1930

Analytical studies on the utilization of the cornstalk

Charles J. Peterson
Iowa State College

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ANALYTICAL STUDIES ON THE UTILIZATION OF THE CORNSTALK

By

Charles J. Peterson

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Plant Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1930

ACKNOWLEDGEMENT

The writer wishes to express his appreciation to Dr. R. M. Hixon for the suggestion of these problems and for the generous advice and encouragement given during the progress of this work. Acknowledgement is also made to Dr. C. H. Werkman for his assistance in the thermophilic fermentation studies of Part IV of this thesis.

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INTRODUCTION

The production of cellulosic material from cornstalks or other agricultural waste materials is not to be considered a new project, for we know that as early as the seventeenth century there were attempts made at Rinimo, Italy, to utilize corn husks as a raw material in the production of paper. In the eighteenth century there were two plants put up in Italy for the production of paper from corn husks. During the nineteenth century, several patents[1] were issued for the production of paper and also cloth from corn husks and stalks. This early work was of a cut and try type and gave us little data other than the specific processes.

Considerable publicity was given to the possibility of producing paper from cornstalks during the period between 1908 and 1912.[2] No specific statement can be found regarding the location of a plant for the production of cornstalk paper about this time. However, it is believed that a plant for this

1. Allison and Hawkins, U.S. Patent. Not consulted (1802).
   Sprague U.S.Patent. Not consulted (1829).
   Shaw British Patent. Not consulted (1837).
   Holland U.S. Patent. 878 (1838).
   de Campoloro U.S. Patent. 29471 (1860).
   Ebenezer U.S. Patent. 29059 (1860).
   Welsback U.S. Patent 38220 (1863).
   Roth U.S. Patent 41642 (1864).
2. Anon Sci. American 99, 274, (1908).
   Anon Harpers Weekly 52, Oct. 31, 27, (1908).
   Anon Sci. American Supplement 72, 430, (1911).

purpose was erected and put into operation at Kankakee, Ill. This plant produced paper after a mechanical separation from both the cornstalk fiber as well as the pith. An agricultural bulletin by Brand[1] is printed on paper made from cornstalks and other agricultural wastes likely produced in this plant.

More recently, about 1927 a similar publicity was given to the production of cellulosic products from agricultural wastes.[2] About this time, a plant was put up at Danville, Ill. for the production of paper from cornstalks. This plant produced paper from the stalk without a previous separation of any kind. Numerous newspapers printed on paper produced by this have been published. At the present time, this plant is operating at only partial capacity probably due to depressed business conditions of the country. A wall board plant has been put up at Dubuque, Iowa, for the production of wall board from cornstalks, and at present is producing wall board of excellent quality.

The cost of production of paper from cornstalks is only slightly less than the cost of production of paper from wood pulp. When one takes into consideration the fact that the

1. Brand. Bureau of Plant Industry. Circular No. 82 (1911).
2. Darrow St. M. 55, 998, Oct. (1926).
   Davis Cur. Hist. 26, 261 My. (1927).
   Paddock Prop. Mech. 51, 67, Ja. (1929).
   Anon. Factory & Ind. Management 77, 262, (1929).
   Arnold Sci. Monthly 28, 463, (1929).
   Miller. Mag. of Business 55, 144, (1929).
   Anon. Business Week p. 8, Ja. 22, (1930).
   Sci. Ampr. 142, 409, (1930).

wood pulp mills have been paid for by previous profits while mills for the production of cornstalk paper have to be built, it is easily seen that the production of paper from cornstalks in competition to the production from wood pulp is hardly economical, when the two celluloses are considered alone. It was due to this economic difficulty, that the mill at Kankakee was forced to cease operating. It is also believed that the mill at Danville is in rather serious difficulties due ohly to this economic reason.

Since the cost of production of cellulose from these two competitive fields is so nearly the same, the existence of the industry for the production of cellulosic products from cornstalks will depend, as in practically all industries, upon the recovery and utilization of the by products. The process of converting plant tissues into cellulosic pulp is accomplished at a loss of about 40 to 50 per cent of the original tissue. In the alkali processes, no satisfactory method of isolation of the dissolved substances has been found which will at the same time permit the recovery of caustic. In the sulfite process, fermentation of the hydrolized sugars has been practiced to a very limited extent but the ligno-sulfonic acids are too soluble to permit convenient isolation. It is estimated that the waste liquors for the annual cellulose production contain at least three million tons of waste on a dry basis. If this material were even dried, its fuel value alone would be

equivalent to about two million tons of coal.[1]

Before any recovery and use could be made of these by products it would be necessary to know of what they consisted. The most logical way of determining these by-products would be to make an analytical study of the cornstalk, the cellulosic residue, and the digestor liquors. Accordingly the first part of this thesis is devoted to an analytical examination of the cornstalk tissue.

Since the present method of pulping cornstalks as well as the other grasses and similar materials is of the alkali type, a study was made of this process for the purpose of determining the constituents removed from the tissue by pulping as well as a possible utilization of the digestor liquor by fermentation. This study is reported in part two of this thesis.

Due to the fact that in the soda process for pulping it is quite uneconomical to sacrifice the soda for the recovery of the by-products, a new process was sought which would make possible the recovery of both the caustic used for pulping as well as the by-products. Part three of this thesis reports the pulping of the cornstalk and other agricultural waste materials by the use of a volatile alkali, which permits the recovery of the alkali as well as the products made soluble during pulping.

1. Eisenbeiss, Papier-Fabrikant. 108, (1924).

It has been known for sometime that cellulosic materials may be fermented by the use of certain bacteria to acetic and formic acids as well as other valuable materials. It was, therefore, thought that agricultural waste materials might be used as a fermentation medium for the commercial production of valuable products. Part four of this thesis reports analytical studies in connection with the fermentation of agricultural waste materials by the use of thermophilic bacteria.

PART I

CHEMICAL EXAMINATION OF THE TISSUE OF THE CORNSTALK

HISTORICAL

The first real analytical work regarding the nature of the carbohydrate materials of the cornstalk tissue was done by Browne and Tollens[1] in 1902. They reported the pentosan content as about 26 per cent and also indicated that this value was approximately constant for the different tissues of the stalk. The next work of any importance was that of Wiley[2] in which he reported the cornstalk as containing 50 to 53 per cent Cross and Bevan cellulose with 35 to 40 per cent. α- cellulose. This work was followed by that of Brand[3] in which he indicated that stalk consisted of a fibrous and a pith material which made distinctly different types of paper. In 1924, Latshaw and Miller[4] made an elemental analysis of the different parts of the corn plant. All of these analyses, except for the values indicated, were primarily of an agricultural nature and of little value for commercial purposes. Recently quite a number of publications of a general descriptive nature[5] have appeared as well as a few which given some

1. Browne and Tollens, Ber. 35, 1457 (1902)
2. Wiley. U. S. D. A. Division of Chem. Bulletin No. 50 (1898)
3. Brand. U. S. D. A. Bureau of Plant Ind. Circular No. 82 (1911)
4. Latshaw and Miller. J. Agri. Research 27, 845 (1924).
5. Rommel, Ind. Eng. Chem. 20, 716, (1928).
   Rommel, Ind. Eng. Chem. News Edition p. 1, May 20, (1928).
   Rommel, Ind. Eng. Chem. News Edition p. 7, July 20, (1928).
   Kirkpatrick, Chem. Met. Eng., 35, 401. (1928).

analytical data[1] along with the general report. A complete bibliography from 1900 to 1928 is given by West[2].

