolyzing char most

likely determined the extent of swelling. The composition of black liquor was

studied to further investigate this hypothesis.

Scale ├──┤

Figure 46. Photograph showing a cross section of a black liquor
particle (700°C, 100%).

COMPOSITIONAL VARIABLES

Kraft black liquor is composed of four main types of components: kraft

lignin (KL), sugar acids (SA), extractives, and inorganics. The four components

were studied to determine their role in the swelling of black liquor during

pyrolysis. Inorganic salts were used for the inorganic portion of this study.

No attempt was made to change the organically bound inorganic species in this

study. The kraft lignin was obtained by precipitation with acid and filtration

from the black liquor. Sugar acids were isolated from the filtrate. The

extractives were separated from loblolly pine by TAPPI standards. Details of

all the procedures can be found in Appendix I.

The solutions of kraft lignin and sugar acids prepared by the addition of

caustic were dilute (20-40%). The kraft lignin samples had high viscosities, as

the solutions approached 40% solids. During the study of the compositional variables, the dilute solutions were pyrolyzed in small metal cups. At 500°C evaporation and pyrolysis occurred as separate processes. Studying the components of black liquor at low initial solids content was assumed not to have an effect on the swelling behavior of these components. This hypothesis was tested by pyrolyzing a 20% solution of black liquor in a metal cup. The swollen volumes of these chars were comparable to the swollen volumes of chars pyrolyzed from a 65% solids liquor in metal cups at 500°C.

An initial factorial experiment was performed with kraft lignin, sugar acids, and inorganic salts. The extractives vary widely in content and composition between species and were investigated separately. The objective of the initial test was to determine what interactions were responsible for the swelling of kraft black liquor. The components of black liquor were mixed in roughly the same ratio as found in black liquor (KL:SA:IN, 4:3:2). The results are shown in Table 22. The 65% solids black liquor used in studying the process variables was tested and used as a reference.

Table 22. Factorial experiment with kraft lignin, sugar acids, and inorganics. Tested in metal cups.

	Vol., cm^3/g
Black liquor (65%)	94
SA:KL, 3:4	100
SA:KL:IN, 3:4:2	60
SA	24
KL:IN, 2:1	19
KL	17
SA:IN, 3:2	4
IN	~ 0

Conditions: 500°C, 1666 cm^3/s, KL - kraft lignin, SA - sugar acid,
IN - solution of Na_2CO_3, Na_2SO_4, Na_2S, and $Na_2S_2O_3$.

The results clearly indicated that there was a large synergistic effect between the sugar acids and the kraft lignin to produce chars with large swollen volumes. The inorganics decreased swelling. The swelling of kraft lignin, sugar acid and mixtures of the two will be discussed first, followed by the inorganics, and then the extractives.

Swelling of Kraft Lignin, Sugar Acids, and Their Mixtures

The isolated forms of kraft lignin and sugar acids were acidic; to simulate kraft black liquor the pH of the sugar acid and kraft lignin solutions were adjusted separately to levels between 10.5 and 13.0 by the addition of 1N NaOH. The solutions were then mixed together.

Figure 47 shows that the effects of changing the relative amounts of kraft lignin and sugar acids on swelling at pH 10.5, 12.0, 13.0. The changes in pH over this range would primarily affect the ionization of the kraft lignin molecules. The highest swelling occurred when the kraft lignin was fully ionized at pH 12 for a 1:1 KL/SA ratio. At pH 10.5 some of the higher molecular weight lignin would precipitate out; the swelling was generally lower for these liquors. Increasing the pH to 13 did not significantly influence swelling, which indicated the sodium hydroxide was not directly involved in the swelling mechanism. The effects of pH on swelling were relatively small and were not studied further.

Table 23 shows the swollen volumes of chars for the kraft lignin, sugar acids, and a 1:1 mixture pyrolyzed at 900°C. The results were similar to what occurred at 500°C, i.e., the 1:1 mixture produced higher swollen chars than either component pyrolyzed separately.

The carbon dioxide evolution curve during the pyrolysis of a kraft lignin particle is shown in Fig. 48. There were two photographs taken, the first during the evaporation of water and the second during pyrolysis. The photographs are

indicated in the figure by dashed lines with the swollen volumes above them. The solid line between the two photographs indicates the point at which the kraft lignin solidified. This point was recorded by activating the camera switch without taking a photograph. The poor swelling ability of the kraft lignin fraction of black liquor was explained by the lack of deformability of the material during the evolution of pyrolysis gases.
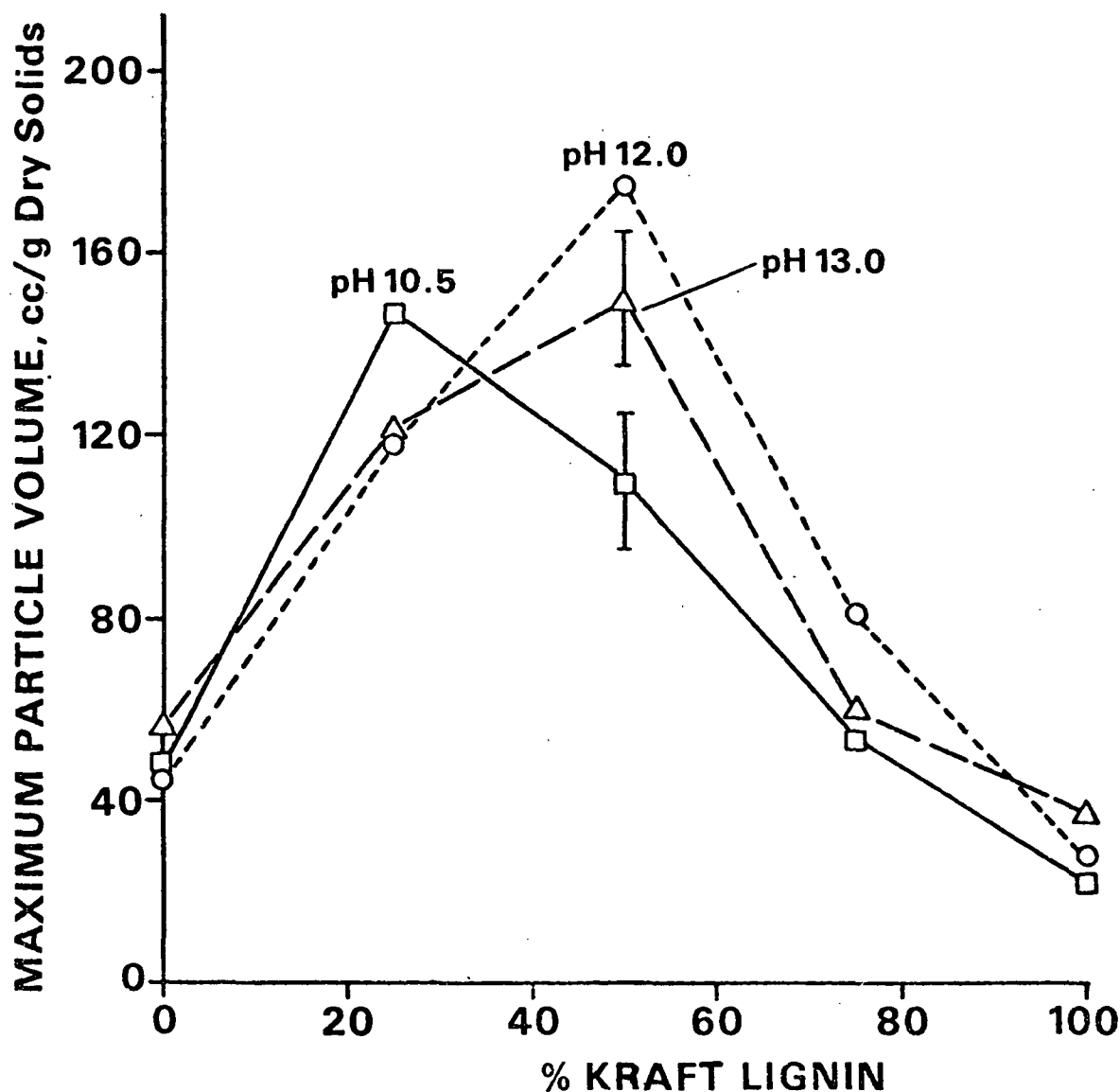
Figure 47. Maximum particle volume of kraft lignin/sugar acid mixtures at different pH (500°C). Brackets indicate 95% confidence interval. Typical softwood black liquor has a 3/2 kraft lignin to sugar acid ratio.

Table 23. Swelling at 900°C of SA, KL, and a mixture of
the two components (average of four replicates).

	SA	KL	1:1 KL/SA
Vol., cm^3/g	22	23	68

LSD - 15 cm^3/g

Least significant difference (LSD) - 26 cm^3/g (averages
differing by 26 or more are significantly different).
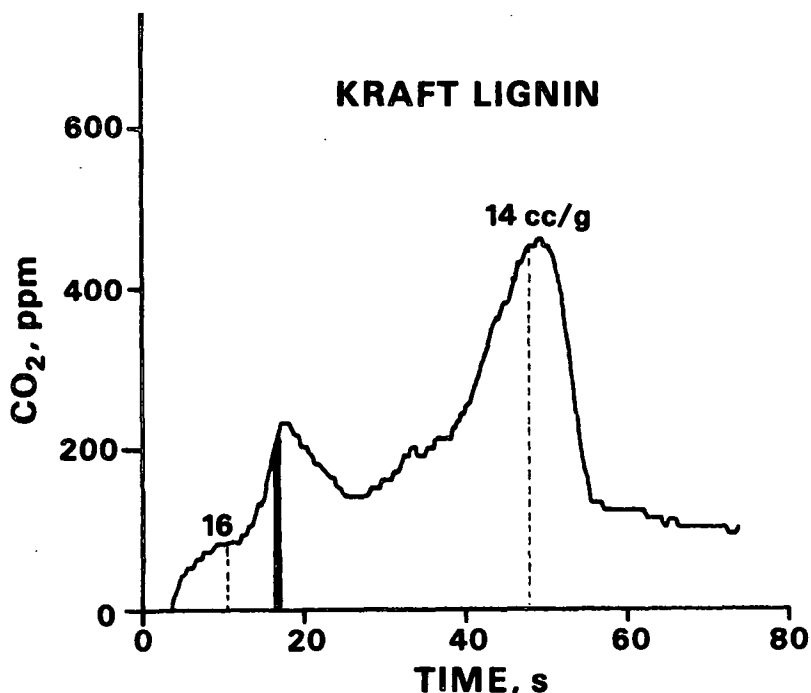
Figure 48. Carbon dioxide vs. time for a kraft lignin particle
(500°C, 99 mg, 46% solids). Photographs indicated by
dashed lines with swollen volumes indicated above the
lines. The solid line indicates the point at which
the lignin ceased to swell.

Figure 49 shows the carbon dioxide evolution curve for the pyrolysis of

sugar acids. The pyrolysis of sugar acids resulted in the evolution of more

pyrolysis gases and produced less char than kraft lignin. The sugar acids were

deformable during pyrolysis which resulted in swelling after evaporation had

been completed. The magnitude of swelling was considerably less for the sugar

acids than black liquor. The final char from sugar acid pyrolysis was spherical

and was composed of a very thin outer layer, which indicated surface tension may have been playing an important role in the swelling of sugar acids.
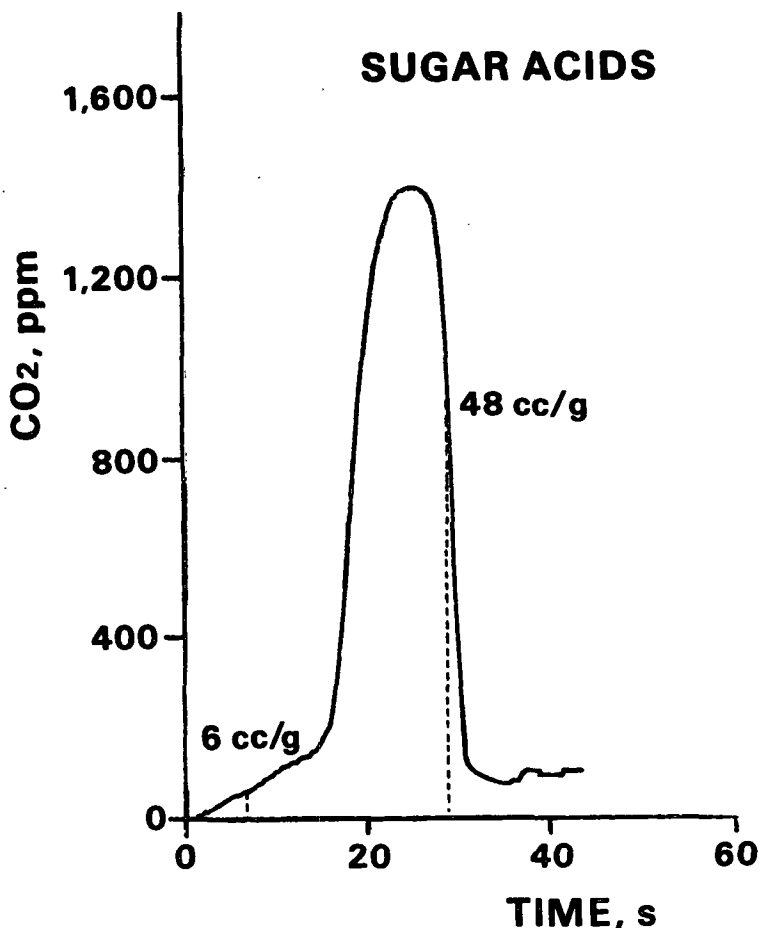
Figure 49.   Carbon dioxide vs. time for sugar acids (500°C, 88 mg, 51% solids). Photographs indicated by dashed lines with swollen volumes indicated above them.

Figure 50 shows the swelling of a 1:1 mixture of KL:SA in relation to the evolution of carbon dioxide. The material was deformable during swelling, much in the same manner as was found for sugar acids, except much more swelling took place.

