AN ABSTRACT OF THE THESIS OF

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Title: THE DETERMINATION OF THE APPROXIMATE MOLECULAR
        WEIGHT, PARTICLE SIZE, AND HOMOGENEITY OF SOME
        SODA LIGNINS

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Commercially available waste liquors were obtained from the Longview Fibre Company and the Crown-Zellerbach plant at Camas, Washington, which employ alkaline methods of pulping. This was done in order to study some of their fundamental chemistry.

The lignin in these waste liquors was precipitated by acidification with sulfuric acid and purified by repeated precipitation from dioxane solution.

The general behavior of lignin obtained in the alkaline pulping processes indicates that the material is colloidally dispersed. A study of diffusion velocity offers a good means of estimating the molecular weight, particle size, and degree of homogeneity of these colloidally dispersed materials.

A membrane diffusion method was used to gain this end. The apparatus must be standardized against a substance whose diffusion coefficient is known. This was accomplished by calibrating the two diffusion cells used with 0.1 N. KCl whose diffusion coefficient is known. By substituting in the equation of Northrop and Anson, the cell constant was determined, from which the diffusion coefficient of an unknown substance can be found:

$$D = \frac{\log_{10} c_o - \log_{10} (c_o - 2c)}{Kt}$$

where c_o is the initial concentration in the cell, c the final concentration which has been attained in the beaker, K the cell constant, t the elapsed time, and D the diffusion coefficient.

In determining the diffusion coefficients of the lignin samples, the same method was used as in determining the cell constants. These solutions were analyzed by means of a Klett-Summerson colorimeter. The two concentrations obtained in this manner were then substituted into the equation previously given. The values for D obtained were then substituted in the Stokes-Einstein equation in order to determine the particle size:

$$D = \frac{RT}{N6\pi\eta r}$$

where D is the diffusion coefficient at infinite dilution, T is the absolute temperature, R is the gas constant, r is the radius of the molecule, η is the viscosity of the solvent, and N is Avogadro's number. The value for r is then substituted into the following equation in order to determine the molecular weight of the lignin:

$$M = 4/3 \pi r^3 dN \quad \text{where r is the radius of the}$$

particle and d is the density of lignin.

It is a well known fact that if the square root of the concentration of a substance is plotted against its diffusion coefficient and extrapolated to infinite dilution, a diffusion coefficient will be obtained which may be used to determine the actual molecular weight of the substance. Since in this study it was possible to deal with only relatively dilute solutions, the diffusion coefficients obtained would not have a very wide range of variation. However, it is believed that a fairly good average value was obtained which could be used to calculate the approximate weight of the lignin. The extrapolated D values for both samples dealt with give a particle size of 1.40×10^{-7} cm. and a molecular weight of approximately 8,500. It is interesting to note that the Longview Fibre Company sample was cooked under somewhat more vigorous conditions of temperature and pressure; nonetheless, about the same results were obtained with both samples, indicating that both plants apparently arrived at approximately the same end point.

In order to determine the homogeneity of these particles, the diffusion cells were set up as before. After diffusing a given amount of time, the solution in the beaker was removed and analyzed and replaced with a fresh solution of dioxane. This was repeated several times. It was found in both cases that as the concentration became less, the calculated values for D also were smaller, indicating that the particles were non-homogeneous.

THE DETERMINATION OF THE APPROXIMATE
MOLECULAR WEIGHT, PARTICLE SIZE, AND
HOMOGENEITY OF SOME SODA LIGNINS

by

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ACKNOWLEDGMENT

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FOREWORD

It has been apparent for many years that there is a plentiful, readily available source of the so-called lignified portion of the wood going to waste in our paper mills. A great deal of work has been done in an attempt to find uses for this lignin as it is found in the waste products from these commercial processes, and some progress has been made in this direction, notably in the field of plastics.

Of course, much fundamental work has been done with the lignin obtained from wood, but since such vigorous methods are necessary to strip the lignin from the wood, it is obvious that the isolated lignin obtained is far different from the lignin found in situ, and hence little is actually known of its constitution. It is generally agreed that lignin is somehow chemically combined with the cellulose in plants from which it is derived.

Any industrial processes for the utilization of lignin will probably be based on the lignin obtained as a by-product in the pulp and paper industry. It, therefore, seems practical to study some of these lignins as they are produced commercially and which are now waste products. Commercially available waste liquors were obtained from various paper mills using alkaline methods of pulping

in order to study some of their fundamental chemistry.
The contribution of this thesis toward that end is an
attempt to determine the approximate molecular weight,
particle size, and homogeneity of some of these lignins
in the hope that it will add to the store of information
available concerning commercial sources of lignin.