LIGNIN DETERMINATION

Lignin may be determined by any one of several methods as the 72% H_2SO_4 method[3], the Willstatter HCl method[4], the 1% HCl method[5], the gaseous HCl method[6], etc. The 72% H_2SO_4 and the Willstatter HCl methods are considered the best, with the 72% H_2SO_4 method being the easier to carry out. The 72% H_2SO_4 method was therefore selected for the determination of the lignin in the cornstalk.

The method of procedure for the 72% H_2SO_4 method indicates that the process is carried out at room temperature. In all cases when the process is carried out at room temperature a black carbonatious residue is obtained. Since the literature reports that the lignin residue from this process, when applied to woods, is usually dark, nothing was thought wrong until it was found impossible to make the lignin value of the same sample check when determined in summer and winter. It was found that the values obtained in summer were much higher than those obtained in winter. This indicated that the temperature

1. Jackson, Paper Mill 50, No. 36, 2, (1927).
   Webber. Ind. Eng. Chem. 21, 270, (1929).
2. West, "Bibliography of Paper Making". p. Lockwood Trade Journal Co. (1929).
3. Schorger, "Chemistry of cellulose and wood," p. 524, McGraw-Hill Book Co. 1926.
4. Willstatter and Kalb, Ber. 55, 2640, (1922).
5. Krull, Diss. Danzig 19, (1916).
6. Konig and Rump, Z. Unters. Nahr. Genussm., 28, 177 (1914).

must be causing the variation as it was the only thing which had been changed in the process.

To verify the fact that temperature change was causing the variation in lignin value, the process was carried out with cornstalk material at several specific temperatures. The results of this investigation are given below.

Temperature °C	Per cent Lignin	Color of Residue
30°	34.3	Black
15°	24.0	Brown
4°	23.7	Light Brown

These values indicate that the lignin value of the cornstalk increases with temperature rise after the temperature passes a certain critical value. A probable explanation for this is that the cellulose and hemicelluloses are hydrolized to the simple sugars which go into solution and at the higher temperature these simple sugars decompose and carbon is precipitated. This precipitated carbon caused the increase in lignin value.

In order to verify the fact that the lignin values obtained at the lower temperature are more nearly the correct values, the lignins of different material have been determined by the Willstatter HCl method and by the 72% H_2SO_4 method at room temperature and at ice box temperature. The results of this investigation are given in Table I.

Table I.

Comparison of the Lignin Values of the Cortex, Vascular Bundles and Pith of the Cornstalk by Different Processes

	Outer Shell	Vascular Bundles	Pith	Total Cornstalk
Room Temperature 72% H_2SO_4	33.5	35.2	32.0	34.3
Cooled 72% H_2SO_4	25.2	22.5	16.5	23.7
Willstatter	25.4	22.0	15.9	22.8

These values indicate that the values obtained by the cold 72% H_2SO_4 method are more nearly the true values of the lignin in the material as they check the values obtained by the Willstatter HCl method.

EXPERIMENTAL

The analytical scheme is fundamentally that recommended by Schwalbe[1] for the examination of plant tissues and the celluloses derived from them. The material used for these experiments consisted of stalks from the baled material selected and cleaned by hand. The selected material was ground to pass a 60-mesh screen unless otherwise indicated. The moisture content of this material was 7.72 per cent on an oven-dry basis of 105°C. The dry tissue ran 3.62 per cent ash and 0.6 per cent either extractable matter. The data reported

1. Schwalbe, Z. Angew. Chem., 32, 125-229, (1919)

below are all calculated on the dry basis.

Cellulose in the Cornstalk

The term "cellulose" in carbohydrate chemistry is generall restricted to the inert substance of the same percentage composition as starch $(C_6H_{10}O_5)_x$ but presumedly more highly polymerized. The term is not so restricted in the less technical language, as indicated by the terms alpha-cellulose, beta-dellulose, and gamma-cellulose used in the analyses of the commercial products. The product obtained by the Cross and Bevan[1] analytical method is reported as cellulose, although it is recognized that this product may contain considerable furfural-yielding material and small quantities of lignin.

The Cross and Bevan determination leaves a residue of 45.5 per cent of the stalk as cellulose pulp. This product contains furfural-yielding material to the equivalent of 17.1 per cent pentosan. The lignin determination by the 72 per cent sulfuric acid method at room temperature gives 5.8 per cent lignin while the Willstatter method indicates 3.3 per cent. The ash ran 0.6 per cent. Variation in the methods of the treatment will, of course, change these values. If the pentosan, lignin, and ash are calculated to per cent of original stalk subtracted from the value for Cross and Bevan cellulose,

1. Cross and Bevan, "Cellulose," p. 94, Longmans, Green and Co., (1916).

the following results are obtained:

	Per cent
Cellulose pulp	45.5
Pentosan	7.8
Lignin, average	2.0
Ash	0.3
Cellulose, by difference	35.4

Hemicellulose in the Cornstalk

The definition of this group of substances is even less precise than the definition for cellulose. It is generally agreed that they are the group of polysaccharides of the tissue which are insoluble in water but soluble in caustic solution, and are more subject to acid hydrolysis than the cellulose. They are subdivided according to the simple sugars obtained by hydrolysis - xylans, galactans, mannans, and mixtures such as galacto-arabans, etc.

A part of the confusion is due to the fact that alkaline extraction does not give a sharp separation between the cellulose and hemicellulose and also removes a portion of the lignin. As would be expected, the values obtained by alkaline extraction of the tissue do not agree with those obtained by acid hydrolysis of the tissue. These difficulties have led to the postulation of many different kinds of hemicelluloses.

With the cornstalk an approximation has been made by 5 per cent alkaline extraction of the tissue followed by analysis of both the residue and filtrate. The tissue was treated three

times for 12, 4, and 4 hours, respectively, with sufficient 5 per cent sodium hydroxide to moisten it at room temperatures. The solutions were pressed off and the residual tissue washed with warm water after each extraction. This treatment dissolved 46.2 per cent of the stalk, leaving 53.8 per cent as residue. Analyses for pentosans by furfural showed 17.3 per cent of the stalk calculated as pentosans in the extract with 7.1 per cent in the residue. The sum of these results, 24.4 per cent, indicates an unaccountable loss in pentosan equivalent to 3.2 per cent of the stalk, since the original tissue contained 27.6 per cent pentosan. A determination of reducing sugars indicated little, if any, reducing sugars other than those calculated as pentosans[1].