The swelling began (indicated by the solid line, Fig. 50) at about the same time that pyrolysis had begun. The swelling of the KL/SA mixture was higher

than the sugar acid solution despite the lower amount of pyrolysis gases given off per unit weight of starting material. The char particle of a 1:1 KL/SA mixture was a foamlike structure with a very high void volume, which was similar to a black liquor char.
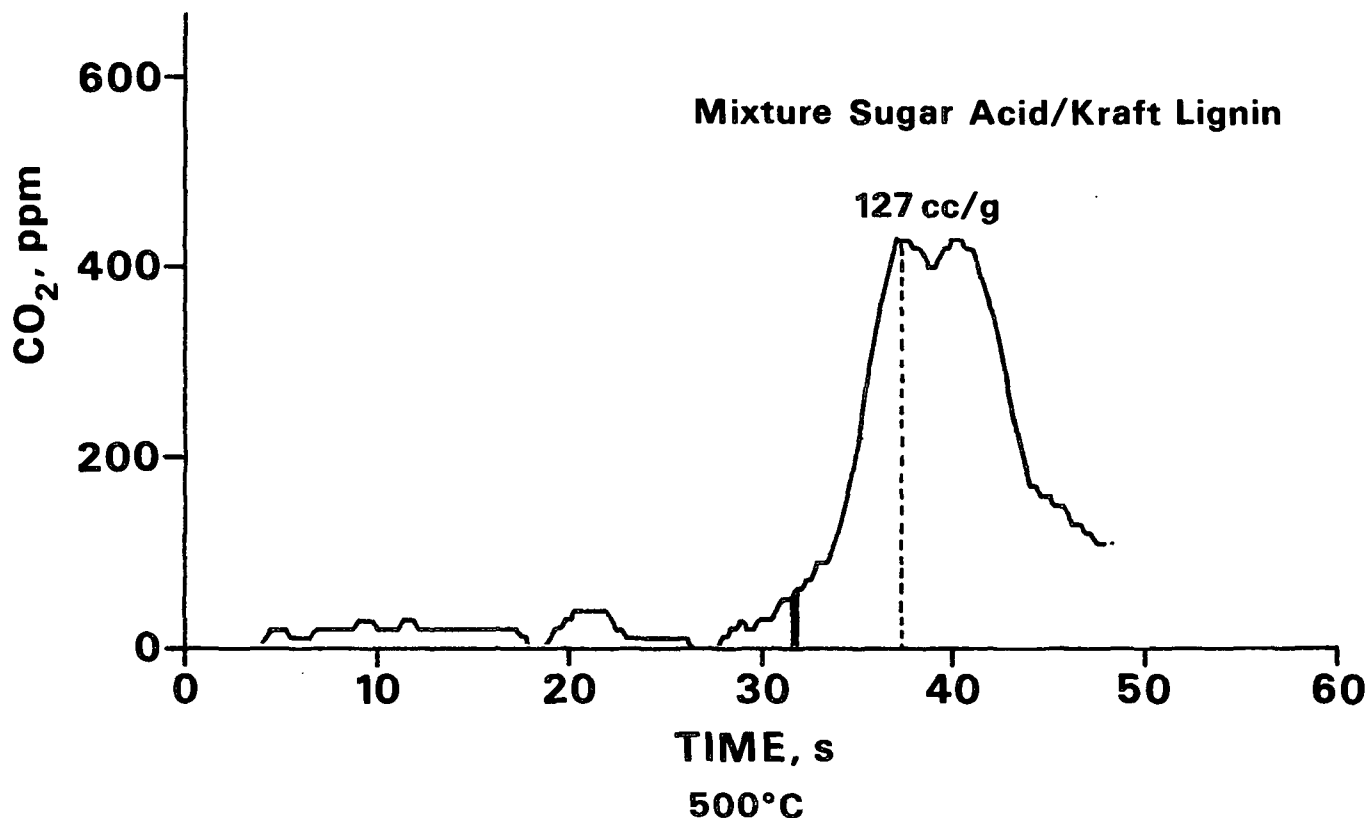
Figure 50. Carbon dioxide vs. time for a 1:1 mixture of kraft lignin and sugar acids (500°C, 123 mg, 48% solids). Photographs indicated by dashed lines with volumes indicated above them. The solid line at 32 seconds indicates the approximate time significant swelling rates (> 1 cm^3/g-s) began.

The synergistic effect of sugar acids and kraft lignin on swollen volume resulted from an apparent optimum in the deformability of the pyrolyzing system. Kraft lignin did not swell during pyrolysis as it formed rigid chars. Sugar acids formed materials during pyrolysis which appeared to have a lower viscosity and allowed more of the pyrolysis gases to escape than a KL/SA mixture. The

combination of KL and SA yielded a substance which was deformable when subjected
to the forces exerted by the pyrolysis gases.

Thermogravimetric analyses were performed on solutions of kraft lignin, sugar
acids, and a 1:1 KL/SA mixture, all possessing nearly the same viscosity (pH
12). The results are shown in Table 24. The weight percent at 200°C was
approximately the percent solids of the solutions.

Table 24 Pyrolysis activity of KL, SA and a mixture of the two
         (pH 12).

| Material | Heating Rate, °C/min. | % Weight at | | % Decomposition[a] |
		200°C	600°C	
KL	5	37.5	27.0	28.0
	20	37.5	27.0	28.0
SA	5	73.0	39.0	46.6
	20	70.5	37.0	47.5 37.5[b]
1:1 SA/KL	5	47.0	30.5	35.1
	20	46.5	29.0	37.6

[a]% Decomposition $= \dfrac{wt.\ (200°C) - wt.\ (600°C)}{wt.\ (200°C)}$.

[b]Average of kraft lignin and sugar acid decompositions.

The results show that the kraft lignin produced more char than the sugar
acids. The char yield of the KL/SA mixture was a combination of the yields of
the two individual components within the error associated with the test. The
kraft lignin and sugar acids appeared to pyrolyze independently of one another.
The thermogravimetric traces of these components can be found in Appendix I.

The molecular weight of kraft lignin to a large extent determines the
rheological properties of kraft black liquor. The molecular weight of kraft
lignin macromolecules covers a wide range. Since swelling appeared to be

related to the deformable characteristics of pyrolyzing particles, the molecular weight of kraft lignin was investigated.

A kraft lignin sample was fractionated into three different molecular weight ranges by ultrafiltration. Kraft lignin molecules are actually present in aggregates and the molecular weight cut off (MWCO) indicated by the membranes does not reflect the true molecular weight of fractionated kraft lignin (Table 3). The fractionated solutions of kraft lignin were mixed with equal weights of sugar acids and then the mixtures were pyrolyzed at 500°C. Procedures can be found in Appendix I. The results are shown in Table 25.

Table 25. Effect of kraft lignin molecular weight on the swelling of 1:1 KL/SA mixtures (average of four replicates).

Kraft Lignin MW	High	Med.	Low
MWCO	> 50,000	20,000-50,000	< 20,000
Vol., cm³/g	48	90	116

LSD - 21 cm³/g

Least significant difference (LSD) - 26 cm³/g (averages differing by 26 or more are significantly different).

The results show that the samples containing the higher molecular weight lignin produced lower swollen volumes than the samples containing lower molecular weight lignin. The largest effect occurred between the high and medium molecular weight samples. Mixtures containing higher molecular weight components had higher viscosities than lower molecular weight components. The effect may be similar to what was observed for black liquor (Fig. 24) where higher viscosities were generally associated with lower swelling. Kraft lignin molecular weight would also influence the physical chemical properties of kraft lignin. Smaller

molecules of lignin would contain a larger surface area to interact with sugar acid molecules per unit volume of lignin. More work is required to determine whether the effect of lignin molecular weight on swollen volume was simply one of molecular size (viscous effects) or whether a difference in physicochemical properties of lignin play an important role in the swelling mechanism.

Inorganic Salt – Sodium Sulfate

The inorganic content of kraft black liquor consists of inorganic salts and organically bound materials. The effect of inorganic salt content on swelling was investigated. No attempt was made to investigate the effect of the organically bound elements (Na,S) on black liquor swelling. Sodium sulfate was used in these experiments as a representative inorganic salt.

The effect of sodium sulfate on the swelling of black liquor is shown in Fig. 51. The solid line indicates the relationship expected between particle volume and sodium sulfate content if the sodium sulfate acted as a diluent. The sodium sulfate acted as a diluent up to the 20% (by weight) addition level. The 25 and 35% data points were significantly different (95% confidence) from the diluent line, indicating the sodium sulfate interfered with the swelling mechanism. An explanation for this occurrence was not obvious.

Extractives

The amount and composition of extractives varies widely depending on many factors: one of the largest factors is the type of tree species. Extractives have been found to adversely affect the swelling of black liquors. The effects have mainly been attributed to certain substances in specific tree species, i.e., ellagic and gallic acid in eucalyptus.
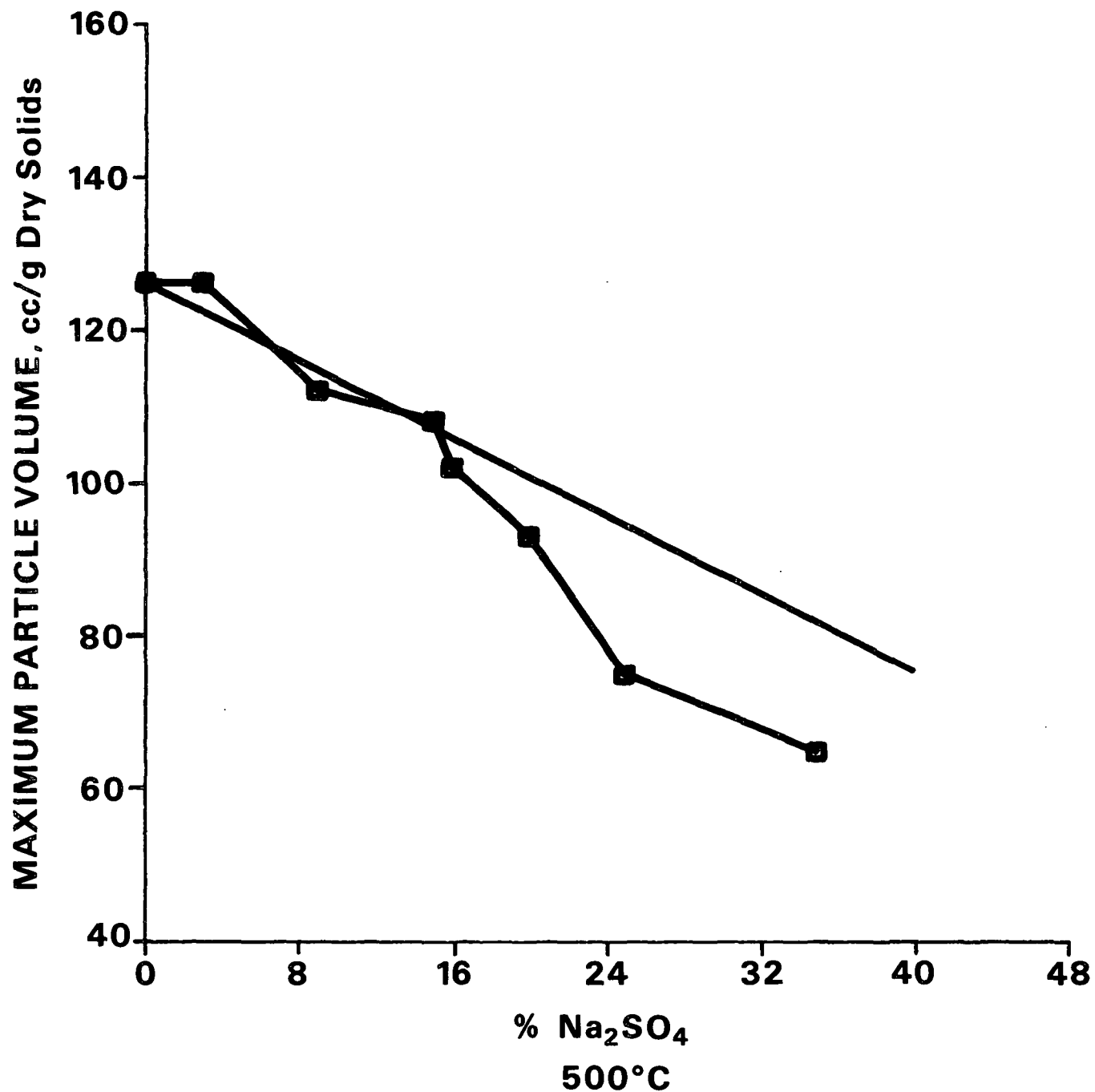
Figure 51. Effect of sodium sulfate concentration (by weight) on the maximum particle volume at 500°C. Solid line indicates relationship if sodium sulfate acted as a diluent to the swelling process.

The objective of this study was to determine how the extractives interfere with swelling. In this investigation, the effect of extractives on swelling was determined in two ways. First, the extractives were isolated and added back to black liquor and second, an extractive free wood was pulped and the resultant liquor was compared to a "normal" liquor with no extractives removed. The extractives were isolated according to TAPPI Standard (T 264 om-82).

Table 26 shows the swelling of three different loblolly pine black liquors. The liquors used in the table came from small bombs and were cooked in the same oil bath under identical conditions. Cooking conditions can be found in Appendix I. The "normal" liquor was not skimmed before concentrating and subsequent pyrolysis. The extractive free black liquor came from the cook using extractive free wood. Extractives (7% by weight) were added to an extractive free liquor for the third black liquor sample. The extractives added back to the black liquor were dissolved in the benzene-alcohol extraction mixture. The benzene-alcohol mixture had no effect on swelling when added to black liquor.

The extractives of loblolly pine were added to black liquor in different quantities as is shown in Fig. 52. The solid line indicates the relationship between particle volume and extractive content if the extractives acted as a diluent. The extractives had a large adverse effect on the swelling of kraft black liquors. The extractives which passed through the pulping process had a lesser effect on swelling than extractives which were isolated from the loblolly pine chips.

Table 26. The effect of extractives on maximum particle swollen volume (average of three replicates).

	Normal	Extractive Free	Ext. Free + 7% Ext. Added
Vol., cm^3/g	46	82	25

LSD - 26 cm^3/g
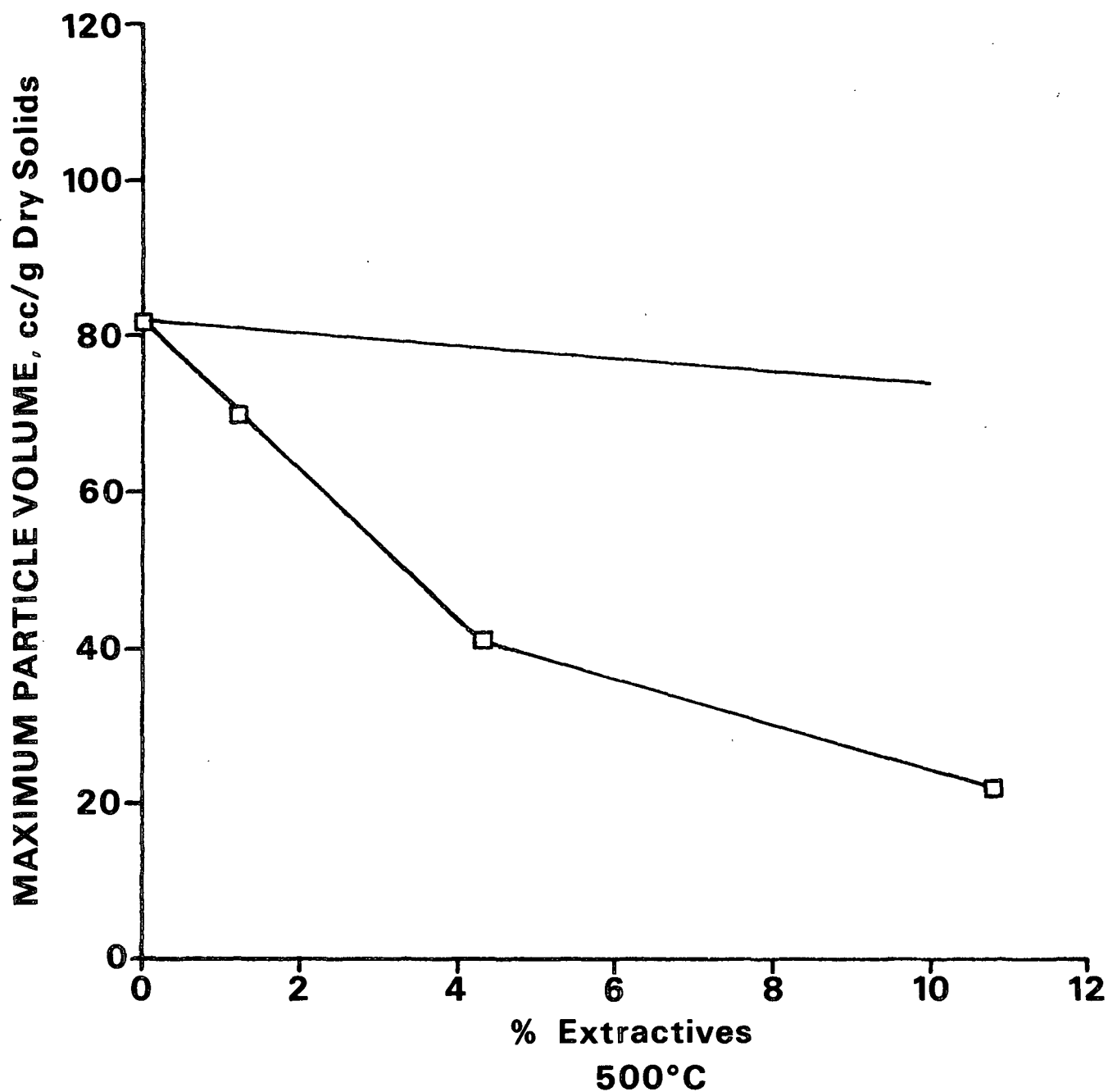
Figure 52. Effect of extractive concentration on the maximum particle
volume (500°C, 63% solids). Solid line indicates relationship
expected if the extractives acted as a diluent and did not
participate in the swelling process.