THE DETERMINATION OF THE APPROXIMATE MOLECULAR WEIGHT, PARTICLE SIZE, AND HOMOGENEITY OF SOME SODA LIGNINS

CHAPTER I

INTRODUCTION

A. METHODS OF DIFFUSION

The general behavior of lignin obtained in the alkaline pulping processes indicates that the material is colloidally dispersed. A study of diffusion velocity offers a good means of estimating the molecular weight, particle size, and homogeneity of these colloidally dispersed materials.

A membrane diffusion method was used to gain this end since it is so much easier to work with than a free diffusion method. There is no danger of mixing and rapid concentration changes are obtained due to the existence of a sharp diffusion gradient in the diaphragm. However, the chief argument which might be used against this method is that the apparatus must be standardized against a substance whose diffusion coefficient is known.

Various methods had been employed before 1929 to separate liquids by means of animal membranes, colloidal membranes, etc. but in this year Northrop and Anson (26) were the first to develop a membrane which was practical

for diffusion. It was found that sintered glass or alundum disks were satisfactory for this purpose.

McBain and his co-workers (5,19,20,21,22) improved further on the cell developed by Northrop. The apparatus developed by them consists of separating two bodies of solutions by a porous membrane which has pores of visible or microscopic size, small enough to prevent the liquid from flowing through en masse and yet much larger than the molecules of the solvent. In this investigation, diaphragms having a pore radius of $2\text{-}5 \times 10^4$ $\overset{o}{A}$ and a diameter and thickness of 5 x 0.2 cm. were used. A drawing of the diffusion cell is shown in Figure 1.
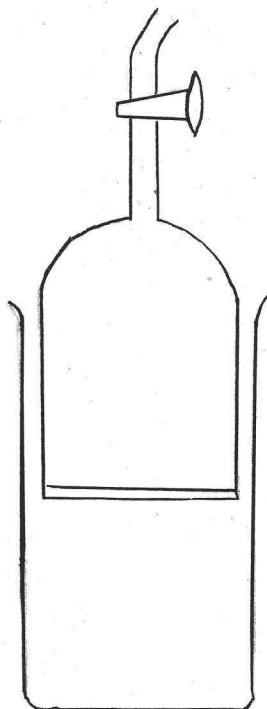
Fig. 1. The Sintered Glass Diffusion Cell

The basic relation for diffusion studies is Fick's equation (8):

$$ds = -Dq \frac{dc}{dx} \quad dt$$

where q is the cross-sectional area, $\frac{dc}{dx}$ is the concentration gradient, ds the amount of solute passing through the membrane in time dt, and D the diffusion coefficient. It can then be seen that D is the amount of material diffusing across unit area in unit time when the concentration gradient is unity.

Einstein (7) has developed an equation for determining particle sizes if the molecules are large, spherical, and uncharged:

$$D = \frac{RT}{N6\pi\eta r}$$

where D is the diffusion coefficient at infinite dilution, T is the absolute temperature, R is the gas constant, r is the radius of the molecule, η is the viscosity of the solvent, and N is Avogadro's number. This equation may now be used to determine particle sizes from the diffusion coefficient.

For membrane diffusion, Northrop and Anson have developed the following relationship:

$$D = \frac{\log_{10} c_0 - \log_{10} (c_0 - 2c)}{Kt}$$

where c_0 is the initial concentration in the cell, c the

final concentration which has been attained in the beaker, K the cell constant, t the elapsed time, and D the diffusion coefficient.

This last equation was utilized in determining the cell constants and the diffusion coefficients in this investigation. The cell constant K is determined for each cell by measuring the diffusion of a substance whose diffusion coefficient is known and substituting in Northrop and Anson's equation. The values for K obtained in this manner, which are different for each cell used, may then be used in calculating all subsequent diffusion coefficients.

Using the values obtained for D and substituting in the Einstein equation, the particle size is determined. The molecular weight may then be determined by making use of the following relationship:

$$M = \frac{4}{3}\pi r^3 dN$$

where r is the radius of the particle, N is Avogadro's number, and d is the density.

B. CHEMICAL NATURE OF LIGNIN

1. Nature of Lignin in situ

For a long time it has been known that in the development of the cell walls of plants, a change occurs in which the cellulose becomes hardened, or lignified. The cell

wall consists of various layers, the middle lamella, the primary wall, and the secondary wall. It has been found that the lignin is largely accumulated in the middle lamella. This lignin differs from species to species and even lignin isolated by different methods from the same species differs in its properties. Hence, since no uniform lignin has ever been isolated, it may be considered somewhat doubtful that there exists a distinct compound which deserves the name lignin. Phillips and Goss (28), working with barley, stated that the percentage of lignin as well as the methoxyl in the lignin increased in a regular manner as the plant developed and matured.