An acid hydrolysis of the tissue was run using 2.5 grams of tissue and 20 cc. of 1.125 specific gravity hydrochloric acid in 200 cc. of water at boiling temperatures under reflux for 2½ hours. This treatment dissolved 40.7 per cent of the cornstalk. A gravimetric Fehling's determination gave a copper equivalent of 26.4 per cent glucose in the solution. A furfural determination gave 20.8 per cent pentosan in the solution and 4.1 per cent in the residue. The sum of these values gives 24.9 per cent pentosan, which indicates an unaccountable loss of 2.7 per cent pentosan from that of the original sample. Since the reducing

1. This statement is based on the equivalent copper value of glucose and xylose as reported by Stone, Ber., 23, 3796 (1890)

values of glucose and xylose are about the same, a subtraction of the furfural value for xylose of 21.5 per cent from the glucose value would indicate that about 4.9 per cent of the stalk as reducing sugars other than xylose might be present.

Table II

Composition of Cornstalk under Various Analytical Treatments
(Results in percentage of original stalk dried at 105°C.)

Designation of Tissue	Original stalk	5% NaOH Extract of Stalk		Acid Hydrolysis	
		46.2% Fraction (soluble)	53.8% Fraction (not soluble)	40.7% Fraction (Soluble)	59.3% Fraction (not soluble
	Per cent	Per cent	Per cent	Per cent	Per cent
Lignins Room Temp.	34.4	26.5 (by diff.)	7.8	14.3 (by diff.)	20.0
Ash	3.6	--	1.6	--	1.4
Hemicellulose:					
Pentosans	27.6	17.3	7.1	20.8	4.1
Hexosans	1.3	None	--	4.9	---
Cellulose by diff.	23.1		37.3		33.8

The residue from the acid hydrolysis, 59.3 per cent of the original stalk, contained 1.4 per cent ash, 4.1 per cent pentosan, and 20.0 per cent lignin based on the original stalk. This would leave 33.8 per cent cellulose in the stalk by difference.

A summary of the results of the three independent series of analytical procedures is given in Table II. It will be observed that the sums of these various procedures check fairly

well for the indicated fractional composition of the cornstalk and that the values for cellulose by difference check roughly with the value 35.4 obtained from the corrected Cross and Bevan value. The analytical procedures upon which these results are based are not considered sufficiently selective to warrant the inclusion of the nitrogenous and ether-soluble fractions, since their magnitudes would be within the experimental error of these values.

Pectin in the Cornstalk

An effort has been made to determine the pectin content of the cornstalk as a means of correlation with retting experiments. A direct isolation failed to give any pectin or pectic acid. An indirect attempt was made by determining galactose on the assumption that all pectins are characterized by yielding mucic acid on oxidation. The quantities of mucic acid obtained were so small that definite identification was doubtful. In this connection attention should be called to the work of Ritter[1], which shows that the middle lamella of basswood tissue consists of lignin and not pectin or calcium pectate. The question arises as to whether a similar change takes place in the lignification of the cornstalk.

Isolation and Analysis of Pentosans from Cornstalk

In preparing xylan or wood gum it is common practice first to extract the tissue with 1 per cent ammonium hydroxide to

1. Ritter, Ind. Eng. Chem., 17, 1195 (1925).

remove the water-soluble constituents, coloring matter, etc. Analysis of this extract gave the following results:

	Per cent
Total solids extracted by 1 per cent ammonia	6.00
Total sugars (calculated as glucose)	2.17
Pentosans (by furfural)	0.85
Galactans (by mucic acid)	Indefinite trace

This analysis indicates that the water-soluble hexose carbohydrates, including starch, are not present to more than 2.0 per cent of the total stalk.

After the preliminary treatment with 1 per cent ammonia, the tissue was extracted with 5 per cent sodium hydroxide as described for the determination of hemicelluloses. Alcohol was added to this extract until precipitation ceased. This usually required a volume-to-volume proportion; in a few cases more alcohol was necessary. The precipitate settled fairly rapidly and was filtered off through paper after about 6 hours standing. The material was reprecipitated by adding alcohol to a 1 per cent sodium hydroxide solution of the material. The yellow, amorphous powder obtained by drying this residue gave the following analysis:

	Per cent
Moisture (loss at 100°C.)	3.15
Pentosan (furfural distillation)	88.00
Lignin (cold 72 per cent sulfuric acid)	2.25
Ash	2.64
Total	96.04
Reducing sugars as xylan (by Fehling)	87.32

In view of the fact that the reducing sugars and furfural determination check, it seems probable that this material is

xylan, with the impurities indicated.

Note-The furfural determinations have been calculated as xylan throughout this paper on this evidence. This fraction is being more closely examined and until that time the furfural values should be interpreted with the usual reservations. Cf. Klingstedt, Z. anal. Chem., 66, 129 (1925). The work of Brown and Tollens, Ber., 35, 1457 (1902), indicates that small amounts of arabinose are to be expected.
The same procedure is frequently used and the precipitated fraction designated as "hemicellulose." Varying amounts of lignin can be brought down with this fraction according to the manipulation details.

Isolation and Analysis of Lignin Fraction

The lignins, although insoluble in either water or alcohol, are quite soluble in a mixture of the two solvents. The filtrate from the isolation of the pentosan fraction was fractionally distilled to remove the alcohol, the lignins remaining in solution in the aqueous sodium hydroxide. When the alcohol was removed, the solution was cooled and acidified, the lignins separating at once. They were purified by twice taking up in 1 per cent sodium hydroxide and reprecipitating by acidification.

The lignins (or lignic acids) were obtained as a light brown, amorphous powder. When suspended in water, they softened at 60°C. to a sticky, resinous oil, which immediately solidified

upon cooling to a brittle, easily pulverized mass. This characteristic changes with time. The analysis of this fraction was as follows:

	Per cent
Moisture (loss at 100°C.)	22.0
Pentosans	Indefinite trace
Reducing sugars (Hydrolysis)	Indefinite trace
Lignin (by 72 per cent sulfuric acid)	76.1
Ash	1.0
Total	99.1
Methoxy content	14.0

Separation and Analysis of Three Structural Tissues of Cornstalk

The matured cornstalk can be easily separated into three different tissues or combinations of tissues: (a) the epidermis and the peripheral vascular bundles or the outer shell of the stalk; (b) the pith or fundamental parenchyma of the stalk (the term "pith" as used by Jackson and by Sherwood apparently includes the vascular bundles as well as the parenchymatous tissues); (c) the inner vascular bundles interspersed through the pith of the stalk. Of these tissues, the outer shell and the central vascular bundles are predominantly fibrous in structure and of woody appearance. The pith is composed of more or less cubical cells of soft and spongy texture.