The amount of carbon dioxide evolved from black liquor with and without

extractives was measured. The results are shown in Table 27. The results show

that the black liquors with extractives gave off about the same amount of pyrolysis gases as the black liquor without extractives. The extractives did not appear to reduce the swelling by interfering with pyrolysis in a manner which would decrease the evolution of pyrolysis gases.

Table 27. Extractive effect on swollen volume and carbon dioxide evolution.

| | | Loblolly Pine (63% solids) | |
		Extractive Free	8.4% Extractives Added
500°C	Vol., cm^3/g	73	29
	CO_2, μg	17 ± 1	21 ± 5
700°C	Vol., cm^3/g	35	26
	CO_2, μg	44 ± 2	50 ± 17

± 1 std. deviation

Photographs were taken during the swelling process of particles with and without extractives. Figures 53 and 54 show the carbon dioxide evolution profiles during pyrolysis; the time at which photographs were taken are indicated by the dashed lines with the volumes displayed above the lines. Figure 53 shows pyrolysis of an extractive free liquor and Fig. 54 shows the same liquor with 8.4% extractives added.

An indication of char deformability during pyrolysis was the shrinking behavior of the particles after attaining maximum volume. The extractive free liquor shrank about 30% after reaching maximum volume. The black liquor with 8.4% extractives added shrank less than 10% after reaching maximum volume. This indicated the extractives influenced swelling by changing the deformable characteristics of black liquor.
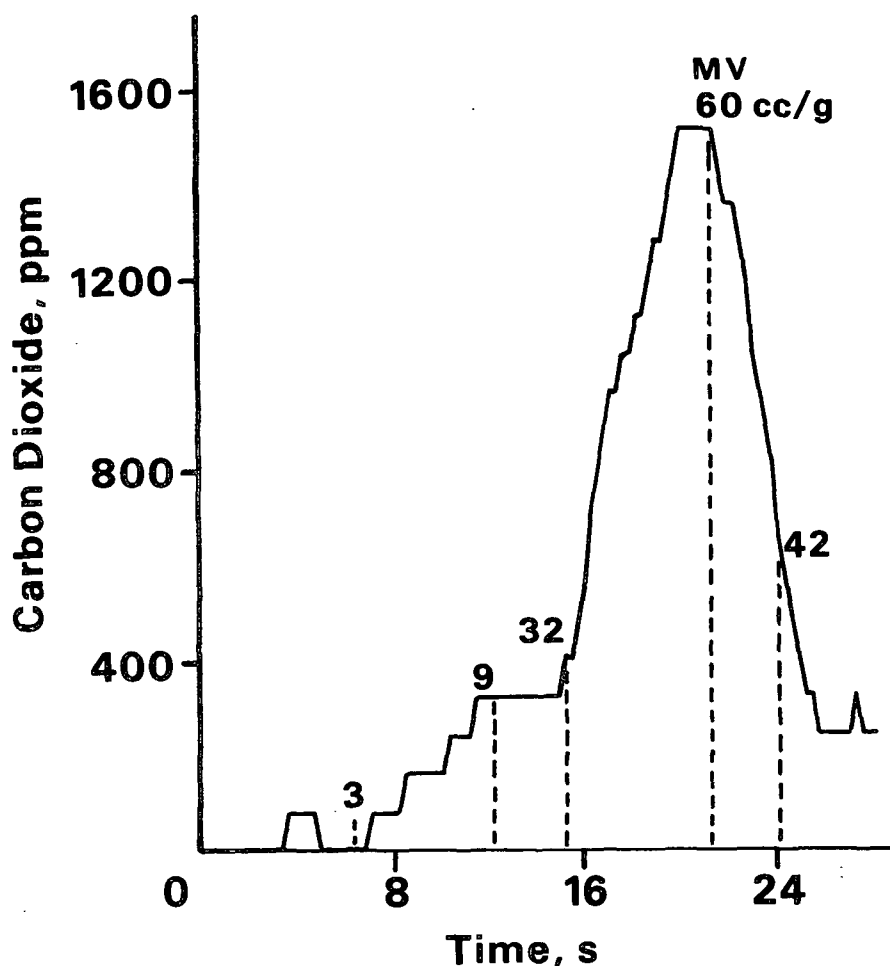
Figure 53. Carbon dioxide profile for an extractive free black liquor particle pyrolyzed at 500°C (63% solids, 38 mg dry wt.). Photographs indicated by lines with the swollen volume displayed above the lines. MV indicates maximum volume.

The effect appeared to be similar to the comparison between black liquor (high char vol.) and sugar acids (low char vol.), where the swelling occurred during pyrolysis, but marked differences occurred in the maximum swollen volume of the chars. The chars with extractives were very different from the chars resulting from sugar acid pyrolysis. The chars containing extractives were dense, hardened, and had a relatively high intrinsic strength, much like other low swelling chars (kraft lignin, HMW KL/SA). All the other chars were very

fragile. The extractives appeared to change the physical properties during pyrolysis in such a way as to interfere with the swelling mechanism by making the chars more rigid during pyrolysis.
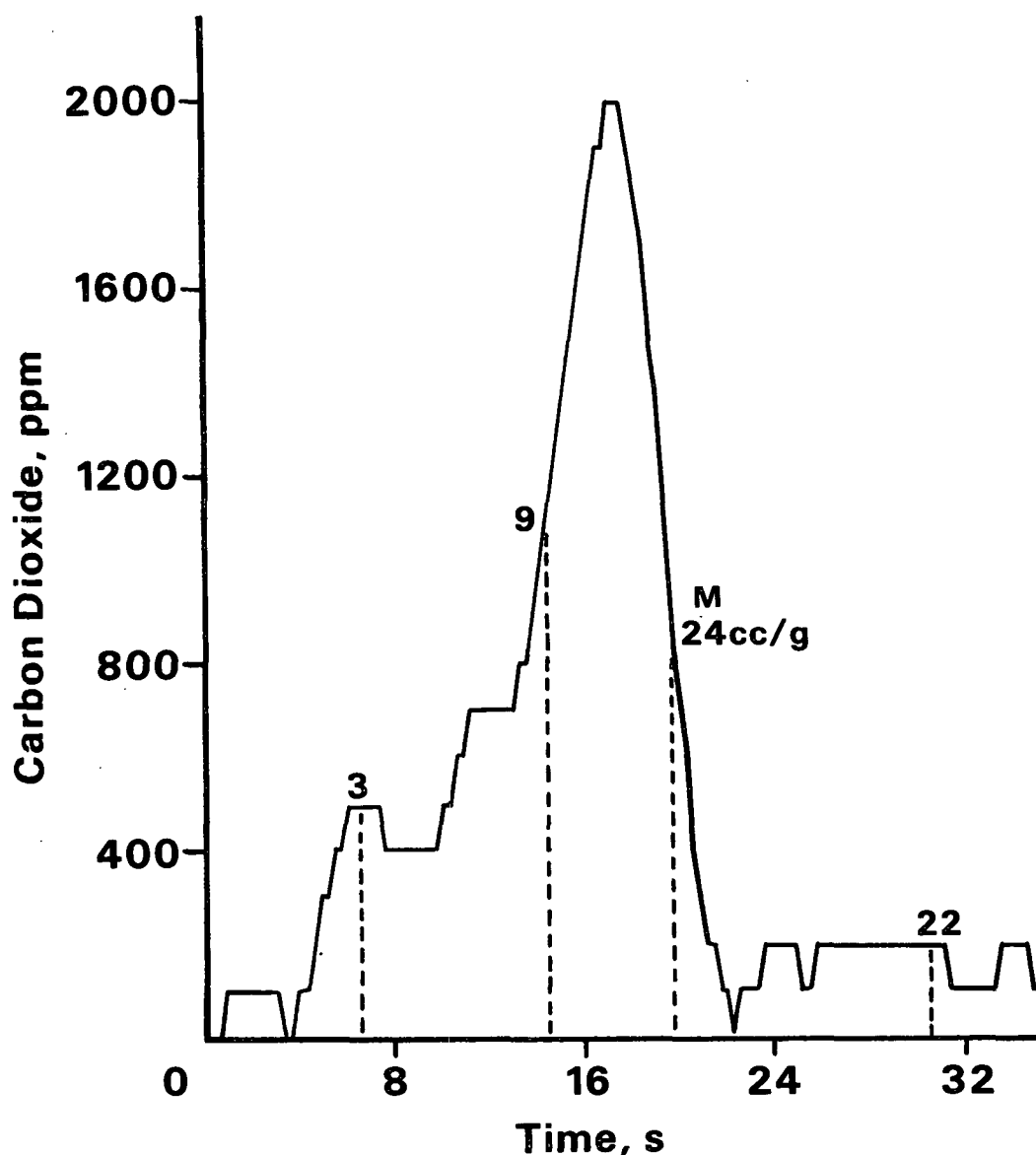
Figure 54. Carbon dioxide profile for an extractive free black liquor particle with 8.4% extractives added (500°C, 63% solids, 30.0 mg). Photographs indicated by lines with swollen volumes displayed above the lines. MV indicates maximum volume.

Surface Characteristics of Chars

The results suggested that the deformable properties of the pyrolyzing char determined the extent of swelling. Quantitatively measuring the dynamic deformable characteristics of chars (e.g., viscosity and surface tension) during pyrolysis was beyond the scope of this investigation. High and low swelling chars were examined using scanning electron and light microscopy to determine if differences in the deformable properties would be revealed in differences in the surface characteristics of the chars.

Two systems were studied: 1) black liquor with and without extractives and 2) sugar acid/kraft lignin (SA/KL) mixtures using high and low molecular weight kraft lignins (HMW KL and LMW KL). Extractives and high molecular weight lignins were the substances found to interfere with the swelling mechanism.

Figures 55-57 show photomicrographs of chars resulting from the pyrolysis of black liquor with and without extractives. Figure 55 shows the formation of bubbles in an extractive free black liquor particle where the char was quenched midway through the pyrolysis. Once pyrolysis was complete, the bubbles collapsed as shown in Fig. 56. The chars without extractives exhibited a tendency to form small bubbles approximately 50-150 microns in diameter. Figure 57 shows this surface structure was not present in chars pyrolyzed from black liquor containing 8.4% extractives.

Figures 58 and 59 show photomicrographs of KL/SA mixtures with HMW and LMW kraft lignins. The highly swollen chars (LMW KL/SA- Fig. 58) showed the formation of bubbles, and the low swollen chars (HMW KL/SA- Fig. 59) did not exhibit this structure and were more dense. The surface features found in the chars formed from the pyrolysis of LMW KL/SA were similar in size and shape to the

char derived from the extractive free black liquor. The highly swollen chars could easily be observed with a microscope by transmitting light through the particles and observing them with a microscope. Chars containing extractives (low swollen volumes) were difficult to observe in this manner due to their dense structure. Breaking apart the outer char layer only marginally alleviated this problem.
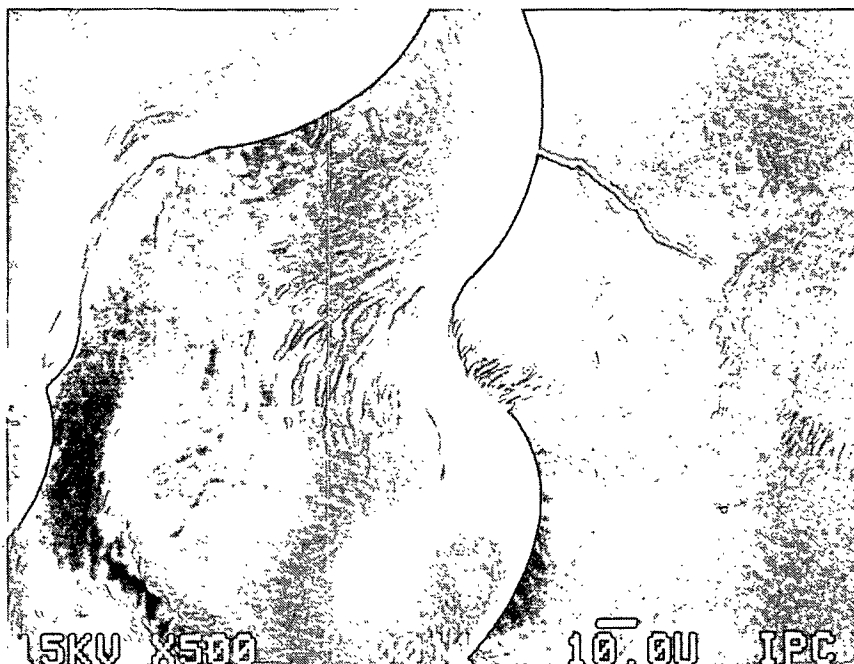
Figure 55. Photomicrograph of a char resulting from the pyrolysis of an extractive free black liquor (63% solids). Quenched midway through pyrolysis.

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 250°C. This temperature corresponds to the decomposition of 2-deoxy-D-arabino-hexonic acid.[31] Other sugar acids would be expected to decompose over the same temperature range. When the sugar acid solution was heated, bubble formation occurred at approximately the same temperature as black liquor. Sugar acids which had been air dried did not swell during pyrolysis.

Figure 56. Photomicrograph of a char resulting from the pyrolysis of an extractive free black liquor (63% solids). Quenched at maximum volume.

Figure 57. Photomicrograph of a char resulting from the pyrolysis of an extractive free black liquor + 8.4% extractives (63% solids). Quenched at maximum volume.
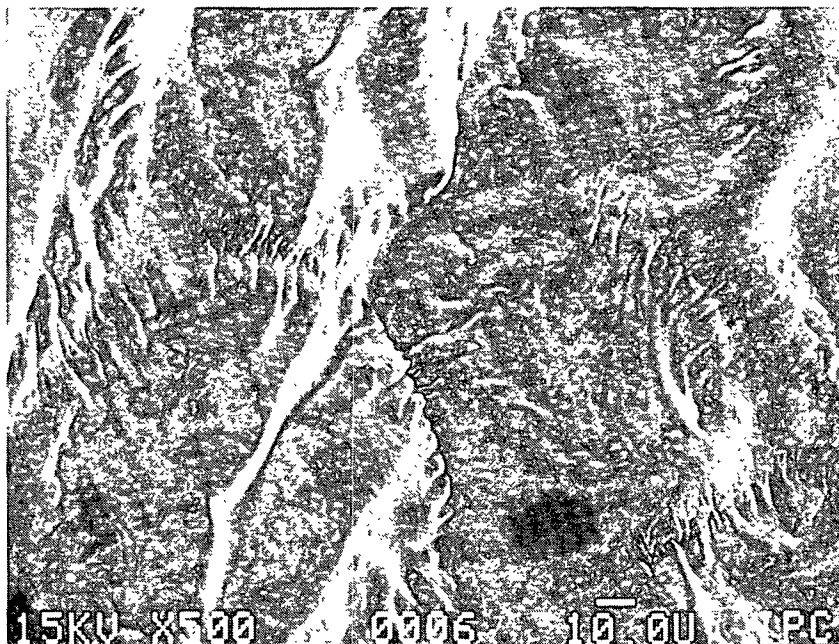
Figure 58. Photomicrograph of a char resulting from the pyrolysis of a 1:1 LMW KL/SA mixture (66% solids). Quenched at maximum volume.