According to many investigators, lignin seems to occur in chemical combination with cellulose and related polysaccharides as an aromatic glucoside. Hagglund and Bjorkman (11), Mehta (24), Phillips (27), Klason (16), Harris, Sherrard, and Mitchell (13), and Norman (25), support this view.

According to Fuchs (10), the formation of lignin may be considered as a biochemical process with enzymatic action involved. That pectins may be regarded as an intermediate stage in lignin formation has been put forth by Ehrlich (6). Therefore, lignin formation may be regarded as an enzymatic process, changing pectins in such a way as to remove the carbon dioxide, water, and oxygen from the

original molecules.

Assuming lignin to be a definite chemical substance
of sorts, various formulae have been suggested to account
for its chemical nature. Klason (15) was the first to sug-
gest an aromatic structure for lignin and considered it a
condensation product of coniferyl alcohol. There is strong
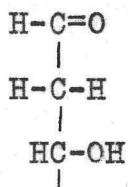evidence that lignin contains an aromatic nucleus due to
the fact that upon degradation aromatic compounds result.

Freudenberg (9) believes that lignin is composed of
the following structural units in which the three carbon
chain may be either I, II, or III, and that these may be
attached to aromatic nuclei IV, V, or VI.
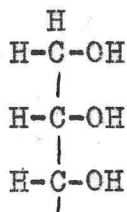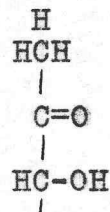
```
      H                                        H
   H-C-OH              H-C=O                   HCH
      |                   |                     |
   H-C-OH              H-C-H                    C=O
      |                   |                     |
   H-C-OH              HC-OH                   HC-OH
      |                   |                     |

      I                  II                   III
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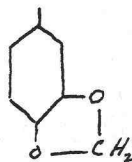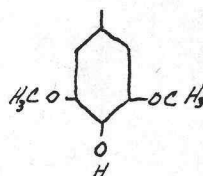

      IV   V   VI

These units, in turn, Freudenberg believes, are poly-
merized to form a chain such as that shown below.
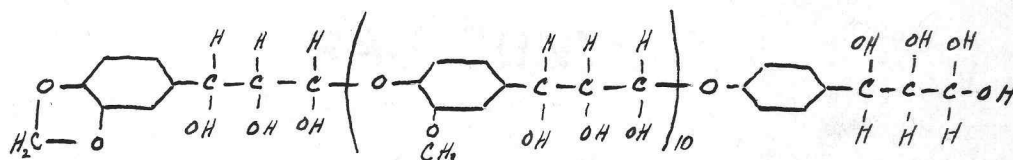
Many other structures have been proposed for this so-
called lignin, but Freudenberg's is perhaps the best known.
However, it must be realized that these structures appear-
ing throughout the literature cannot be accepted for the
true structure of lignin. No constitutional formula for
lignin at the present time can be proposed because of our
incomplete knowledge of the chemistry of this substance.

2. NATURE OF THE SODA LIGNINS

An important application of Freudenberg's formula is
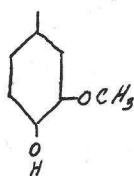concerned with its relationship to pulp manufacture. The
various processes used in pulp manufacture make use of the
fact that when wood is treated with various chemicals, the
lignin of the lignified tissues is removed, leaving behind
the cellulose as unchanged as possible. This is quite dif-
ficult to do because the lignin seems to stick to the cell

membrane. None of the processes having industrial application have been able to overcome this difficulty; and, since vigorous chemical action must be employed in order to remove the lignin from the rest of the wood with which it is apparently chemically combined, it seems very likely that the lignin resulting is altered to some extent from the form in which it existed originally in the wood.

Until recent years, little attention has been paid to what could be done with the black liquor left at the end of alkaline pulping processes since it has always been disposed of by burning for soda recovery. Now the possibilities of the greater usefulness of this liquor have been realized. As far back as 1909, Rinman (32) found that humus substances could be precipitated from black liquor by the addition of carbon dioxide. The next year, Hough (14) found that this ligneous matter could be precipitated by acidification with sulfuric acid. Cram (4) in 1914 suggested that the precipitate formed by treating the liquor with hydrochloric acid could be used for the preparation of paper size, dyestuff, wood stain, and varnish.