It was presumed that most of the lignin content of the cornstalk would be found in the vascular bundles and that the hemicellulose would be largely concentrated in the parenchymatous tissues. The analytical data (Table III) do not support this

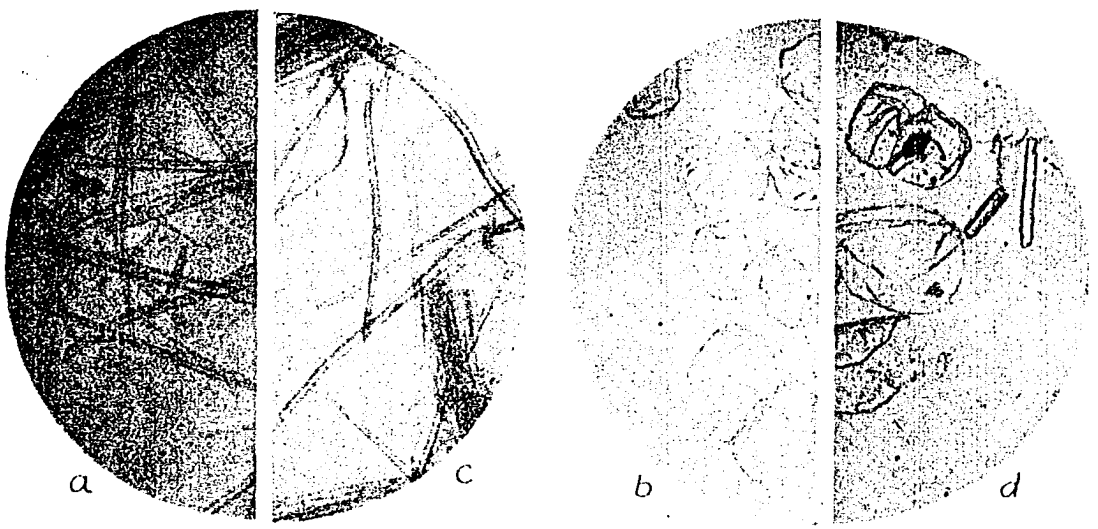
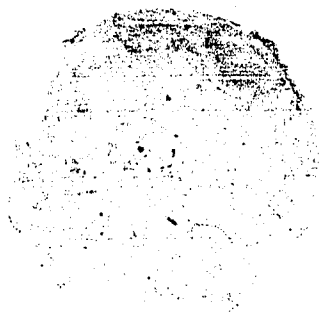


Figure 1—Photomicrographs of Cellulose Pulp from the Cornstalk Prepared by the de Vains Process

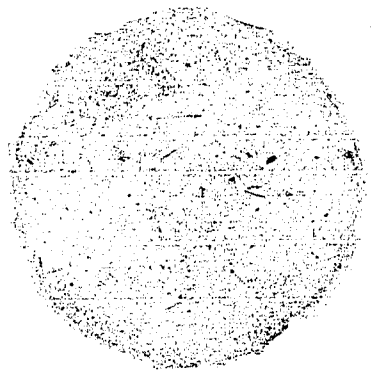
a and *b* from vascular bundles and parenchyma carefully dissected out. *c* and *d* from mechanically separated prosenchymatous and parenchymatous tissues.

Samples of Paper made from



Hand Separated
Pith

Hand Separated
Fiber



Hand Separated
Outer Shell

Mechanically Separated
Pith

Mechanically Separated
Fibers

presumption, the analyses of these different tissues being about the same as that for the total stalk. To obtain these data the outer shell of the stalk was peeled off with a sharp knife, the inner pith cylinder softened in water, and the vascular bundles separated from the pith by carfully pulling out each fiber and scraping away the softer parenchymatous tissue. The separated tissues were then analyzed as previously described for the total stalk except that the cellulose pulp was obtained by a modification of the de Vains process instead of by the Cross and Bevan analytical method. It will be observed that the values for cellulose by difference check roughly with the value reported for the total stalk. (Table III).

Although these tissues had approximately the same chemical composition, the physical nature of the cellulose pulp prepared from the pith was very different from that prepared from the other tissues. The pulp prepared from the vascular bundles and outer shell was distinctly fibrous in texture and formed a good mat in filtering. The pulp prepared from the pith had no visible fiber and in appearance resembled the gelatinized celluloses. Photomicrographs of these pulps are shown in Figure 1a and b. These tissues had no mechanical treatment and it is difficult to believe that treatment with 1 per cent caustic as used in the preparation of the material would cause such a degree of gelatinization. It seems more probable that this property is due to the original subdivision of the tissue

into thin-walled, isodimetric cells rather than to the chemical nature of the cellulose.

Table III

Comparison of Compositions of the Cortex, Vascular Bundles, and Pith of the Cornstalk

	Outer Shell	Vascular Bundles	Pith	Total Cornstalk
	Per cent	Per cent	Per cent	Per cent
Pentosan	25.9	26.4	27.7	27.6
Lignin R. T.	33.6	35.2	32.0	34.3
Lignin (cold 72%)	25.2	22.5	16.5	23.7
Cellulose pulp	55.9	50.2	50.1	52.6
Pentosans in pulp	16.6	15.1	12.2	14.2
Cellulose (by difference)	39.3	37.1	37.9	38.4

The tedious task of dissecting these tissues would handicap any great extension of the above studies. Since these results indicated such a decided difference in the physical nature of these tissues a mechanical device for separating the parenchymatous tissues from the shell and vascular bundles has been developed[1]. The success of the separation can be judged by comparing the photomicrographs c and d in Figure 1 with those of the corresponding hand-separated tissues. Paper from each of these materials is seen on page 21.

1. The machine patented by Sherwood, U. S. Patent 627,882 (1899), apparently separated the shell from the central portion of the stalk, the term "pith" being used to designate the central parenchyma and vascular bundles as well. The same applies to U. S. Patents 720,850 and 720,851 (1903).

It should be emphasized that these statements are not to be interpreted to mean that paper cannot be made from the pith of the cornstalk. Sheets prepared from the mechanically separated pith resemble the rice paper of the Chinese. The facts that the pith is very bulky, that it will yield to milder chemical treatment than the rest of the stalk, and that it is almost impossible to bleach it to a white pulp indicate that it would be more economical to separate it from the more fibrous tissues which constitute about 80 per cent of the stalk.

SUMMARY

It is pointed out that the 72% H_2SO_4 method for the lignin determination gives high results, and a modification of this method is suggested in which the temperature is controlled.

An analytical examination of the cornstalk indicates that it consists primarily of lignin (approximately 24 per cent), pentosan (approximately 27 per cent), cellulose (Approximately 36 per cent). There is little polyhexose material subject to acid hydrolysis (2 to 6 per cent) and no pectic material could be definitely identified.

Directions are given for the isolation from the cornstalk by alkali extraction of a pentosan fraction (with about 25 per cent impurity as ash and lignin) and of a lignin fraction (apparently containing no carbohydrates).

The shell, pith, and vascular bundles have been dissected from the cornstalk and analyzed. The composition of these

tissues does not vary greatly from that of the total stalk. The cellulose pulp prepared from the pith dries to a parchment-like paper.

PART II

THE PARTITION OF THE CONSTITUENTS OF THE CORNSTALK BY THE ACTION OF ALKALI.

INTRODUCTION

The present industrial process for pulping the cornstalk[1], like the industrial processes for the other grasses, is of the alkali type. In this process, the pentosan and lignin bodies removed by the caustic are sacrificed for the more valuable alkali used in the treatment. The following study reports the partition of the three predominant classes of compounds of the cornstalk under alkali treatment; the object of the study being to obtain data bearing on the feasibility of the fermentation of the pentosans in the alkali liquor.