Figure 59. Photomicrograph of a char resulting from the pyrolysis of a 1:1 HMW KL/SA mixture (41% solids). Quenched at maximum volume.

Analysis of the surface characteristics of chars was only found to be of value where large differences in swollen volumes existed. Smaller differences in swollen volume did not reveal any notable differences in the surface characteristics of the chars, i.e., chars differing in solids content and in inorganic contents all exhibited bubble formation. The formation of bubbles appeared to distinguish very low swelling chars from high swelling chars.

SUMMARY OF THE RESULTS

Of the process variables investigated, the pyrolysis temperature had the largest influence on the swollen volume of chars derived from black liquor. The temperature appeared to influence the swelling by changing the ability of the pyrolyzing black liquor to deform when subjected to the forces created by the production of pyrolysis gases. Pyrolyzing black liquor particles appeared to be the most deformable at 500°C, which resulted in maximum char volumes between 300 and 900°C. The initial solid content of black liquor had a relatively small effect on swelling. Initial solids contents above 85% produced lower swollen volumes than liquors below 80% solids. The initial solids content of black liquor only influenced char volume when pyrolyzed between 400 and 700°C. Chars differing in original solids content were analyzed by ^{13}C NMR. The analysis showed the carboxyl content correlated well with the swollen volumes of the chars.

The heating rate changed the swelling rate of black liquor, but did not change the final particle volume under the conditions tested. The particle size did not affect the particle volume attained during pyrolysis per unit weight of starting material. Adding steam to the gaseous environment surrounding the pyrolyzing particle did not affect the swelling behavior of dry black liquor particles.

The components of kraft black liquor had a large influence on black liquor swelling. The pH, over the range found in mill black liquors, only affected the swollen volume to a small extent. Sugar acids and kraft lignin swelled significantly when mixed together. A 1:1 ratio of the two components produced chars having the highest char volumes. Chars pyrolyzed from kraft lignin were rigid

and did not swell significantly. Sugar acids formed very spherical chars and swelled during the evolution of pyrolysis gases. The sugar acid material appeared to be too fluid to accommodate large swollen volumes. The mixture of these two materials produced materials which were highly deformable during pyrolysis. Inorganic salts acted as a diluent when added to black liquor. Extractives appeared to interfere with the swelling mechanism by increasing the viscous properties of black liquor during pyrolysis. The effects of the compositional variables on swollen volume determined at 500°C were also found to occur at 900°C.

The analysis of char surface characteristics revealed differences between high and low volume chars. High volume chars, such as those derived from extractive free black liquor and low molecular weight kraft lignin mixed with sugar acids, formed small bubbles during pyrolysis. Black liquor containing extractives (4-10%) and high molecular weight kraft lignin mixed with sugar acids produced low volume chars and did not show signs of having formed bubbles during pyrolysis.

DISCUSSION OF THE SWELLING MECHANISM OF BLACK LIQUOR

The swelling of black liquor began at approximately the same time pyrolysis gases began evolving. A pyrolyzing black liquor particle would expand until the pyrolysis process was just about complete. The amount of pyrolysis gases evolved did not correlate with a change in particle volume as the pyrolysis proceeded. Pyrolyzing particles tended to swell more (for a given amount of gas evolved) later in the process, which indicated intermediate species present during the pyrolysis process would be important in swelling. The rate of pyrolysis gas production influenced the swelling rate but not the extent of swelling. These conclusions were reached through the study of the heating rate, the particle size, and the pyrolysis temperature.

The viscous properties of the pyrolyzing material appeared to be a factor in determining the extent of black liquor swelling during pyrolysis. A pyrolysis temperature of 500°C resulted in maximum swelling of black liquor for the temperature range (300-900°C) investigated. The material appeared to flow more easily as the temperature was increased from 300 to 500°C. Kraft lignin, when pyrolyzed, begins to produce tars at approximately 350°C. The combination of tar production and a lowering of the molecular weight (through pyrolytic decomposition) may be responsible for the increased deformability of black liquor between 300 and 500°C.

The decrease in black liquor char volume, as the pyrolysis temperature was increased between 500 and 900°C, appeared to result from the outer char layer restricting the growth of the pyrolyzing particle. At higher temperatures (700-900°C), an outer char layer developed, while the interior of the particle was still a viscous mass undergoing pyrolysis. As the interior of the particle pyrolyzed, the outer char restricted further swelling. This was evidenced by

the breaking apart of the outer shell to accommodate swelling. Nonuniformities in swelling (shape, appendages) occurred more frequently as the pyrolysis temperature was increased. At 500°C, the char that formed would readily deform when subjected to the internal forces generated by the production of pyrolysis gases. Analysis of the compositional variables was performed to further elucidate the importance of the viscous properties of black liquor during pyrolysis.

The investigation into the compositional variables revealed that a combination of kraft lignin and sugar acids was responsible for the large swollen volumes of black liquor chars. Kraft lignin and sugar acids pyrolyzed separately only swelled to a minimal extent. An equal weight of kraft lignin and sugar acids resulted in the largest char volumes.

Analysis of the surface characteristics of highly swollen chars and very low volume chars revealed the formation of small bubbles (50-150 microns in diameter) in highly swollen chars which were absent in very low volume chars. This relationship only held for large differences in swollen volume, i.e., chars differing in inorganic content and chars derived from black liquors at different initial solids content all had similar surface characteristics. Bubble formation in black liquor was found to be initiated at approximately 250°C. The formation of bubbles was an indication that surface active forces could play an important role in swelling.

The evidence also suggested pyrolysis intermediates are responsible for black liquor swelling. Bubble formation was found to distinguish high and very low swelling chars. Bubble formation began at 250°C. A major portion of the organic decomposition (evolution of pyrolysis gases) in black liquor occurs between 250 and 400°C; the major increase in swelling occurs between 400 and 500°C. Also the higher swelling rates tended to occur near the end of the swelling period.

The sugar acids appear to play a more active role in determining the extent of swelling during black liquor pyrolysis than kraft lignin. The carboxyl content (which can be attributed to the sugar acids) correlated well with the swollen volumes of the chars. The temperature at which bubble formation occurs in black liquor corresponds to the decomposition temperature of sugar acids. A solution of sugar acids was found to form bubbles at 250°C.

A sugar acid solution was allowed to dry in air. The resulting sugar crystals did not swell upon pyrolysis. When black liquor was dried, the swelling during pyrolysis was only reduced by approximately 25%. This indicated some type of interaction occurred between kraft lignin and sugar acids in black liquor to prevent crystallization of the sugar acids.

The role of kraft lignin is difficult to define. Although bubbles form at low temperatures (240-260°C), maximum swelling occurs at 500°C. Both cellulosic and ligneous materials form highly aromatic chars similar in structure at 500°C. Kraft lignin, when added to sugar acids in a 1:1 ratio, appeared to increase the viscosity just enough to result in a deformable material which would swell upon pyrolysis. Kraft lignin also appeared to stabilize the bubbles, which allowed for significant swelling to take place during pyrolysis.

The swelling mechanism appeared to be dependent on the rheological properties of black liquor. Conceivably, both surface tension and viscosity could play important roles in swelling. The rheological properties are dependent on the dynamic composition of black liquor as it changes with temperature. More work needs to be done to isolate the specific influences various structural aspects of kraft lignin and sugar acids have on the swelling mechanism.

CONCLUSIONS

The swelling of black liquor particles began and finished at approximately the same time at which the pyrolysis gases began evolving and ceased to evolve. Despite this close relationship between swelling and pyrolysis, there was no correlation between the amount of gas evolved and the change in char volume during the pyrolysis of black liquor particles.

The rheological properties, including both surface active and viscous forces, appeared to determine the extent of swelling during pyrolysis. The black liquor composition had the largest influence on the swelling behavior of black liquor during pyrolysis. An interaction between kraft lignin and sugar acids was responsible for the swelling behavior of black liquor during pyrolysis. Other compositional variables such as increasing the extractive content, increasing the inorganic content, or increasing kraft lignin molecular weight reduced the extent of black liquor swelling during pyrolysis.

RECOMMENDATIONS

Further research is warranted in several areas: 1) black liquor swelling as it relates to combustion, 2) measurement of char rheological properties during swelling, and 3) model compound studies.

The results suggest a good method for studying the effect of black liquor swelling on combustion. The molecular weight of lignin in KL/SA mixtures could be used to change the magnitude of char swelling during combustion. The combustion characteristics of the synthetic black liquors could then be investigated.

The rheological properties of black liquor chars at high temperatures (> 400°C) may reveal information which would be pertinent to the swelling of black liquor. The viscosity may be obtained in a manner similar to Fong et al.[61] However, one must be wary of using black liquor in devices designed to accommodate coal during pyrolysis. A 100% solids black liquor was sent to BCR National Laboratory at the University of Pittsburgh to be tested with an Arnu Audibert dilatometer. Black liquor swelled past the maximum measuring point on the instrument before reaching the starting temperature (300°C) for the test. There are two important points to remember: 1) black liquor begins swelling at a lower temperature than coal and 2) black liquor swells to a larger extent than coal.

Any attempt to measure rheological properties of black liquor at high temperatures should also investigate sugar acids and black liquor with extractives. These materials are all deformable throughout the evolution of pyrolysis gases at 500°C, but the resulting chars have very different characteristics from one another.

The similarity between the surface characteristics and the swelling behavior of black liquor and SA/KL mixtures show that a synthetic black liquor can be produced which behaves like black liquor. A model compound system could be used to further study black liquor swelling. As a first approach, model compounds of sugar acids could be used with isolated kraft lignin. Solid state NMR has been used to study chars from the pyrolysis of wood, cellulose, and lignin, and this investigation has shown that it would be a useful tool in future investigations involving black liquor chars.

ACKNOWLEDGMENTS

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APPENDIX I

EXPERIMENTAL METHODS AND MATERIALS

APPARATUS

A schematic of the single particle reactor is shown in Fig. 35. The particles were heated by a gas stream in a 50 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 around 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 (1.6 cm in diameter) located right below the particle was used to withdraw gas samples at a constant flow rate (0.029 m^3/sec). An Infrared Industries Inc. model 702 gas analyzer was used to monitor the evolution of carbon dioxide and carbon monoxide. This system had a 4.0 second delay time and a first order time constant of 3.6 seconds. A Beckman Industries model 865 infrared water vapor analyzer was obtained during the work on the compositional variables. The gases were detected by infrared instrumentation. When the water vapor 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: reaction time, particle mass, gas temperature, CO, CO_2, and H_2O concentration and a camera switch reading. The data could be collected about seven times a second. The camera switch reading was simply an on-off switch connected to the camera switch; one could record the times at which photographs were taken automatically by using the on-off switch.

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 bypass 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 shown in Table 28. A large batch of loblolly pine wood was cooked and yielded 5 gallons of black liquor which was used over the course of this investigation. Small bombs were cooked under the same conditions. The black liquors obtained from the small bombs were used to investigate the effect of extractives on swelling.

The black liquor was concentrated to approximately 25% solids on a hot plate, and the soap residues were skimmed off. The black liquors were then evaporated in a rotavapor under a 95 kPa vacuum in a water bath at 80°C until approximately a 65% solids solution was attained. No extractives were removed from the black liquors obtained from the small bombs. 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 sample was left in the oven overnight to obtain a 100% solids black liquor.

Table 28. 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		

Large Cook Test Results

Yield	45.7%		
Kappa no.	25.7	BL solids	16.5%

Small Bombs

	Extractive Free		Normal	
Batch no.	5	6	7	8
O.D. wt. grams	80	60	80	60
Kappa no.	32	38	32	35

At the beginning of the study the 100% solids black liquor was ground with a mortar and pestle, then pressed into pellets using a pellet press. A wire was simultaneously pressed with the black liquor solids, which allowed one to attach the pellets to the microbalance. Two sets of dies were used for making two different size pellets (6.3 and 4.8 mm in diameter, approximately 3 mm in height). The process was found to affect the swelling process and therefore was not used after the initial studies.

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 4 hours. Finally, the chips were placed in boiling distilled water for 1 hour.

The extractives were concentrated to about 60% solids in a rotavapor at 95

kPa vacuum and 60°C. The extractives with solvent were added to black liquor

and mixed thoroughly. The solvent (benzene-alcohol mixture) was added to black

liquor and was found to have no effect on black liquor swelling during pyrolysis.

MEASUREMENT OF BLACK LIQUOR CHAR VOLUME

Direct methods to measure the volume of pyrolyzed black liquor particles

have been described elsewhere.[5,6] The methods used fine silica or dried pulp

balls to measure the displacement of the media by the char particles. A

suitable procedure was devised, as details of these procedures were not given.

The procedure devised used a relatively coarse sand and varied the container

size (5-30 mL flasks) according to the particle size. A coarser sand was found

to settle more uniformly and gave more reproducible results than a finer sand.

Container size was varied because large percentages of sand displacement pro-

vided greater accuracy. The accuracy of the method was determined by measuring

the known volumes of ball bearings. The results are shown in Table 29.

Table 29. Volume measurement by the displacement of sand.

Ball Bearings Diameter, cm	Volumes, cm^3	
	Calculated	Measured
1.90	3.64	3.62
1.50	1.80	1.82
0.79	0.26	0.25
0.63	0.13	0.04

Standard error of difference (95%) - ± 0.05 cm^3.

The particles described in the literature were pyrolyzed at relatively low

temperatures (400°C). These particles were more dense, yielding particles with

a relatively high char matrix strength. At higher temperatures the char particles

were too fragile to be measured by the displacement of sand. Also, at these

temperatures the particle could not be removed from the reactor without some oxidation taking place (resulting in a change in volume).

To gain a better understanding of the kraft black liquor swelling, the measurement of the particle volume during pyrolysis was desirable. An indirect measurement of particle volume was sought. 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 projected particle area represented a circle. To increase the sensitivity of the procedure, the negatives were put in an enlarger and the images of the particles were enlarged to the desired size and were then traced on paper. A photograph of a ball bearing in the reactor was used for calibration purposes. This method was compared to the displacement of sand method for a number of char particles varying in size and shape. The results are shown in Table 30. The volume measurements given in the text were divided by the original weight of the particle; by doing this particles differing in particle size and moisture content, and pyrolyzed at different temperatures, could be compared on the same basis.

Table 30. Comparison of volume measurement techniques.

	Volumes, cm^3	
Particle ID	Sand Method	Planimeter Method
1R	1.79	1.70
1B	1.62	1.72
2I	0.10	0.07
1Q	1.74	1.67
7A	0.25	0.39
1DD	1.26	1.03
1Z	2.09	1.90
1U	1.48	1.40

Standard error of difference (95%) - ± 0.09 cm^3.