H. F. Lewis (17) made an extensive study of the recovery of chemicals by the Goodell process from the lignin removed from wood in the Kraft process. This involves the separation, drying of black liquor, destructive distillation of the black liquor solids, etc.

The greatest use to which this precipitated lignin has been put is as a plastic. Synthetic resins were prepared at an early date by Conner (3) and Phillips (29). Conner mixed the lignin with an aldehyde and a phenolic substance, while Phillips reacted the lignin with various aromatic amines and with furfural to yield various condensation products.

Wallace (35), Reboulet (31), and Hambly (12) are also among those who have seen the possibilities of the plastic masses obtained by the acidification of the black liquors.

The synthetic plastic, Meadol (30), has been prepared commercially by acidifying the black liquor with carbon dioxide obtained from flue gas. The addition of carbon dioxide precipitates about thirty per cent of the total organic matter in the liquor, which is subsequently washed with dilute sulfuric acid and water and dried. It was found that the product is soluble in dilute alkali and polar organic solvents, has about twenty-one and one-half per cent methoxyl and eight and one-half percent hydroxyl groups, and can be used as a thermoplastic resin.

Further study of this commercial lignin has revealed many new derivatives. As many as 26 esters of mono- and dibasic aliphatic acids, as well as esters of several aromatic acids, have been characterized (2,18). Along the same lines, Wallace (34) found that when the lignin

obtained by precipitating the black liquor with sulfuric acid is heated with an organic polycarboxylic acid, a fusible resin is obtained containing many ether and ester groups.

It would seem that actually, except for the work done by the Mead Corporation, little has been done to develop the possibilities of the lignin precipitated from the spent alkaline liquors. Obviously, the pulp plants were more interested in improving the quality of the pulp produced rather than what could be done with the waste products. But now, most plants are becoming interested in the many possibilities presented by these liquors.

CHAPTER II

MATERIALS USED

Experiments were carried out with commercial black liquors which were obtained from the Longview Fibre Company, Longview, Washington, and the Crown-Zellerbach Paper Company, Camas, Washington.

The lignin which was dissolved in these alkali liquors was first precipitated by acidification with 7.2 per cent sulfuric acid. The acid was added slowly to the liquor with rapid stirring. There was little or no evidence of heating. It was necessary to determine the ideal pH at which to precipitate these lignins in order to obtain the most easily filterable lignin with which to work. After precipitating at pH's of 2, 4, and 6, using a pH meter for purposes of accuracy, it was found that a pH of 4 was about the best at which to work since a somewhat gummy precipitate was obtained upon precipitation at a pH of 6. The acidified lignin was digested for about one-half hour on a hot plate and then filtered. At the end of this time, it was very easy to filter. The light brown precipitate was washed thoroughly and then dissolved in hot dioxane, in which it is readily soluble.

Various other solvents were tested, such as ethyl alcohol, methyl alcohol, ethanolamine and alcohol,

pyridine, dry acetone, wet acetone, chloroform, benzene, ethyl acetate, dioxane, octyl alcohol, and hexyl alcohol. Lignin was readily soluble in sodium hydroxide and in pyridine, but these two were discarded as possibilities (the sodium hydroxide would have attacked the diffusion cell and hence would have made any sort of accurate results impossible; the pyridine rejected for obvious reasons). The lignin was quite soluble in wet acetone but dioxane was deemed the best solvent with which to do further experiments.