Separation of Tissue

The material used in these studies consisted of the two distinct types of structural tissue in the cornstalk; the pith (parenchymatous tissue), and the outer shell together with the fibrovascular bundles from the central portions of the stalk. These tissues were separated by first chopping the stalk, freed from leaves and dirt, in a Wiley mill without screens. When the mill is run at low speed (240 r.p.m.), this will break the stalks into pieces one to two inches in length and crush the outer shell of all pieces. The cubical pith cells are then screened from the

1. Kirkpatrick, Chem. and Met. Eng., 35, 401 (1928).

fibrovascular bundles and outer shell by the use of a wash roll in an ordinary beating engine; the beater roll being set with at least 1/4" clearance and the wash roll being covered with a 10 mesh screen. Concentration of wash water and prevention of water waste can be obtained by returning the water from the wash roll to the beater after filtering out the pith by means of 60 mesh screen[1]. The separation is completed in about 45 minutes with the experimental apparatus used in this laboratory. A schematic diagram of which is shown in figure II. The average of seven such separations gave the following results:

Pith material	26%
Fibrous material	63%
Water soluble material	9.0%
Loss (by diff.)	2.0%

It should be emphasized that the separation of these tissues is made without chemical treatment of the stalk, and while a Hollander is used in the separation, that the tissue is not "beaten" in the usual sense of the word. Many other kinds of washing machines could be developed for the same purpose, the fundamentals involved being merely the rubbing out of the soft pith and the separation of these cubical cells from the more fibrous and resistant tissue. This separation, if used commercially, would take the place of the hot water washing shown in the flow-sheet for the commercial preparation of paper from cornstalks[2].

1. A patent covering the essentials of this apparatus has been issued to Kumagama and Shimomura, B. P. 299740, Chem. Abs. 23, 3574, 1929.
2. Kirkpatrick, Chem. and Met. Eng., 35, 401 (1928).

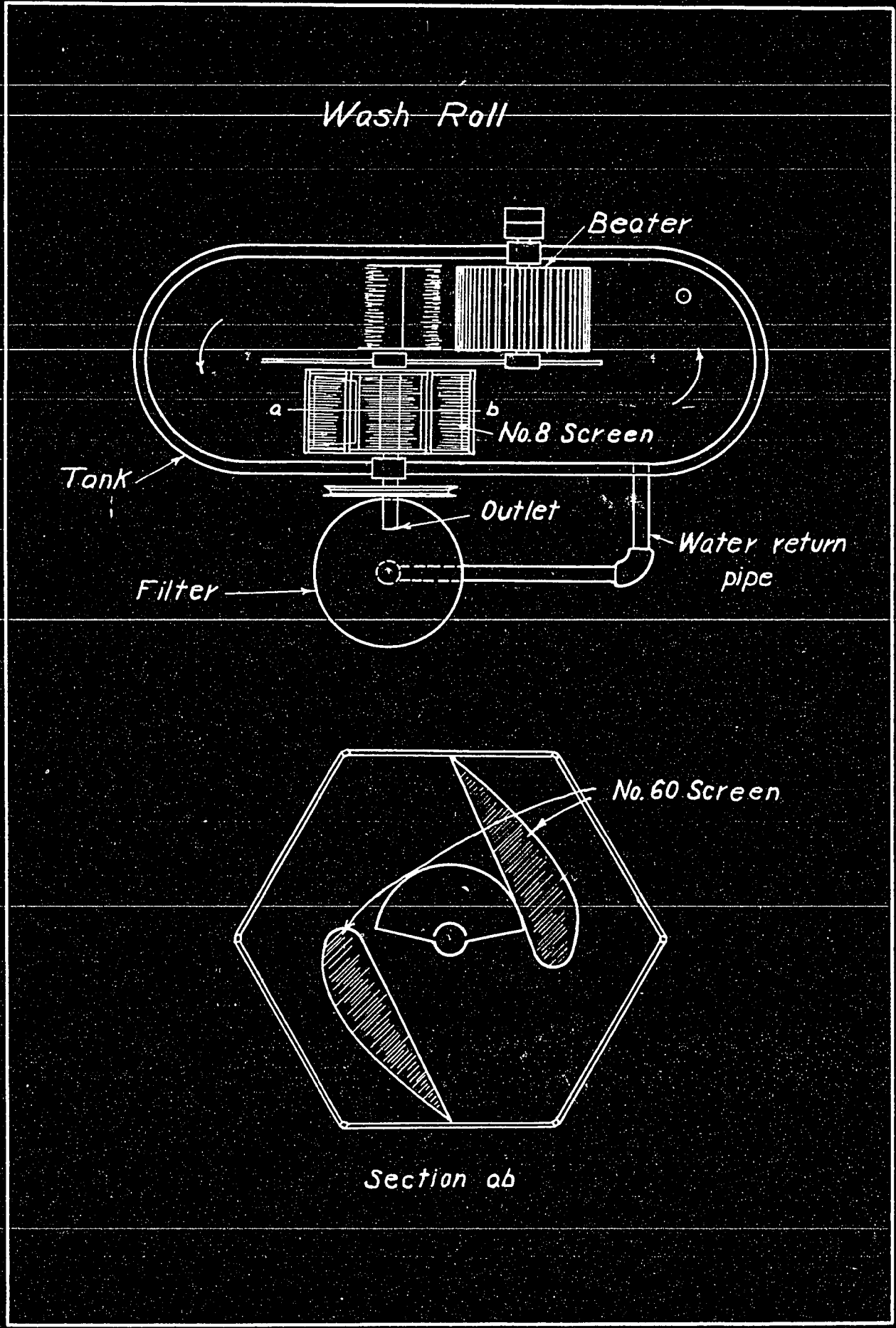

Wash Roll
Beater
a
b
No. 8 Screen
Tank
Outlet
Water return pipe
Filter
No. 60 Screen
Section ab

Fig. 2

Pulping of Tissue

The chemical treatment reported for the two tissues of the cornstalk consists essentially of the de Vains process. The literature regarding the de Vains process consists principally of patents[1] and descriptions of plant operations. Analytical studies have been made on esparto grass[2] and on flax straw[3]. Waentig[4] has made an extensive study of the action of chlorine and chlorine dioxide in the process. A number of studies have been made in the Chemical Engr. Dept. of Iowa State College on the application of this process to the production of cellulose from the cornstalk[5]. A bibliography from 1900 to 1928 is given by West[6].

The de Vains process consists of three distinct steps:

1. Preliminary treatment with dilute alkali to partially deligrify the tissues.
2. Chlorination of the pulp from the alkali treatment to convert the residual lignin into soluble compounds.