MEASUREMENT OF THE HEAT FLUX TO THE PARTICLE

The heat flux to the particle was determined by measuring the rate of evap-
oration of water from small metal cups. The metal cups were formed in the shape
of half spheres (nominally about 6 mm in diameter). The surface area of the cup
was determined by weighing the cup and knowing the weight per unit area of the
metal. The evaporation rate was determined by a linear regression of the
constant evaporation zone from a mass vs. time plot. A typical plot of mass
vs. time is shown in Fig. 60.
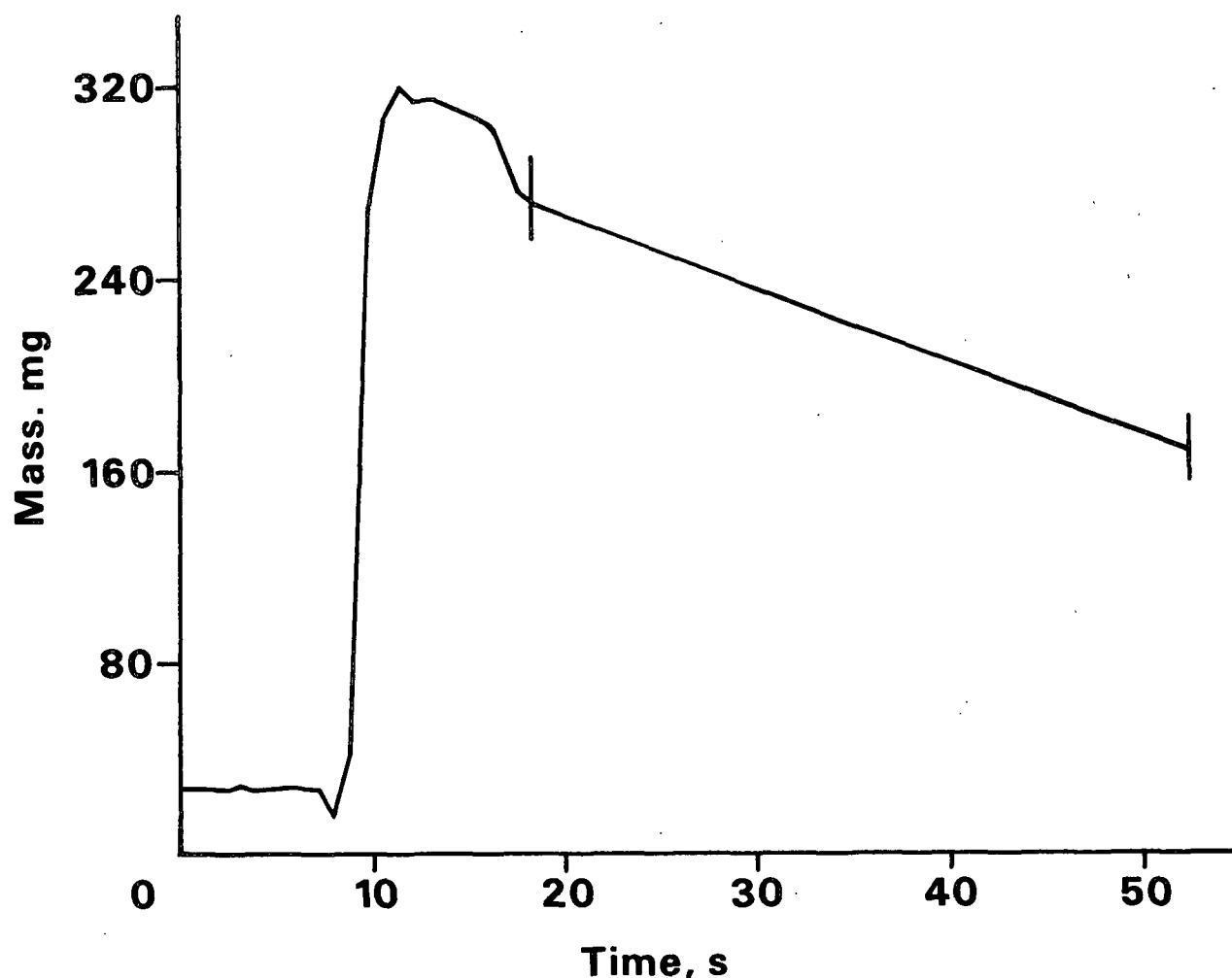
Figure 60. Mass vs. time for the evaporation of water (725°C, no
flow rate, 3.04 mg/s).

The heat flux can also be determined from a relationship developed for the forced convection heat transfer to a single sphere.[76] The heat transfer coefficient (h) can be determined from Eq. (1) with the heat flux determined from Eq. (2).

$$Nu = \frac{hD}{k} = 2.0 + 0.60 \; Re^{1/2} \; Pr^{1/3} \tag{1}$$

$$Q = h(T_\infty - To) \tag{2}$$

where: Nu – Nusselt no., h – heat transfer coefficient ($W/m^2-°K$),

D – diameter of the particle (m), k – thermal conductivity

of particle ($W/m-°K$), Re – Reynolds no., Pr – Prandtl no.,

T_∞ – gas temp. (°K), To – particle temp. (°K),

Q – convective heat flux (W/m^2).

The calculated and measured values of heat flux compared well for the range of reactor conditions tested: 600-900°C and 833-2500 cm^3/s. Calculations showed a laminar velocity profile existed in the reactor under these conditions. The measured values were corrected for radiation by comparing the evaporation rates with the surrounding walls preheated and at room temperature. The radiation component was about 15% of the total heat transferred at 800°C. Figure 60 shows there is a good correlation between the measured and calculated values.

A sample calculation for the velocity of the gas stream in the reactor is shown below.

A = (0.05 m)(0.05 m) = 2.5 x 10^{-3} m^2

T1 = 700°C = 973°K

V = 1666 cm^3/s at std. conditions, vol. flow

T2 = 298°K

$\overline{v}$ = avg. velocity, v_c = velocity at center

$$\overline{v} = \frac{V}{A} = \frac{(1.67 \times 10^{-3} \text{ m}^3/\text{s})}{(2.5 \times 10^{-3} \text{ m}^2)} = 0.645 \text{ m /s @ std.}$$

$$v1 = \frac{T1}{T2} v2 \qquad \overline{v} = \frac{(973°K)(0.645 \text{ m/s})}{298°K} = 2.1 \text{ m/s}$$

$$v_c = 2 \, \overline{v} \text{ for laminar flow}$$

$$v_c = 4.2 \text{ m/s}$$
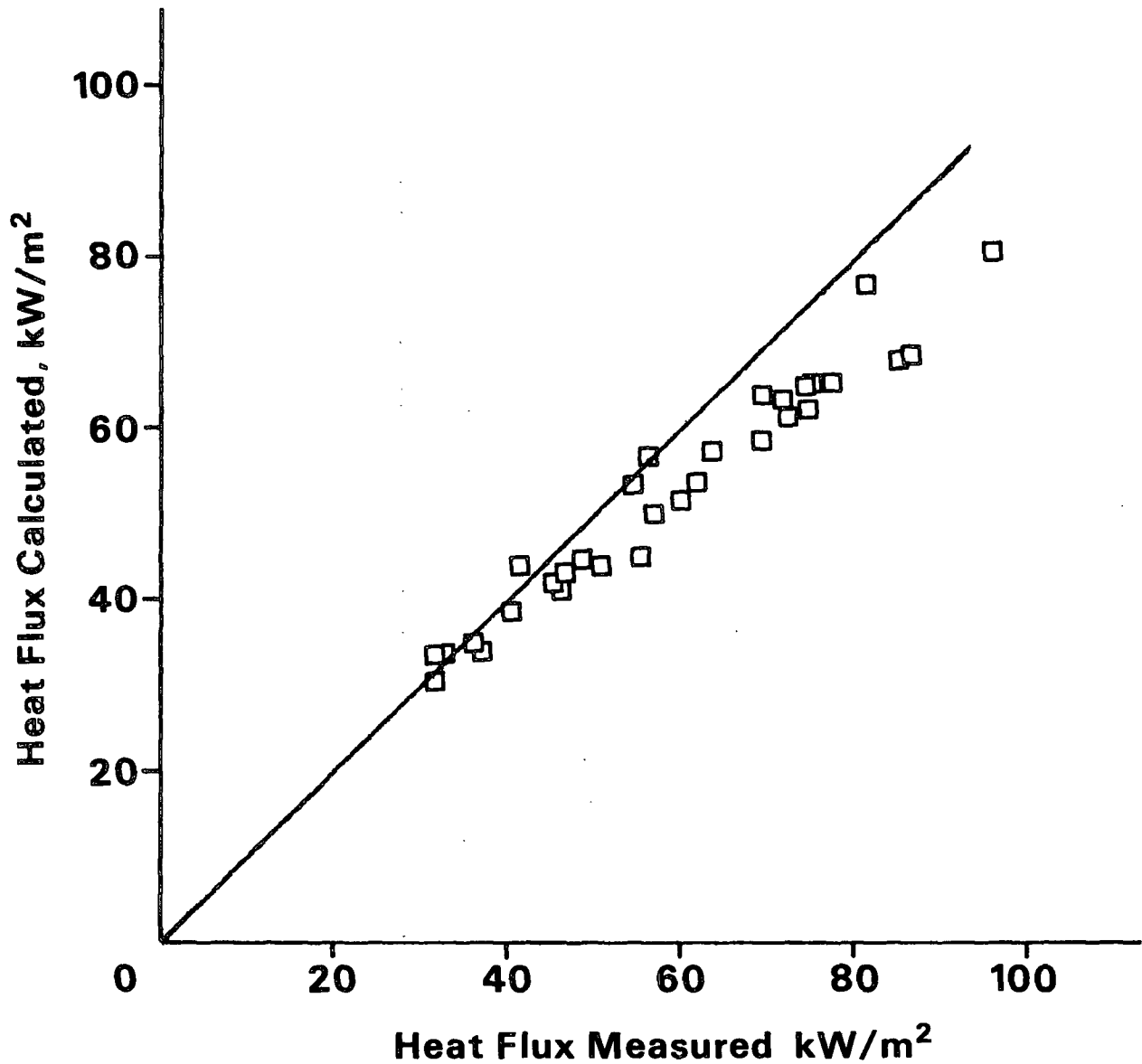
Figure 61. Convective heat flux in the single particle reactor, measured vs. calculated. Measured values corrected for radiation. The line drawn assumes the measured and calculated values were equal.

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 water to approximately 15% solids. The pH was gradually lowered to 2.5 with 1N sulfuric acid. The solution was centrifuged for an hour at 2000 rpm. The precipitated kraft lignin was washed and centrifuged two times. Sulfuric acid was added to keep the pH below 2.5. The resultant precipitate was kept under water in cold storage. Kraft lignin stored in this way could later be transformed to a sodium salt by adding caustic.

The remaining filtrate was concentrated (almost to dryness) in a rotavapor at 95 kPa and 80°C. Acetic acid corresponding to double the volume of sugar acid solution was added and allowed to stand overnight. The precipitated inorganic material was removed, and after vacuum evaporation a syrupy product was obtained. Distilled water was added to give about a 30% solution. Any additional inorganic precipitate formed at this point was removed by filtration.

The solution was then passed through a column of Dowex 50 - X8 (H$^+$) ion exchange resin (100 cm^3 of resin to 250 cm^3 of solution) to remove sodium ions. The solution was then mixed with Dowex 3 (OH$^-$) for approximately 10 minutes (50 cm^3 of resin to 250 cm^3 of solution) to neutralize the liberated hydrogen ions. The solution was next passed through a column filled with adsorbent resin (Amberlite XAD - 8, 250 cm^3 resin to 50 cm^3 solution). The solution was then placed in a beaker with Amberlite XAD - 2 and allowed to stand overnight. The amberlite products were used to remove some of the colored materials such as lower molecular weight lignins which did not precipitate during acidification. This solution was then evaporated in a rotavapor to approximately 30% solids and

placed in cold storage. This procedure basically follows the procedure given by Alen and Sjostrom.[12,14] The procedure yields what was termed a "crude hydroxy acid" fraction. The amounts of individual components yielded from this procedure are shown in Table 4.

The resulting solutions of kraft lignin and sugar acids were acidic, and the pH was raised to simulate kraft black liquor. The active alkali of black liquor is usually measured by titrating a sample down to a pH of 8.3. To determine the alkalinity of the sugar acid and the kraft lignin fractions the alkali (1$\underline{N}$ NaOH) added from pH 8.3 was measured and an active alkali calculated according to Eq. (3). The active alkali of kraft lignin and sugar acid solutions are shown in Table 31.

$$\left(\frac{mL \ of \ NaOH}{g \ of \ solids}\right) \left(\frac{40 \ g \ NaOH}{1000 \ mL \ NaOH}\right) \left(\frac{62 \ g \ Na_2O}{80 \ g \ NaOH}\right) \times 100 = \% \ AA \ as \ Na_2O \qquad (3)$$

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 1$\underline{N}$ NaOH and diluted to a 1% solids content. This solution was put through the ultrafiltration process. The ultrafiltration process only lasted a few minutes under these conditions. The temperature was 60°C during the ultrafiltration process.

Table 31. Active alkali as a function
of pH for sugar acid and
kraft lignin solutions.

Active Alkali (in percent as Na$_2$O)

pH	KL	SA
10.5	2.4%	3.4%
12.0	5.9	4.0
13.0	7.9	5.7

The concentrate retained on the 50,000 MWCO membrane represented the high molecular weight fraction. The medium molecular weight fraction were 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 optimum swelling. The samples were acidified, washed and then brought back up to a pH of 12. This produced samples which swelled extensively in some cases.

THERMOGRAVIMETRIC ANALYSIS OF BLACK LIQUOR COMPONENTS

Thermogravimetric analysis was performed on kraft lignin (35% solids), hydroxy acid (70% solids), and 1:1 KL/HA mixtures (45% solids). All the tests were performed with the solutions at pH 12 and nearly the same viscosities. At least two runs were conducted with each sample. All the experiments were conducted under a 60 mL/min. flowing nitrogen atmosphere. Thermogravimetric traces of each of the solutions analyzed are shown in Fig. 62-64.