The solution was then filtered to remove any dioxane-insoluble materials and then slowly poured into rapidly stirred ether to reprecipitate the lignin. Twenty times the volume of the dioxane was used for this purpose since it was found that by using too small a volume of ether a gummy precipitate was obtained. This material was dried in an oven at 60° C. and powdered. Since it is probable that not all the ether-soluble material was removed by one extraction, the powdered lignin was again dissolved in dioxane, reprecipitated by pouring into ether, filtered, dried, and ground to a fine powder.

In order to carry out diffusion experiments with these lignins it was necessary to determine some means of analyzing the material in the cell and that which had diffused out into the solvent in a given amount of time. A

Klett-Summerson colorimeter was obtained for this purpose.
It was then necessary to set up a series of standards for
both of the samples of purified lignin dissolved in di-
oxane. A weighed amount of lignin was dissolved in diox-
ane and diluted to 250 ml. Solutions of varying concentra-
tion were then made up from the original solutions of known
concentration. Readings were taken with the colorimeter
and the results plotted against grams of lignin dissolved
in 100 ml. of solution. It was then possible to determine
the concentrations of the solutions easily after diffusion.

CHAPTER III

EXPERIMENTAL PROCEDURES

A. DETERMINATION OF THE CELL CONSTANTS

As was mentioned before, membrane diffusion cells must
be calibrated by the use of a substance whose diffusion co-
efficient is known. In the present series of experiments,
0.1 N. KCl was used for determining the cell constants.
Gas-free distilled water was used to wash out the cells by
means of suction. After no gas bubbles remained in the
membrane, the cell was filled with 0.1 N. KCl and the ex-
cess solution remaining in the tip above the stop-cocks re-
moved by means of suction. The cell was then placed in a
beaker of distilled water whose volume equaled that of the
cell. The cell was then placed in a thermostat held at
20° C. $\pm$ 0.2. After a preliminary diffusion of 150 minutes
to set up a constant rate of diffusion, the cell was re-
moved from the beaker of water and solution adhering to the
outside of the cell was removed by wiping with a clean
cloth. The cell was then transferred to another beaker of
distilled water containing an amount equal to the volume
of the cell. This water had first been brought to the
temperature of the thermostat. This was then allowed to
diffuse, after which the solution in the beaker and that
in the cell were analyzed to determine how much KCl had

diffused out in a given amount of time.

In analyzing the solutions, the concentrations were determined by titrating with 0.1 N. $AgNO_3$, using dichloro-fluorescin as an adsorption indicator. In drawing out the solution in the cell prior to analysis, care was taken to discard the first few milliliters. Both the solutions within the cell and the beaker were analyzed by this meth-od and the results substituted in the equation by Northrop and Anson (28). The accepted value for 0.1 N. KCl at 20°C. is 1.67 cm^2/day or 1.94 x 10^{-5} cm^2/second. The latter value for D was used in calculating cell contents since the results therefrom came out in whole numbers. The values obtained for the cell constants may be found in Table I.

B. PROCEDURE FOR DETERMINING THE MOLECULAR WEIGHTS OF THE PRECIPITATED LIGNINS

The soda lignins obtained from the Longview Fibre Company and the Crown-Zellerbach Paper Company were used in the diffusion experiments. The two cells whose con-stants had previously been determined were used in carry-ing out diffusion experiments with these precipitated lig-nins. The lignin samples were first dissolved in dioxane and then placed in the diffusion cells. Using the method described in Chapter IIIA, the cells were first thoroughly rinsed with distilled water which had been boiled and