1. de Vains
   U. S. Patent 1,106,994
   U. S. Patent 1,500,060
   U. S. Patent 1,556,497
   U. S. Patent 1,593,487
   British Patent 189,561
   British Patent 197,329
   British Patent 198,975
   British Patent 201,488
   British Patent 208,551
2. Mutti and Venturi, Ann. Chim. Applicata, 17, 391 (1927)
3. Schafer, Bray and Peterson, Paper Trade J. 84, No.8,207(1927)
4. Waentig, Z. angew. Chem., 41, 493, 977, 1001 (1928)
5. Webber, Ind. Eng. Chem., 21, 270 (1928)
   Roberts, B. S. Thesis, Iowa State College (1927) (In manuscript)
6. West, "Bibliography of Paper Making", p. 202
   Lockwood Trade Journal Co., (1929).

3. Extraction of the chlorinated lignins with either solium sulfite or caustic solutions.

It was expected that each of these treatments would cause sufficient chemical change that a three dimensional diagram would be necessary to portray the results graphically. Accordingly, three variations in each treatment were made giving a total of twenty-seven samples for the study. The expected variation in the second and third treatments was not found, the greater portion of the chemical change taking place in the first treatment with dilute caustic. While the second and third treatment caused little chemical change, they did cause considerable change in the ease of bleaching of the pulp.

In applying these treatments to the cornstalk tissues, quantitative procedures were followed thruout rather than pulping processes. The tissue, excepting the pith, was ground to pass a 60 mesh screen. The material used had a moisture content of 5.63% on an oven-dry basis of 105 degrees. The dry tissue ran 1.44% ash. All results reported below are on the oven-dry basis unless otherwise indicated.

In the study of the pulping of the fibrous material, twenty-seven samples of twenty-five grams each were weighed out to give three variable treatments of each of the three steps in the procedure. These samples were then grouped as shown in Table IVto give all the possible combinations of:

1. Alkali treatment with concentrations of 0.5, 1.0 and 2.0

TABLE IV

Results of Various Treatment o

Sample No.	Treatment				ANALYSIS OF LIQUORS				
					NaOH		Chlorination		Na
	Conc. NaOH in %	Vol. NaOH in cc	Chlorination time in Mins.	Conc. $NaSO_3$ in %	Combustible Residue	Pentosan	Combustible Residue	Pentosan	Combustible Residu
1	0.5	250	15	1.0	14.64	1.58	1.53	0.15	2.38
2	0.5	250	15	2.0	14.64	1.58	1.53	0.15	4.01
3	0.5	250	15	4.0	14.64	1.58	1.53	0.15	6.68
4	0.5	250	30	1.0	14.64	1.58	1.77	0.16	2.39
5	0.5	250	30	2.0	14.64	1.58	1.77	0.16	2.26
6	0.5	250	30	4.0	14.64	1.58	1.77	0.16	2.27
7	0.5	250	60	1.0	14.64	1.58	2.41	0.17	6.71
8	0.5	250	60	2.0	14.64	1.58	2.41	0.17	5.11
9	0.5	250	60	4.0	14.64	1.58	2.41	0.17	4.63
10	1.0	250	15	1.0	24.75	3.61	1.41	0.24	1.93
11	1.0	250	15	2.0	24.75	3.61	1.41	0.24	----
12	1.0	250	15	4.0	24.75	3.61	1.41	0.24	----
13	1.0	250	30	1.0	24.75	3.61	1.60	0.34	2.14
14	1.0	250	30	2.0	24.75	3.61	1.60	0.34	2.30
15	1.0	250	30	4.0	24.75	3.61	1.60	0.34	2.14
16	1.0	250	60	1.0	24.75	3.61	1.64	0.30	2.41
17	1.0	250	60	2.0	24.75	3.61	1.64	0.30	2.58
18	1.0	250	60	4.0	24.75	3.61	1.64	0.30	2.58
19	2.0	250	15	1.0	30.20	7.53	1.20	0.12	3.42
20	2.0	250	15	2.0	30.20	7.53	1.20	0.12	2.82
21	2.0	250	15	4.0	30.20	7.53	1.20	0.12	2.20
22	2.0	250	30	1.0	30.20	7.53	1.46	0.20	2.11
23	2.0	250	30	2.0	30.20	7.53	1.46	0.20	1.78
24	2.0	250	30	4.0	30.20	7.53	1.46	0.20	2.73
25	2.0	250	60	1.0	30.20	7.53	1.84	0.17	2.22
26	2.0	250	60	2.0	30.20	7.53	1.84	0.17	1.99
27	2.0	250	60	4.0	30.20	7.53	1.84	0.17	1.44

TABLE V

Effect of Caustic Concentrati

45	0.1	750	30	2.0					
46	0.2	750	30	2.0					
47	0.3	750	30	2.0					
37	0.5	750	30	2.0	25.75	5.22	2.86	0.52	2.58
38	1.0	750	30	2.0	29.00	6.78	2.56	0.27	2.64
39	2.0	750	30	2.0	33.00	9.23	2.29	0.20	2.92

TABLE IV

Treatment on Fibrous Material

IQUORS nation		Na_2SO_3		Total Combust: ible mat ter Removed	Total Pentosan Removed	Yield of Pulp	Analysis of Pulp			
	Pento san	Combust ible Residue	Pento san				Ash	Pentosan	Lignin	α Cel lose
	0.15	2.38	-	18.55	-	72.2	0.25	22.25	13.62	52.
	0.15	4.01	-	20.18	-	71.0	0.29	21.12	13.47	50.
	0.15	6.68	-	23.85	-	68.4	0.25	19.51	12.86	47.
	0.16	2.59	0.71	18.80	2.45	68.0	0.32	18.90	11.19	49.
	0.16	2.26	0.75	18.67	2.49	66.5	0.26	18.41	10.79	47.
	0.16	2.27	0.65	18.66	2.39	67.3	0.21	19.17	10.52	48.
	0.17	6.71	0.89	23.76	2.64	63.1	0.29	17.86	10.40	44.
	0.17	5.11	1.26	22.16	3.01	62.8	0.30	18.94	7.04	43.
	0.17	4.63	1.18	21.68	2.93	63.1	0.26	18.55	7.58	44.
	0.24	1.93	0.58	27.09	4.43	57.1	0.15	17.29	4.32	42.
	0.24	----	0.42	---	4.27	56.9	0.13	17.80	4.57	42.
	0.24	----	0.42	----	4.27	57.2	0.11	16.96	4.84	39.
	0.34	2.14	0.72	28.49	4.67	56.0	0.10	17.45	3.41	40.
	0.34	2.30	0.69	28.65	4.64	56.5	0.13	17.90	3.12	40.
	0.34	2.14	0.54	28.49	4.49	56.5	0.10	17.95	3.24	40.
	0.30	2.41	0.87	28.80	4.78	56.1	0.16	17.67	3.34	39.
	0.30	2.58	0.95	28.97	4.86	55.1	0.14	17.05	2.92	38.
	0.30	2.58	0.84	28.97	4.75	54.8	0.18	16.50	2.84	38.
	0.12	3.42	0.44	34.82	8.09	53.2	0.21	15.25	3.02	37.
	0.12	2.82	0.39	34.22	8.04	55.1	0.16	15.30	3.18	41.
	0.12	2.20	0.30	33.60	7.95	57.5	0.14	18.30	3.54	43.
	0.20	2.11	0.67	33.77	8.40	52.8	0.14	14.60	2.26	38.
	0.20	1.78	0.60	33.44	8.33	51.8	0.15	14.39	2.16	38.
	0.20	2.73	0.63	34.39	8.36	51.8	0.17	14.07	2.18	37.
	0.17	2.22	0.92	34.26	8.62	52.1	0.27	14.82	2.53	37.
	0.17	1.99	0.78	34.01	8.48	51.9	0.25	14.38	2.36	38.
	0.17	1.44	0.73	33.48	8.43	50.9	0.25	13.70	2.39	38.