CP/MAS ^{13}C NMR ANALYSIS OF BLACK LIQUOR CHARS

Four black liquor samples were pyrolyzed at 500°C. The samples were pyrolyzed with the surrounding walls at room temperature for the start of the test. The chars were quenched by diverting the hot nitrogen gas away from the particle and flowing nitrogen at room temperature past the particle. The samples were quenched at the point of maximum swelling (before pyrolysis had been completed). The chars were analyzed with a CP/MAS ^{13}C NMR spectrometer by the Weyerhaeuser Company. The samples differed in solids content and represented two different swelling levels. The 65 and 73% black liquors swelled more upon pyrolysis than the 86 and 100% black liquors. Sample calculations and the spectra are presented in the following pages.
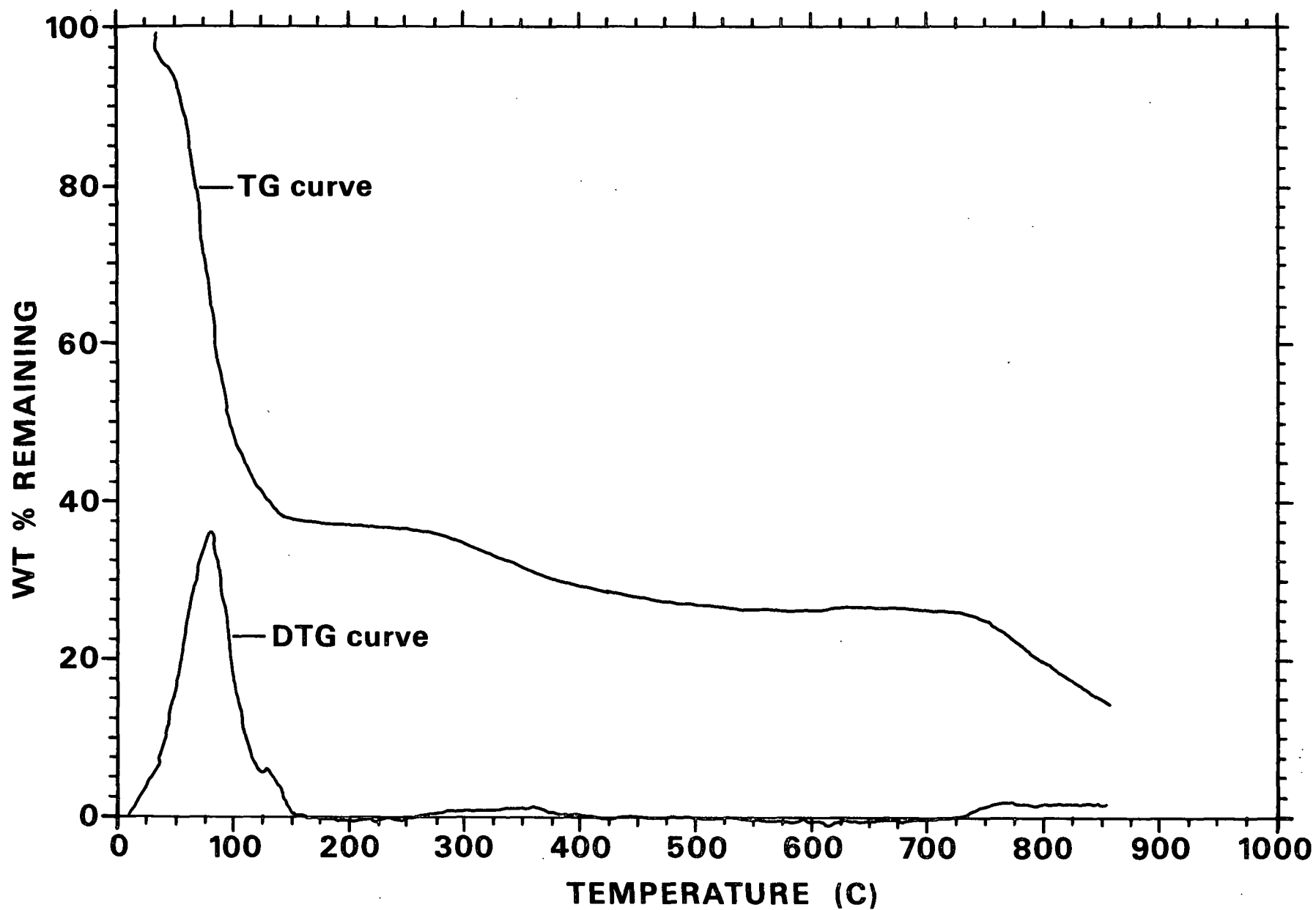
Figure 62. Thermogravimetric (TG) trace and derivative thermogravimetric (DTG) trace of kraft lignin at 5°C/min.
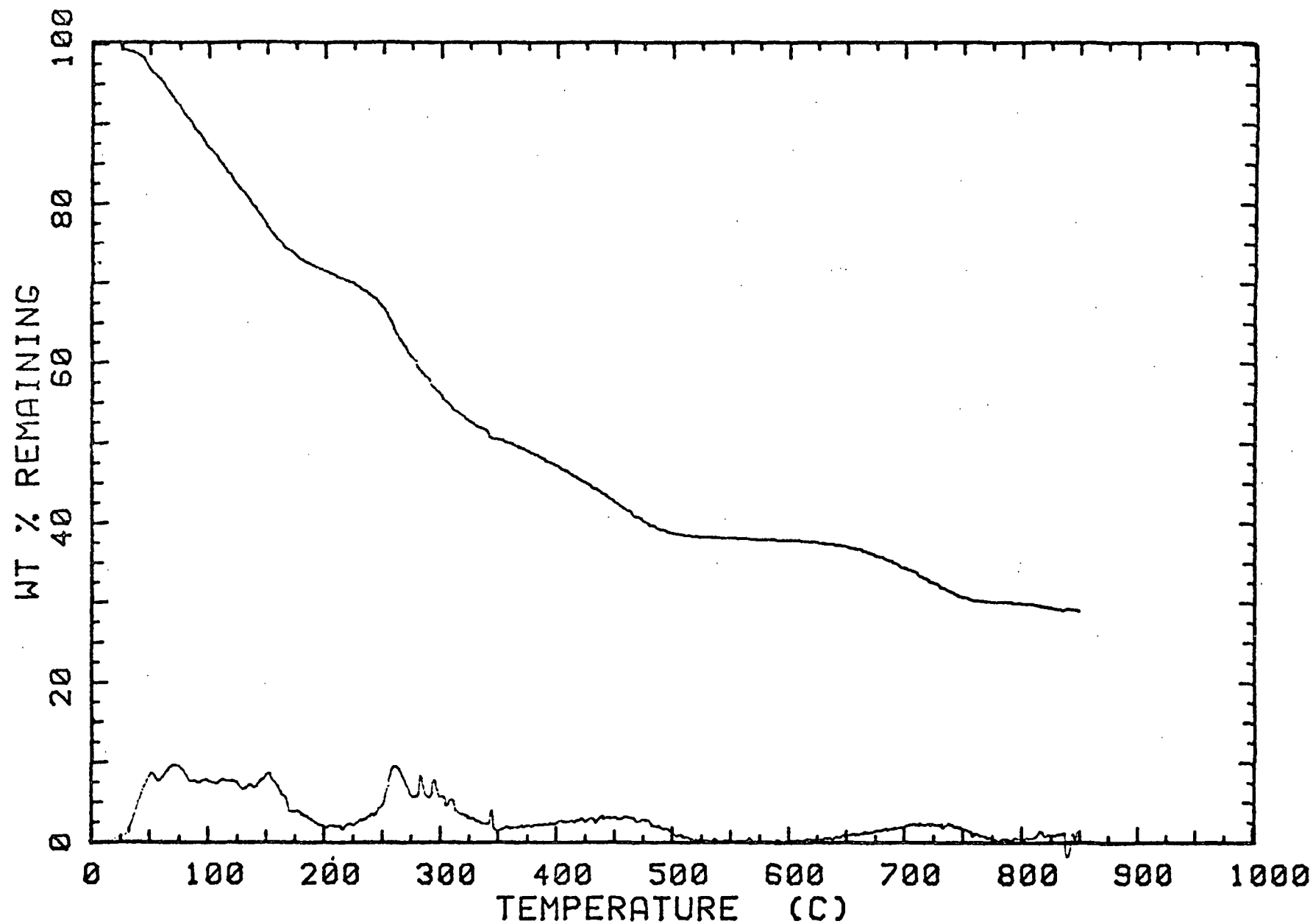
Figure 63. Thermogravimetric trace of sugar acids at 5°C/min.
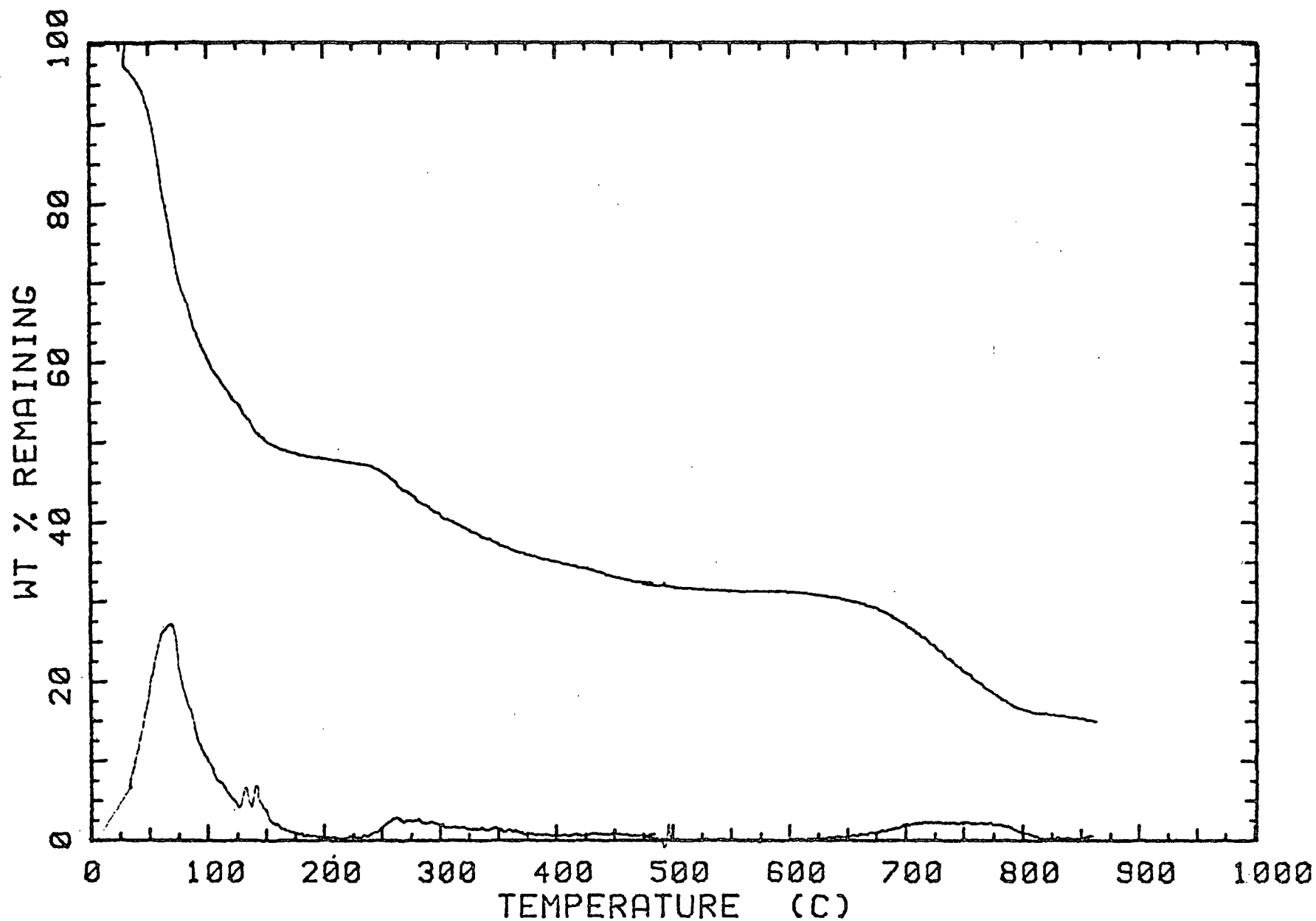
Figure 64. Thermogravimetric trace of KL/SA 1:1 at 5°C/min.

UNDERSTANDING YOUR S-100 OUTPUT

L. W. Amos - 1/9/84

1. Cross Polarization Pulse Sequence:
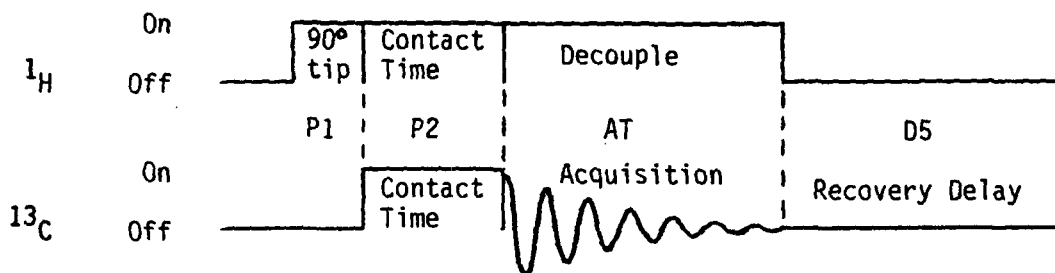
Typically,   P1 $\sim$ 5 μs   P2 $\sim$ 2 ms   AT $\sim$ 25 - 100 ms   D5 $\sim$ 0.5 - 1.0 s

2. Parameter names and their meanings:

NA	Number of acquisitions
SIZE	Number of computer data words used in Fourier transformation
QPD	Quadrature phase detector; number of phases per cycle
ABC	Automatic baseline control
ADC	Number of bits used in analog-digital converter
AI	Absolute intensity
SW	Spectral width in Hz on each side of transmitter pulse, normally located at 100 ppm
DW	Sampling time per data point in μs
RG	Acquisition trigger delay in μs
DE	Acquisition hardware delay (ringdown) in μs
F2	Proton decoupling frequency in MHz/power level
OF	Spectral referencing offset in Hz
SF	Spectrometer frequency (observe nucleus, normally ^{13}C) in MHz/power level
EM	Exponential multiplication (sensitivity enhancement) line broadening in Hz
PA, PB	Zero- and first-order phase corrections, respectively, in degrees
S/N	Signal-to-noise ratio
TT	Total time for data acquisition
SCALE	Horizontal frequency axis scale

3. Upper lefthand corner:

Top line: FILENAME   OPERATOR   DATE FILED
Following lines: Sample description and spin rate

ANALYTICAL WORKSHEET

Weyerhaeuser Company
Analytical Laboratories
Tacoma, Washington

SAMPLE NUMBER(S)
BLK. LIQUOR CHAR #4   p. 1 of 3

ANALYSIS FOR
INTENSITY CORREC'N. FOR SSB's.

SERVICE REQUEST NUMBER
12791

METHOD NUMBER
CP/MAS NMR   10350

DATA

Have SSB from arom. region; appears from ~270 to ~220 δ; upfield SSB is under aliphatics (expect UFSSB max at ~15δ). Arom. region runs from ~165 to ~90 δ, max, ~129 δ. Need to correct arom. & aliph. integrals for arom. SSB's; can work back & forth between two integrations: −X1 (300 to −100 δ) and −X2 (~270 to ~−30δ). Wind up with results on the basis of the −X2 values.

CHAR 4. BAF:	Range, δ	−X1 Raw Int.	−X2 Raw. Int.	Range, δ
(LFSSB)	300 − 220	4.34	0.34	220−196
	220 − 209	0.41		
−COO−	220 − 165	8.82	8.45	220−165
(Raw Arom)	165 − 90	49.68	54.21	165−90
(Raw Aliph)	90 − −30	36.40	37.35	90 − −30
	{Σ 220 to −30}	94.90	100.01	{Σ 220 to −30}

From −X1, $\frac{LFSSB}{Arom} = \frac{4.34}{49.68} = 0.0874$

$(2)\left(\frac{LFSSB}{Arom}\right) = 0.1747$

$(2)(LFSSB) = 8.68$

For −X2, $SSB = (Arom)\left(\frac{LFSSB}{Arom}\right) = (54.21)(0.0874)$
$= 4.74$

	−X1 Corrected Int.	−X2 Corrected Int.		
−COO− 220−165	8.82	8.45	220−165	−COO−
Arom [Raw + 2·LFSSB]	58.36	63.69	[Raw +2·SSB]	Arom.
Aliph [Raw −1·LFSSB]	32.06	32.61	[Raw −1. SSB]	Aliph.
{Total 220 to −30}	99.24	104.75	{Total, 220 to −30}	

94.90 + 4.34 = 99.24 ↰

Σ 104.75 = 100.01 + 4.74

$\frac{Arom}{Aliph} = 1.82$ 1.95 $= \frac{Arom.}{Aliph}$.