evacuated and then filled with dioxane from which the dissolved air had also been removed. The dioxane was then slowly replaced in the cell by drawing the gas-free lignin solution into it. This procedure, of course, diluted the solution somewhat, but was deemed necessary. The cell was then placed in a close-fitting beaker containing an amount of dioxane equal to that in the cell and placed in the thermostat. This was then allowed to diffuse for several hours in order to set up a constant diffusion gradient and also to allow the cell to come to the temperature in the thermostat. At the end of this time, the cell was transferred to another beaker of dioxane of equal volume and allowed to diffuse for a long enough period of time to allow enough diffusion to permit analysis of the solution in the beaker by means of the colorimeter.

During diffusion, the cell was partially sealed with rubber to minimize evaporation of the dioxane. From the readings taken with the colorimeter, the concentrations of the solutions within the cell and the beaker were determined and the results substituted in the equation of Northrop and Anson to obtain the diffusion coefficient. The values so obtained were then substituted in the Stokes-Einstein equation in order to determine the particle size and hence the molecular weight of the lignins.

C. PROCEDURE FOR STUDYING THE HOMOGENEITY
OF THE LIGNIN SAMPLES

In order to study the homogeneity of these particles,
the diffusion cells were set up as previously described.
The particles were allowed to diffuse for a given unit
of time. The solution in the beaker was then removed and
analyzed and replaced by a fresh solution of dioxane
without disturbing the solution in the cell. This was
repeated several times, analyzing the solution in the
beaker each time to determine how much lignin had diffused
out. At the end of the series of runs, the solution in
the cell was analyzed and, knowing how much lignin had
diffused out for each run, the concentration in the cells
at the beginning of each run was determined. From these
data, the diffusion coefficient for each run was calcu-
lated and the variation of each D value with concentration
determined.

CHAPTER IV

RESULTS AND CONCLUSIONS

A. HOMOGENEITY OF LIGNIN PARTICLES

In determining the homogeneity of these lignin par-
ticles, it was found, as shown in Table II, that as the
solutions in the diffusion cell became less concentrated,
the values for the diffusion coefficient became less. If
the particles had all been the same size, the diffusion
coefficient should have become larger as the concentration
went down. If not homogeneous, the smaller particles
would have diffused out first, leaving the larger par-
ticles which would, of course, diffuse out at a much slow-
er rate. Since this was true with both samples used, it
is safe to state that the particles with which we were
dealing in these experiments were nonhomogeneous.

B. THE APPROXIMATE MOLECULAR WEIGHT OF LIGNIN

It is a well known fact that if the square root of
the concentration of a substance is plotted against its
diffusion coefficient and extrapolated to infinite dilu-
tion, a diffusion coefficient will be obtained which may
be used to determine the actual molecular weight of the
substance. As is obvious from Figures II and III, it was
possible to deal with only relatively dilute solutions.
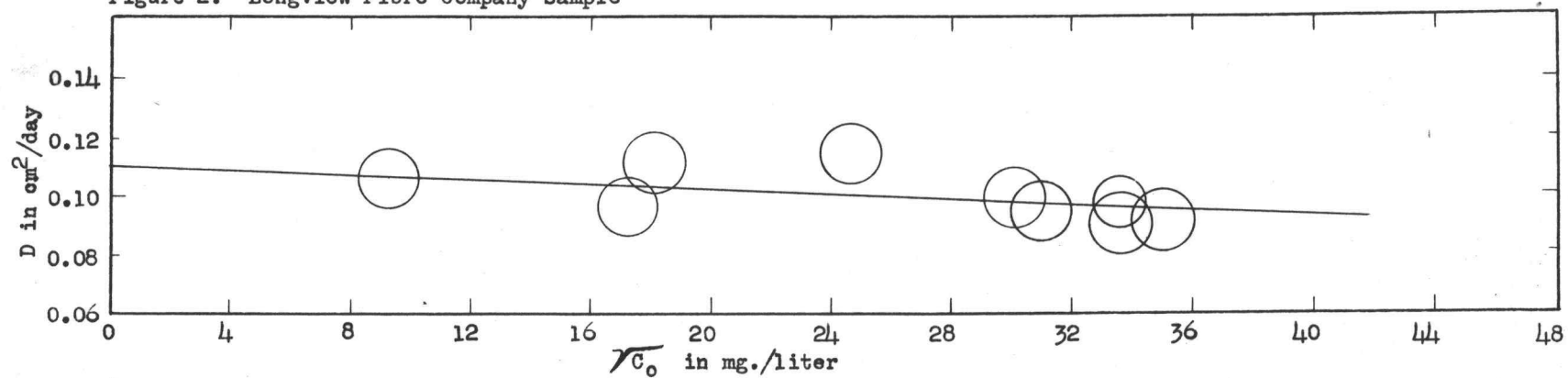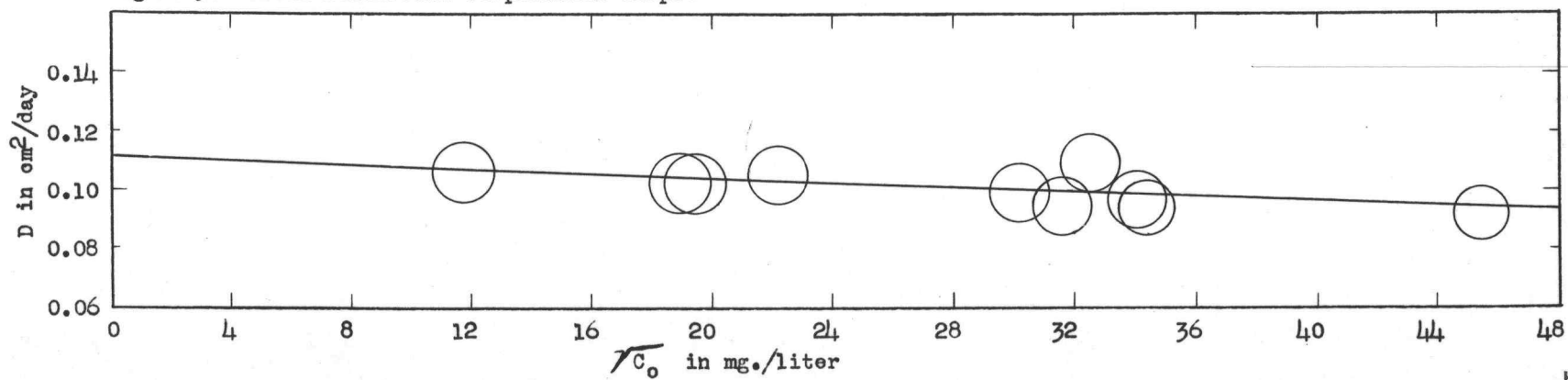
Figure 2. Longview Fibre Company Sample

Figure 3. Crown-Zellerbach Corporation Sample