TABLE V

Concentration on Pith Pulping

					67.8 60.0 58.8				
0.52	2.58	0.99	31.19	6.73	57.2	0.54	14.50	4.78	41.
0.27	2.64	1.07	34.20	8.12	53.3	0.43	12.48	3.82	38.
0.20	2.92	1.22	38.21	11.15	48.9	0.37	3.40	2.97	35.

ld: f lp:	Analysis of Pulp				Combustible matter yield of pulp	Pentosan Removed Pentosan in Pulp	Total Solids Water soluble material
	Ash	Pentosan	Lignin	∝ Cellulose			
.2	0.25	22.25	13.62	52.00	90.75	- -	99.95
.0	0.29	21.12	13.47	50.32	91.18	- -	100.38
.4	0.25	19.51	12.86	47.87	92.25	- -	101.45
.0	0.32	18.90	11.19	49.38	86.80	21.35	96.00
.5	0.26	18.41	10.79	47.45	85.17	20.90	94.37
.3	0.21	19.17	10.52	48.98	85.36	21.56	96.16
.1	0.29	17.86	10.40	44.00	86.86	20.50	96.06
.8	0.30	18.94	7.04	43.18	84.96	21.95	94.16
.1	0.26	18.55	7.58	44.35	84.78	21.48	93.98
.1	0.15	17.29	4.32	42.02	84.19	22.72	93.39
.9	0.13	17.80	4.57	42.40	---	22.07	- -
.2	0.11	16.96	4.84	39.40	---	21.23	- -
.0	0.10	17.45	3.41	40.20	84.49	22.12	93.69
.5	0.13	17.90	3.12	40.60	84.30	22.54	93.50
.5	0.10	17.95	3.24	40.45	84.99	22.44	94.19
.1	0.16	17.67	3.34	39.35	84.90	22.45	94.10
.1	0.14	17.05	2.92	38.76	84.07	21.91	93.27
.8	0.18	16.50	2.84	38.30	83.77	21.25	92.97
.2	0.21	15.25	3.02	37.00	88.02	23.34	97.22
.1	0.16	15.30	3.18	41.00	89.32	23.34	98.52
.5	0.14	18.30	3.54	43.75	91.10	26.25	100.30
.8	0.14	14.60	2.26	38.90	86.58	23.00	95.78
.8	0.15	14.39	2.16	38.20	85.24	22.72	94.44
.8	0.17	14.07	2.18	37.60	86.19	22.43	95.39
.1	0.27	14.82	2.53	37.85	86.36	23.44	95.56
.9	0.25	14.38	2.36	38.90	85.91	23.86	95.11
.9	0.25	13.70	2.39	38.28	84.38	22.13	93.58
.8							
.0							
.8							
.2	0.54	14.50	4.78	41.55	88.39	21.23	97.59
.3	0.43	12.48	3.82	38.75	87.50	20.60	96.70
.9	0.37	5.40	2.97	35.60	86.11	20.55	95.31

volume per cent sodium hydroxide.

2. Chlorination with chlorine gas at a constant rate of 100 cc. per minute for 15, 30 and 60 minutes.
3. Treatment with 1, 2 and 4% sodium sulfite.

The exact pulping procedure is given in detail below. The results are tabulated in Table IV and are shown graphically in Fig. III

The results for the pulping of the pith are tabulated in Table V. The pulping of the pith was carried out in exactly the same manner as the pulping of the fibrous material except 750 cc. caustic solution were used for each 25 grams of tissue. This increase in volume of caustic is necessitated by the bulky nature of the pith.

LABORATORY PROCEDURE

Twenty-five gram samples were used, the smallest volume of sodium hydroxide of the indicated concentration sufficient to cover the sample was added (250 cc. for the fibrous material 750 cc. for the pith). The beaker was brought to boiling on an electric hot plate at a constant rate and held at the boiling temperature for thirty minutes, the volume being kept constant by the addition of water. The hot alkaline extract was filtered from the tissue by suction through a cloth filter, the tissue was washed until the washings came through colorless. An aliquot of the combined liquor and washings was taken for pentosan determination by furfural distillation and another