ANALYST   L. W. Amos

DATE   12-2-85

NB NUMBER

WITNESS

DATE

PAGE NUMBER

Material: **BLACK LIQUOR CHARS**
Analytical Laboratories
Tacoma, Washington

Analysis For: **INTENSITY ADJUSTMENTS – p.2 of 3**   DATA

Service Request ___**12791**___

Method ___**CP/MAS NMR**___

SAMPLE →	1 (64%)			2 (73%)			
SPECTRUM No. →	10354	-X1	-X2	10353	-X1	-X2	
RAW INTENSITY:	FREQ.	INT.	INT.	FREQ.	INT.	INT.	
LOW-FIELD SSB	300 to 225	4.44	—	300 to 220	4.36	—	
CARBOXYL	225 to 161	10.22	10.20	220 to 161	11.27	11.28	
AROMATIC	161 to 93	50.53	53.87	161 to 88	48.94	53.66	
ALIPHATIC	93 to -30	34.33	35.92	88 to -30	34.69	35.05	
TOTAL	225 to -30	95.08	99.99	220 to -30	94.90	99.99	
LFSSB/AROM.		0.0879	—		0.0891	—	
CALCD. SSB		—	4.73		—	4.78	
CORRECTED INTENSITY:							
CARBOXYL		10.22	10.20		11.27	11.28	
AROMATIC		59.41	63.33		57.66	63.22	
ALIPHATIC		29.89	31.19		30.33	30.27	
TOTAL		99.52	104.72		99.26	104.77	
RATIOS:							
ALIPH/AROMATIC		0.503	0.492		0.526	0.479	
-COO-/AROMATIC		0.172	0.161		0.196	0.178	
(ALIPH. + -COO-)/AROM.		0.675	0.654		0.722	0.657	
COO/ALIPH		0.34	.327		.373	.372	

Comments: _____

_____

_____

ANALYST **L. W. Amos**

WITNESS

DATE **1-9-96**

NB NUMBER

PAGE NUMBER 2/1

WEYERHAEUSER TECHNOLOGY CENTER
Analytical Laboratories
Tacoma, Washington
DATA

Material: BLACK LIQUOR CHARS

Analysis For: INTENSITY ADJUSTMENTS p. 3 of 3

Service Request: 12791

Method: CP/MAS NMR

SAMPLE →	3 (86%)			4 (100%)			
SPECTRUM No. →	10352	-X1	-X2	10350	-X1	-X2	
RAW INTENSITY:	FREQ.	INT.	INT.	FREQ.	INT.	INT.	
LOW-FIELD SSB	300 to 220 (217)	5.14	—	300 to 220	4.34	—	
CARBOXYL	(217) 220 to 168	8.49	7.75	220 to 165	8.82	8.45	
AROMATIC	168 to 93 (94)	51.80	57.05	165 to 90	49.68	54.21	
ALIPHATIC	(94) 93 to -30	34.16	35.19	90 to -30	36.40	37.35	
TOTAL	(217) 220 to -30	94.45	≠99.99	220 to -30	94.90	100.01	
LFSSB/AROM.		0.0992	—		0.0874	—	
CALCD. SSB		—	5.66		—	4.74	
CORRECTED INTENSITY:							
CARBOXYL		8.49	7.75		8.82	8.45	
AROMATIC		62.08	68.37		58.36	63.69	
ALIPHATIC		29.02	29.53		32.06	32.61	
TOTAL		99.59	105.65		99.24	104.75	
RATIOS:							
ALIPH/AROMATIC		0.468	0.432		0.549	0.512	
-COO-/AROMATIC		0.137	0.113		0.151	0.133	
(ALIPH. + -COO-)/AROM.		0.604	0.545		0.700	0.645	
-COO- ...		0.293	0.261		0.245	0.260	

Comments:

ANALYST: L. W. Amos

WITNESS:

DATE: 1-9-86

DATE:

NB NUMBER:

PAGE NUMBER:

3/80 FORM 6008 PRINT SHOP/TACOMA

BLCHAR   001   AMOS   06NOV85
BLK LIQ CHAR (64%)
3010 RPS; NEW SF

BLCHAR.1

>
FROM   220.19   TO   -30.17 ppm
  INTEGRAL=   100.00
FROM   220.19   TO   192.98 ppm
  INTEGRAL=   1.50
FROM   220.19   TO   171.45 ppm
  INTEGRAL=   6.79
FROM   220.19   TO   161.07 ppm
  INTEGRAL=   10.20
FROM   161.07   TO   92.95 ppm
  INTEGRAL=   53.87
FROM   92.95   TO   64.95 ppm
  INTEGRAL=   5.75
FROM   92.95   TO   51.06 ppm
  INTEGRAL=   11.82
FROM   92.95   TO   -18.04 ppm
  INTEGRAL=   35.74
FROM   92.95   TO   -30.17 ppm
  INTEGRAL=   35.92

128.731

145.971

182.062
173.616
166.814

87.327
75.450
68.600

56.329
48.147
40.628
32.088
25.703
15.435

200   150   100   50   0   PPM
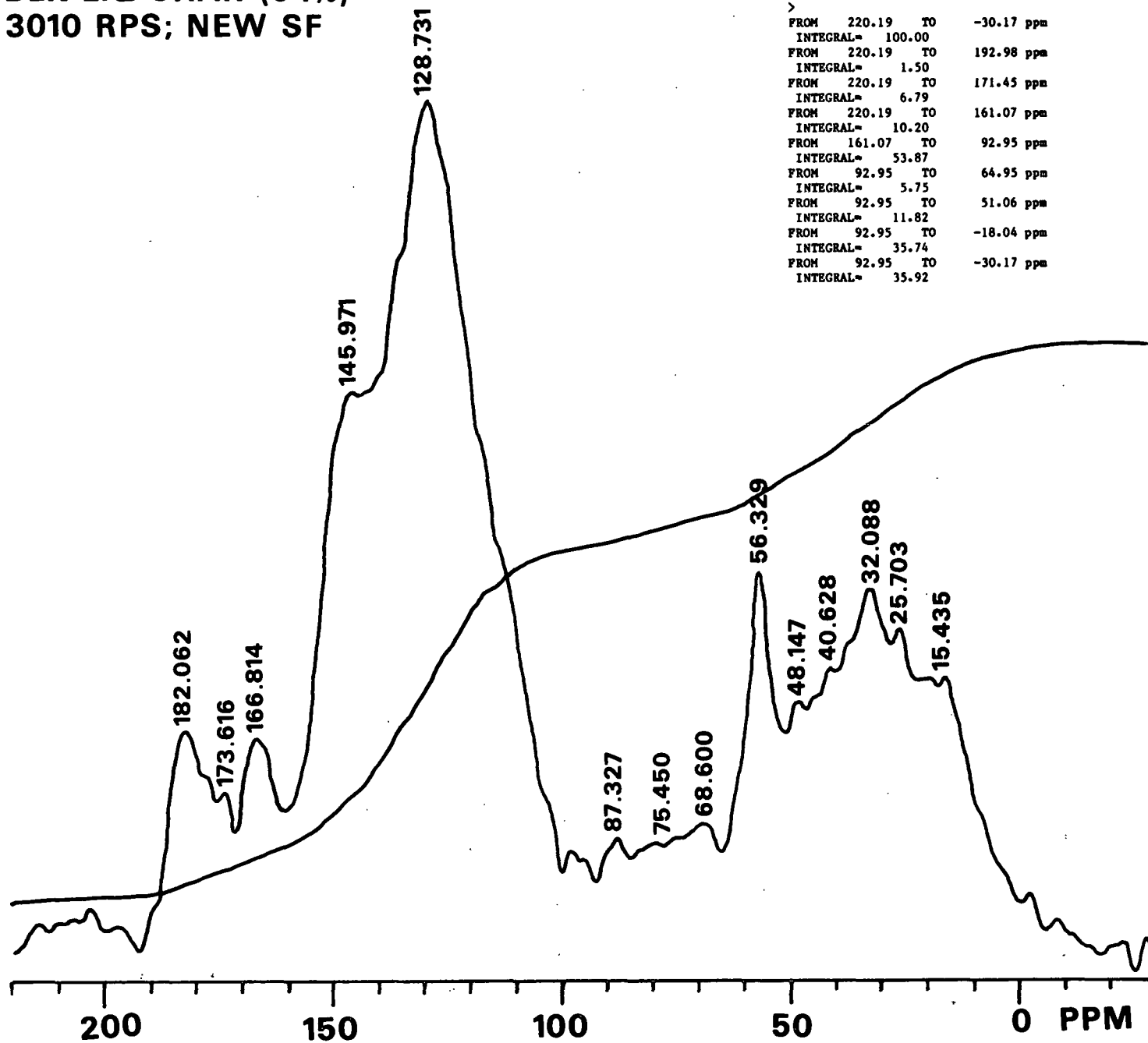
BLCHAR. 002 AMOS
BLK LIQ CHAR (73%)
NEW SF ; 2900 RPS

12NOV85

BLCHAR.2

>
FROM   220.19   TO   -30.17 ppm
  INTEGRAL=   100.00
FROM   220.19   TO   200.03 ppm
  INTEGRAL=   0.30
FROM   220.19   TO   164.99 ppm
  INTEGRAL=   10.09
FROM   220.19   TO   161.07 ppm
  INTEGRAL=   11.28
FROM   161.07   TO   97.06 ppm
  INTEGRAL=   52.13
FROM   161.07   TO   88.05 ppm
  INTEGRAL=   53.66
FROM   88.05   TO   65.93 ppm
  INTEGRAL=   4.39
FROM   88.05   TO   50.08 ppm
  INTEGRAL=   11.02
FROM   88.05   TO   -17.06 ppm
  INTEGRAL=   35.04
FROM   88.05   TO   -30.17 ppm
  INTEGRAL=   35.05

Peak labels: 181.323, 169.509, 163.626, 144.994, 130.368, 100.014, 80.428, 56.345, 46.739, 35.444, 31.212, 24.957, 17.395

200   150   100   50   0 PPM
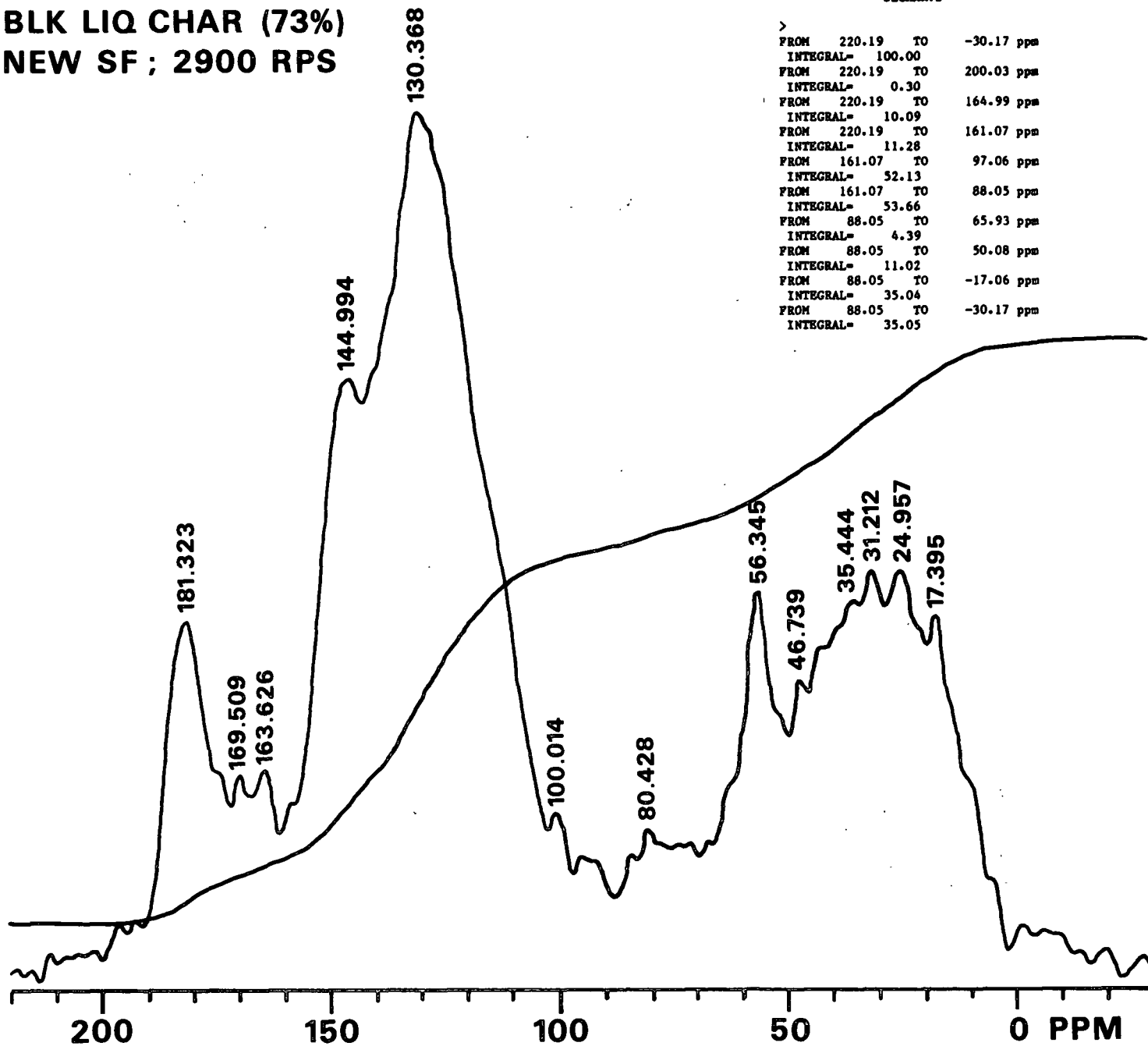
BLK LIQ CHAR (86%)