Hence, the diffusion coefficients obtained would not have a very wide range of variation. However, by following the usual plan of extrapolation to infinite dilution, it is believed that a fairly good average value will be obtained which may be used to calculate the approximate molecular weight of the lignin. It is also believed that the experimental values for D may be considered accurate to the extent of ± 0.01 cm^2/day. For this reason, each experimental point is shown with a radius of 0.01 cm^2/day. The extrapolated D values for both samples give a radius of 1.40×10^{-7} cm. and a molecular weight of 8,538. These results may be seen to be a pretty good average of the values obtained when dealing with dilute solutions of the two lignin samples dissolved in dioxane as a solvent. It must be borne in mind, however, that since we are dealing with nonhomogeneous particles, the molecular weights of the smaller particles which are diffusing out first are what are actually being measured. However, the results obtained still give a basis upon which to compare the two samples.

C. RELATIONSHIP OF RESULTS TO COOKING PROCEDURE USED

The results show that the molecular weight of the Longview Fibre Company lignin is comparable to that obtained using the lignin sample obtained from the

Crown-Zellerbach Corporation. A study of the conditions
under which the wood was cooked in both cases was deemed
necessary to account for the results. The Longview Fibre
Company used Douglas fir alone and held their cook at a
temperature of 360° F. for a period of an hour. It took
one hour and forty-five minutes to bring the cook to a
maximum pressure of 120 pounds per square inch where it
was held for sixty minutes. Although there were no defi-
nite data to tell the exact ratio of alkali to wood,
there is indicated a range of 18-20 per cent active alkali
based on the oven-dry weight of wood charged. Turning now
to the conditions under which the Crown-Zellerbach mill at
Camas, Washington cooked their wood, it was found that
using a ratio of 25 per cent hemlock to 75 per cent Douglas
fir, the top temperature under which the wood was cooked
was at 344° F. It took 62 minutes to bring their pressure
up to 106 pounds per square inch where it was held for a
period of 32 minutes. A little more exact information con-
cerning the charge was available from this cook. Five
hundred and eighty-six pounds of active Na_2O were used per
ton of air-dry pulp. This charge, when based on the weight
of the oven-dry wood, is 13.7 per cent active chemical,
used at a concentration of 7.1 pounds per cubic foot of
total alkali as Na_2O and 5.8 pounds per cubic foot of
active alkali as Na_2O. The sulfidity was found to be 25.4

per cent and the concentration of sulfide expressed as Na_2O of 1.80 pounds per cubic foot.

It should be further noted that the Longview Fibre Company uses a stationary digester while the Crown-Zellerbach plant uses a rotary digester.

From a consideration of the information available, it is apparent that the Longview Fibre Company used more vigorous methods of cooking than the Crown-Zellerbach people. It took them a longer period of time to bring the cook to its top pressure which was higher than that used for the other cook. Also, a slightly higher temperature was used in the case of the first cook. It is apparent then that although somewhat more vigorous cooking conditions were employed at the Longview plant, similar results as to the particle size and molecular weight of the lignins were obtained, indicating that both plants arrived at about the same end point, even though they used varied conditions.

The results given are, obviously, only approximate and yet generalizations may be made from them which have been summarized in this chapter. It is hoped that this fundamental study into one phase of the nature of soda lignins will add to the already rapidly growing store of information with which we in the northwest are particularly concerned.

CHAPTER V

SUMMARY