INTGR SPEC; 2900 RPS

CHAR3.BAF

```
>
FROM     220.19    TO      -30.17 ppm
 INTEGRAL=   100.00
FROM     220.19    TO      200.03 ppm
 INTEGRAL=     0.74
FROM     220.19    TO      191.02 ppm
 INTEGRAL=     1.12
FROM     220.19    TO      167.53 ppm
 INTEGRAL=     7.75
FROM     167.53    TO       93.93 ppm
 INTEGRAL=    57.05
FROM      93.93    TO       72.98 ppm
 INTEGRAL=     3.36
FROM      93.93    TO       64.95 ppm
 INTEGRAL=     4.73
FROM      93.93    TO       50.47 ppm
 INTEGRAL=    10.44
FROM      93.93    TO      -10.01 ppm
 INTEGRAL=    35.19
FROM      93.93    TO      -30.17 ppm
 INTEGRAL=    35.19
```
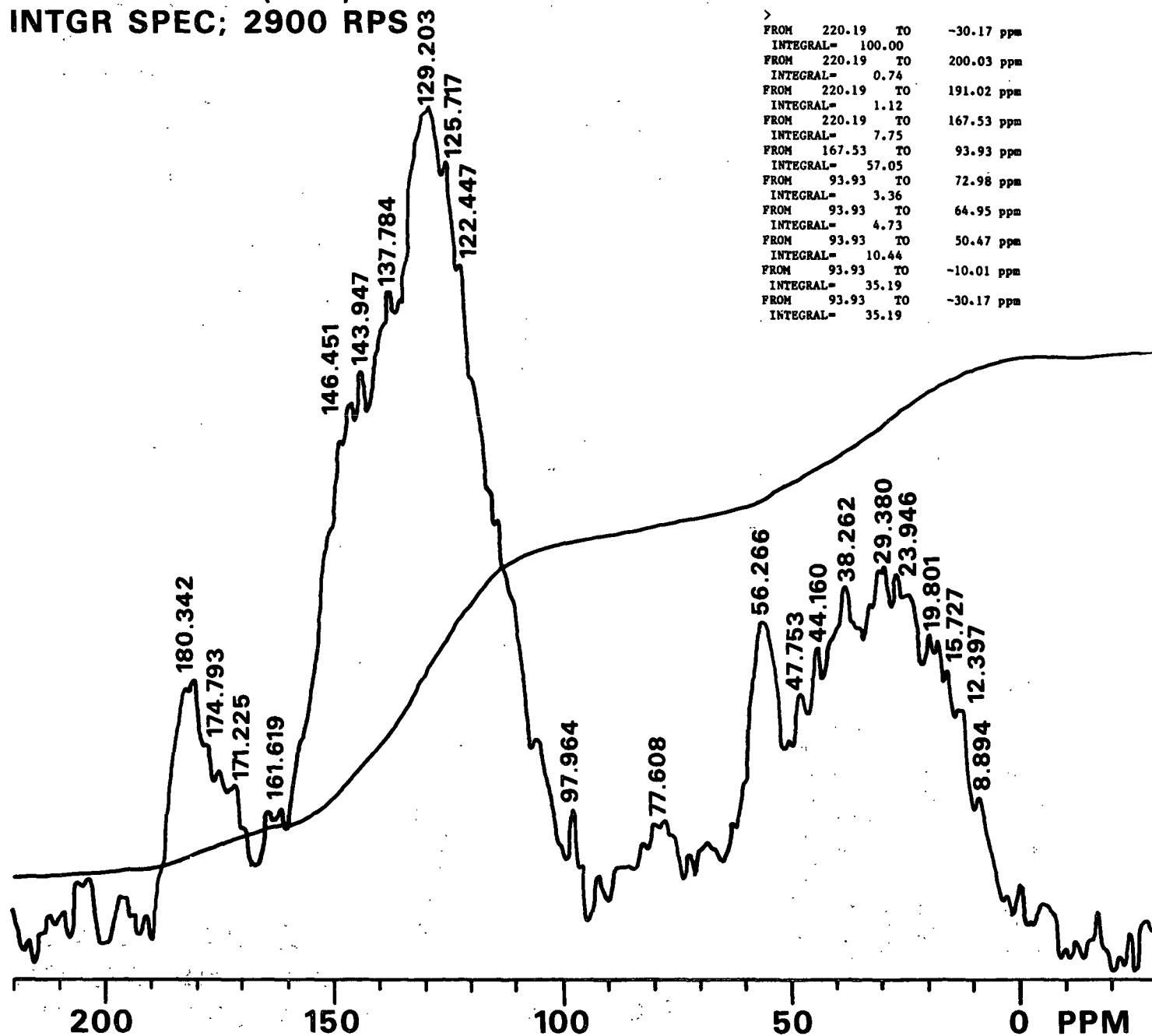
CHAR4   BAF   AMOS   18NOV85
BKL LIQ   CHAR (100%)
NEW SF   2900 RPS

CHAR4.BAF

```
>
FROM    220.19    TO       -30.17 ppm
  INTEGRAL=   100.00
FROM    220.19    TO       195.92 ppm
  INTEGRAL=     0.34
FROM    195.92    TO       164.99 ppm
  INTEGRAL=     8.11
FROM    195.92    TO        90.01 ppm
  INTEGRAL=    62.32
FROM     90.01    TO        72.00 ppm
  INTEGRAL=     3.89
FROM     72.00    TO       -14.90 ppm
  INTEGRAL=    33.46
FROM    -14.90    TO       -30.17 ppm
  INTEGRAL=    -0.02
```

129.330
133.881
145.728
138.921
182.380
172.355
102.183
80.604
74.129
55.945
45.900
40.209
30.646
25.859
22.504
14.710

200   150   100   50   0 PPM
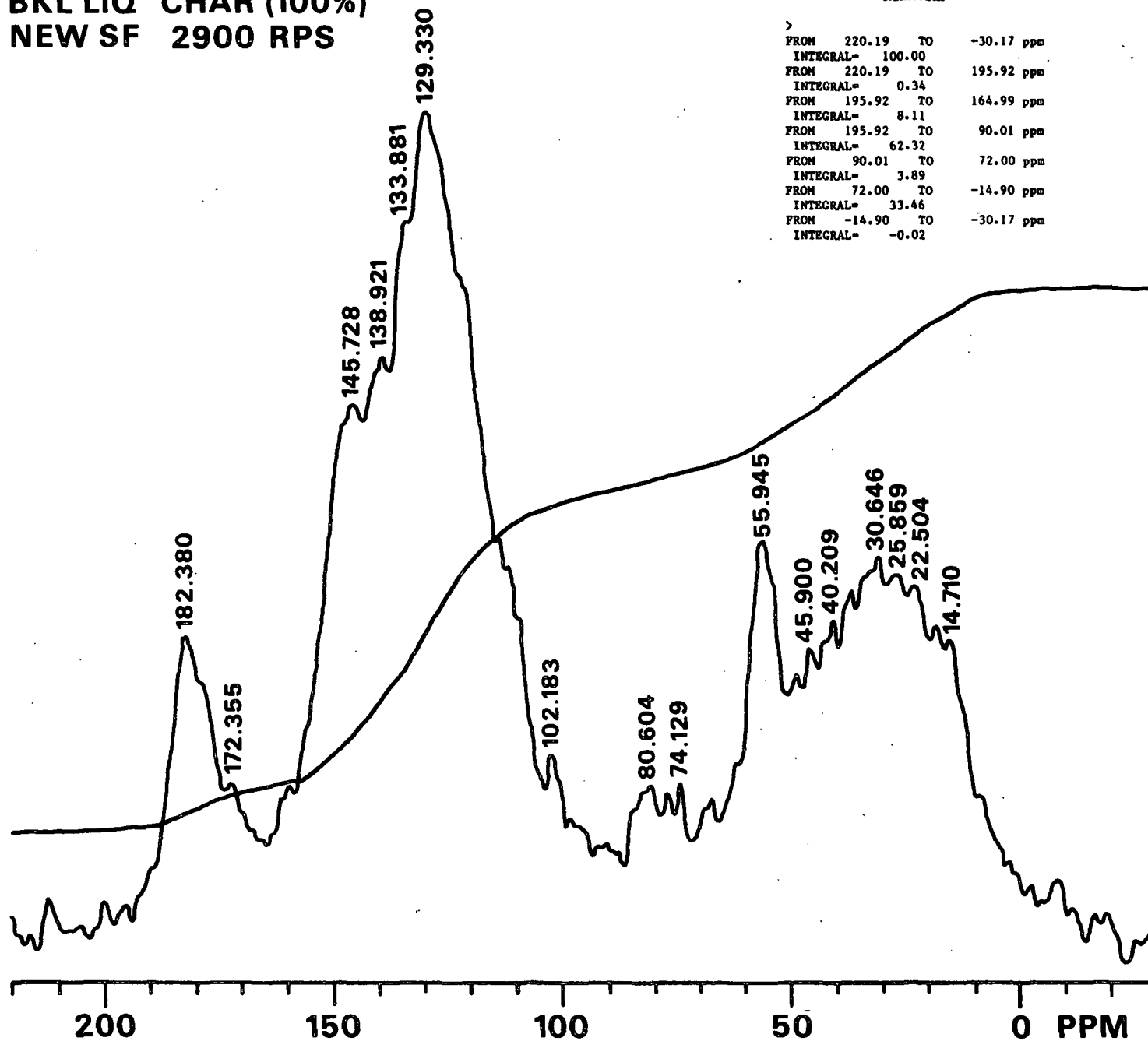
APPENDIX II

STATISTICS

Test 25. 2^3 Factorial experiment: temperature, % solids and heating rate (Table 14 and 15).

	+	−
a − Temperature	500°C	400°C
b − % Solids	100%	65%
c − Flow rate	833 cm^3/s	2500cm^3/s

SWOLLEN VOLUME, cm^3/g original solids

Flow Rate	833 cm^3/s		2500 cm^3/s	
% Solids	65%	100%	65%	100%
Temperature				
400°C	71	52	70	36
	72	42	84	40
500°C	183	52	190	55
	217	60	198	50

TIME TO MAXIMUM VOLUME, s

Flow Rate	833 cm^3/s		2500 cm^3/s	
% Solids	65%	100%	65%	100%
Temperature				
400°C	64	48	54	32
	65		43	
500°C	38	26	28	22
	38	32	28	

TIME TO SWOLLEN VOLUME					SWOLLEN VOLUME			
DF	SS	MS	F		DF	SS	MS	F
1	722	722	36.5(2)	a	1	8978	8978	77 (2)
1	288	288	14.6(1)	b	1	15312	15312	132 (2)
1	40	40	2.1	ab	1	6160	6160	53 (2)
1	312	312	15.8(1)	c	1	24	24	0.2
1	32	32	1.6	ac	1	4	4	0.03
1	2	2	0.1	bc	1	18	18	0.2
1	0.5	0.5	0.03	abc	1	32	32	0.3
4	79	19.75		error	7	811	116	

F (0.99,1,4) = 21.2   F (0.99,1,7) = 12.2
F (0.95,1,4) = 7.71

(1) − significant at 95% confidence level
(2) − significant at 99% confidence level

Test 50. Physical structure of black liquor (Table 17)

Swollen Volume, cm^3/g original solids

Type	1	2	3	4
	58	132	86	57
	78	86	102	65
	61	86	88	72
	73	108	136	88
	88			
mean	69	103	103	72

Type
1 - particles in the form of a pellet
2 - particles in the form of a single dry particle
3 - ground dried black liquor dried at 100 C
4 - ground dried black liquor dried at 140 C
    all pyrolysis runs were performed in small metal cups

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
Equality of cell means	3	4537	1512	4.95
Error	13	3969	305	

LSD - 26 cm^3/g
Confidence Level (CL) - 98% CL - level at which one can reject
the hypothesis that the cell means come from the same sample
space. CL of 95% indicates means are different with a 95%
confidence.

Sample Calculation for the Least Significant Difference

Standard error of difference between 2 means is

$$SE = \left(\frac{2MSE}{n}\right)^{1/2} \quad \text{for even replicates} \tag{4}$$

$$\text{if uneven replicates} \quad n = \frac{a}{\sum \frac{1}{n_i}} \tag{5}$$

$$LSD = (t\ (1-\alpha/2,v)(SE) \tag{6}$$

MSE - mean square of error
  n - number of replicates
  a - number of treatments
 ni - replicate size for each treatment
  v - degrees of freedom

For Test 50

$$n = \frac{4}{(\frac{1}{5} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4})} = 4.21$$

$$SE = [\frac{(2)(305)}{4.21}]^{1/2} = 12.0$$

$$t\ (0.95,13) = 2.160$$

$$LSD = (12.0)(2.160) = 26.0$$

Thus, for two means in this test to be significantly different from one another at the 95% confidence level the means must differ by 26 or more.

Test 48. Effect of moisture content on swelling (Table 18 and 19)

Swollen Volume, cm^3/g original solids

% Solids	100%	96%	86%	73%	65%	100H
	97	106	69	105	125	83
	79	91	63	101	115	66
	84	89	72	132	124	
		83	87	136		
mean	87	95	68	113	121	75

100H - black liquor dried at 140°C instead of 100°C

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
Equality of cell means	5	6241	1248	11.82
Error	11	1161	106	

LSD - 17 cm3/g
CL - 99+%

Test 51. Effect of solids content on swelling (Table 20) 500°C

Swollen Volume, cm3/g original solids

% Solids	65%	86%	100%
	158	128	75
	287	100	64
	195	114	113
	106		108
	192		
mean	196	114	90

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
Equality of cell means	2	24306	12153	17.82
Error	8	5456	682	

LSD - 44 cm^3/g
CL - 99+%

Test 51. Effect of solids content on swelling (Table 20) 700°C

Swollen Volume, cm^3/g original solids

% Solids	65%	86%	100%
	78	68	38
	159	43	53
	86	39	56
	103	50	61
mean	97	50	52

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
Equality of cell means	2	5589	2795	13.71
Error	9	1834	204	

LSD - 23 cm^3/g
CL - 99+%

Test 51. Effect of solids content on swelling (Table 20) 900°C

Swollen Volume, cm^3/g original solids

% Solids	65%	86%	100%
	35	41	50
	63	32	36
	42	27	40
	50	40	32
mean	48	35	40

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
Equality of cell means	2	383	182	2.27
Error	9	720	80	

LSD - 15 cm^3/g
CL - 84%

Test 40. Effect of black liquor composition on swelling (Table 23)

Swollen Volume, cm^3/g original solids

Substance	SA	KL	SA:KL 1:1
	19	15	76
	24	27	84
	22	21	59
	23	29	53
mean	22	23	68

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
Equality of cell means	2	5523	2761	32.70
Error	9	760	84	

LSD - 15 cm^3/g
CL - 99+%

Test 54. Effect of kraft lignin molecular weight on swelling (Table 25)

Swollen Volume, cm^3/g original solids

MW of Kraft Lignin	High	Med.	Low
	68	78	123
	33	88	109
	44	97	106
		96	127
mean	48	90	116

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
Equality of cell means	2	7924	3962	26.59
Error	8	1192	149	

LSD - 21 cm^3/g
CL - 99+%

Effect of extractives on swelling (Table 26)

Type	NORM	EF	7% ADDED
Vol., cm^3/g	48	109	26
	47	60	19
	44	68	31
		95	
		95	
		64	
mean	46	82	25

NORM - black liquor which had not been skimmed from normal wood
EF - black liquor from extractive free wood
7% ADDED - extractive free black liquor with 7% extractives added

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
Equality of cell means	2	7010	3505	14.66
Error	9	2152	239	

LSD - 26 cm^3/g
CL - 99+%

Statistics for Fig. 47

Swollen Volume cm^3/g original solids

KL:HA	HA	1:3	1:1	3:1	KL
pH 10.5	38	141	116	74	22
	57	136	94	34	
	163	120	54		
mean	48	147	110	54	
pH 12.0	41	129	179	51	28
	47	123	167	88	
		101	179	105	
mean	44	118	175	81	28
pH 13.0	77	124	139	63	31
	51	120	146	46	43
	40	122	164	71	
mean	56	122	150	60	37

Analysis of variance did not include hydroxy acid and kraft lignin samples, i.e., the 0 and 100 % KL.

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
% Kraft Lignin	2	32032	16016	66 (2)
pH	2	2081	1040	4.33(1)
Interaction	4	7066	1767	7.35(1)
Error	18	4327	240	

LSD - 27 cm^3/g
(1) - significant at 95% confidence level
(2) - significant at 99% confidence level

Test 53. Effect of inorganic on swelling (Fig. 51)

Swollen Volume, cm^3/g original solids

% Na_2SO_4	0%	15%	20%	25%	35%
	152	107	110	88	89
	139	132	99	99	111
	130	127	124	105	103
	86	134	130	107	90
	123	135			
mean	126	127	116	100	100

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
Equality of cell means	4	3589	897	4.06
Error	19	4198	220	

LSD - 21 cm^3/g
CL - 98%

Test 45. Effect of extractives on swelling (Fig. 52)

Swollen Volume, cm^3/g original solids

% Extractives	0%	1.2%	4.3%	10.8%	B
	109	50	46	24	122
	60	86	40	33	103
	68	61	34	23	58
	95	84	50	21	
	95				
	64				
mean	82	70	43	25	95

B - benzene/ethyl alcohol solvent mixture added to extractive free black liquor, approximately a couple of mg.

Analysis of Variance Table

Source of Variation	DF	SS	MS	F Value
Equality of cell means	4	12664	3166	9.38
Error	16	5396	337	

LSD - 28 cm^3/g
CL - 99+%