Samples of black liquor were obtained from the Longview Fibre Company and the Crown-Zellerbach Corporation plant at Camas, Washington. The lignin dissolved therein was precipitated by acidification with sulfuric acid, purified by precipitation from dioxane, and finally dissolved in dioxane for use in the diffusion studies. A membrane diffusion cell was utilized in determining the diffusion coefficients of the lignin particles, from which their approximate molecular weight, particle size, and degree of homogeneity were determined.

CHAPTER VI

DATA

Table I. Determination of Cell Constants

Cell #1	No. Min. Run	K	Cell #2	No. Min. Run	K
Run 2	2665	2.12	Run 2	2665	3.05
Run 4	960	2.35	Run 3	480	3.13
Run 5	1815	2.21	Run 4	995	3.13
			Run 5	1815	3.07

Average K for Cell #1 = 2.23   Average K for Cell #2 = 3.10

Table II. Determination of Homogeneity of Samples

A. Longview Fibre Company:

Time in Minutes	c_o^*	c^*	D^*
505	3751	8.49	0.1519
725	3742	10.42	0.1293
890	3723	10.04	0.1023
550	3713	6.18	0.1021

B. Crown-Zellerbach Corporation:

Time in Minutes	c_o^*	c^*	D^*
505	1398	2.78	0.1265
725	1395	4.44	0.1070
890	1386	4.44	0.1051
550	1382	5.00	0.0986

$*c_o$ = original concentration in mg/liter
  c = amount diffused out in given time in mg/liter
  D = diffusion coefficient

Table III. Molecular Weight Determinations

A. Longview Fibre Company sample
(K for cell used = 2.23)

Run	Time in minutes	c_o	c	D in cm^2 per day	r in cm x 10^{-7}	Molecular weight
1	2360	1227	7.72	0.09030	1.63	15,400
2	1350	1131	4.01	0.08840	1.67	16,450
3	1440	1132	4.63	0.09632	1.53	12,720
4	1440	961.2	3.86	0.09412	1.57	13,630
5	1440	914.8	3.86	0.09875	1.49	11,800
6	2700	607.7	5.55	0.1151	1.28	7,452
7	1365	333.5	1.54	0.1116	1.32	8,189
8	2700	295.7	2.32	0.09773	1.51	12,180
9	4320	86.1	1.16	0.1055	1.40	9,685
10	Extrapolated to infinite dilution			0.1100	1.40	8,538

B. Crown-Zellerbach Corporation sample
(K for cell used = 3.10)

Run	Time in minutes	c_o	c	D in cm^2 per day	r in cm x 10^{-7}	Molecular weight
1	895	2072	7.22	0.09288	1.59	14,180
2	1440	1183	6.66	0.09484	1.55	13,320
3	1440	1161	6.66	0.09697	1.52	12,460
4	2360	1055	11.1	0.1091	1.35	8,751
5	1440	1005	5.55	0.09350	1.58	13,900
6	1350	904.1	5.00	0.09951	1.48	11,530
7	2700	494.2	5.77	0.1055	1.40	9,679
8	1365	379.6	2.22	0.1035	1.42	10,240
9	2700	359.3	4.11	0.1037	1.42	10,190
10	4320	135.8	2.56	0.1074	1.37	9,173
11	Extrapolated to infinite dilution			0.1100	1.40	8,538

CHAPTER VII

SAMPLE CALCULATIONS

A. Calculations of Cell Constants

Data: Normality of KCl in cell after diffusion = 0.09706
Normality of KCl in beaker after diffusion = 0.00674 = c
Normality of KCl in cell before diffusion = 0.10374 = c_o
Value of D for 0.1 N.KCl at 20^o C. = 1.94×10^{-5} cm^2/sec.
Diffusion time, t = 995 minutes

$$K = \frac{\log_{10} c_o - \log_{10} (c_o - 2c)}{Dt}$$

$$= \frac{\log_{10} 0.10374 - \log_{10} (0.10374 - 2 \times 0.00674)}{1.94 \times 10^{-5} \times 995}$$

= 3.3 = value for Cell #2, Run #4

B. Calculations of Diffusion Coefficients

Data: c_o = 1227 mg/liter
c^o = 7.7 mg/liter
K = 2.23
t = 2360 minutes

$$D = \frac{\log_{10} c_o - \log_{10} (c_o - 2c)}{K \times t \text{ in minutes}} = cm^2/\text{second}$$

$$= \frac{\log_{10} c_o - \log_{10} (c_o - 2c)}{K \times t \text{ in minutes}} \times 86,400 = cm^2/\text{day}$$

$$= \frac{\log_{10} 1227 - \log_{10} (1227 - 15.4)}{2.23 \times 2360} \times 86{,}400$$

$$= 0.09177 \ cm^2/day$$

C. Calculations of Particle Sizes

$$D = \frac{RT}{6\pi N\eta r}$$

where $R = 8.314 \times 10^7$
$T = 293$ A.
$N = 6.02 \times 10^{23}$
η = viscosity of dioxane
$= 0.0126 \ cm^{-1}g.sec.^{-1}$
D = diffusion coefficient for the run

$$r = \frac{8.314 \times 10^7 \times 293}{6 \times \pi \times 6.02 \times 10^{23} \times 0.0126 \times 0.09177}$$

$$r = 1.61 \times 10^{-7} \ cm.$$

D. Calculations of Molecular Weights

$$M = \frac{4}{3} \pi N d r^3$$

where d of lignin = 1.41 gm/cc. (33) and r for the run = 1.61 x 10^{-7} cm.

$$M = \frac{4}{3} \times 6.02 \times 10^{23} \times 1.41 \times (1.61 \times 10^{-7})^3$$

$$= 14{,}700$$

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