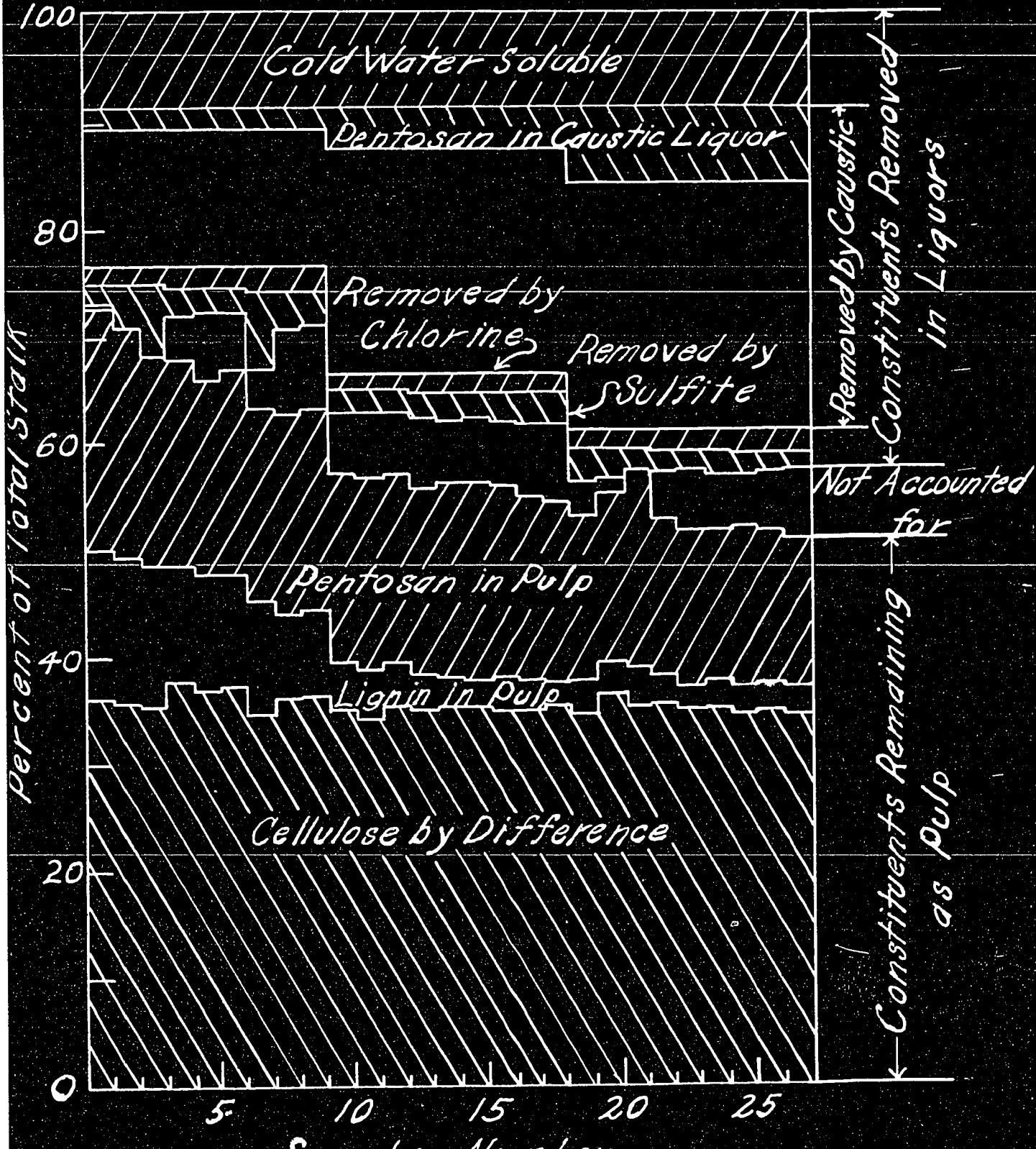


Fig 3 Diagram of Partition of Fibrous Material With Various Treatments From Data of Table I

aliquot was taken for the determination of total organic matter extracted from the stalk, this analysis being made by evaporating the solution at 110 degrees and burning out the organic matter.

The tissue after washing was transferred with 400 cc. of water and stirred until uniformly distributed. The tissue was then subjected to the action of chlorine gas for the indicated time, the rate of chlorination being controlled by a flowmeter delivering the gas stream. After chlorination, the liquor was filtered off and the tissue washed until the washings were free from chlorine. Aliquots of the combined liquor and washings were run for pentosan and total organic matter removed from the stalk.

The tissue was finally treated with 500 cc. of sodium sulfite solution of the indicated strength, the suspension brought to boiling and boiled for five minutes. The hot sodium sulfite extract was filtered off and the residue washed until the washings came through colorless. Aliquots of the combined liquor and washings were run for pentosan and total organic matter removed.

The tissue resulting from these three treatments was bleached with permanganate solution followed by sulfurous acid solution, dried in a vacuum oven at 60 degrees, and analyzed for ash, pentosan, lignin and α cellulose content.

Destruction of Pentosan by Cooking

The total pentosan accounted for in no case checked the amount, approximately 26%, in the original tissue. Experiments in which pentosan, extracted from cornstalks with 5% sodium hydroxide solution, was treated with caustic solution indicated a corresponding destruction, the destruction being greater the higher the concentration of caustic. The data are shown in Table VI. During the progress of this investigation, an article appeared by Aronovsky and Gortner[1] which shows similar results when wood is treated with water alone. This destruction is possibly due to the dehydration of the pentosan material with the production of furfural.

DISCUSSION OF RESULTS

The quantity of organic mater removed by each of the three treatments indicated that the initial caustic treatment was the only variable which removed appreciable quantities of material, although the quantity of organic matter removed increased slightly with increased time of chlorination as well as increased concentration of sodium sulfite. This result is in harmony with the work of Ritter[2] which indicates that a short period of chlorination is sufficient to chlorinate all the exposed lignin. In the treatment of the pith as well as in the treatment of the

1. Aronovsky and Gortner, Ind. Eng. Chem., 22, 264 (1930).
2. Ritter, Ind. Eng. Chem., 16, 947 (1924).

Table VI

Destruction of Pentosan by Cooking

Sample No.	Treatment				Pentosan in sample	Pentosan found after cook in gms.	Pentosan Decomposed in gms.	Per cent Pentosan Decomposed
	Conc. NaOH in %	Vol. NaOH in cc	Pressure of cook in #/	Time of cook in Mins.				
1	1.0	50	35	30	.3502	.3223	.0279	7.95
2	2.0	50	35	30	.3500	.3147	.0353	10.10
3	3.0	50	35	30	.3511	.2918	.0593	16.90

fibers an increase in caustic concentration caused a decrease in the yield of pulp, α-cellulose content, lignin content, and pentosan content of the pulp and an increase in the organic matter removed. See figures IV, V, VI, VII.

In the case of the fibers, the 2.0% caustic treatment produced a good white pulp while the 1.0% and 0.5% caustic treatment produced a dark colored insufficiently treated pulp. On testing intermediate concentrations, it was found that 1.2% caustic failed to give an entirely satisfactory pulp while 1.3% caustic gave a satisfactory pulp. See tableVII. This calculated to be 12.5% sodium hydroxide on the weight of the dry fibers. The actual dilution of the caustic solution has little effect for a pulp may be obtained from as dilute a solution as 0.5% caustic concentration when the ratio of dry fiber tissue to caustic solution is 1 to 30.

In the case of the pith material, the 2.0%, 1.0% and 0.5% caustic treatments all gave satisfactory pulps. On testing lower concentrations, it was found that a satisfactory pulp was obtained with 0.3% but not with 0.2% caustic solution when 30 cc. caustic solution were used per gram of material. See Table V . This calculated to be 7.5% sodium hydroxide on the dry material.

Fig.V indicates that the lignin left in the pulp tends to approach a minimum value with increased caustic concentration, however, it is not completely removed.

Fig.VI indicates that the α-cellulose content when a good

Table VII

Effect of Caustic Concentration on Pulping Fiberous Material

Sample No.	Treatment: Conc. NaOH in %	Vol. NaOH in cc.	Chlorination time in Mins.	Conc. Na_2SO_3 in %	ANALYSIS OF LIQUORS: NaOH: combustible Residue	NaOH: Pentosan	Chlorination: Combustible Residue	Chlorination: Pentosan	Na_2SO_3: Combustible Residue	Na_2SO_3: Pentosan	Total combustible matter removed	T P R
33	0.25	250	30	2.0	5.82	0.41						
34	0.25	500	30	2.0	13.21	1.24						
35	0.25	1000	30	2.0	20.50	3.68						
36	0.25	2000	30	2.0	24.60	4.34						
5	0.5	250	30	2.0	14.64	1.58	1.77	0.16	2.26	0.91	18.67	
29	0.5	500	30	2.0	25.90	3.86	1.64	0.24	2.10	0.67	29.64	
30	0.5	750	30	2.0	28.50	5.83	1.52	0.20	1.95	0.65	31.79	
59	0.5	1000	30	2.0	26.65	5.20						
14	1.0	250	30	2.0	24.75	3.61	1.60	0.34	2.30	0.69	28.65	
31	1.0	500	30	2.0	31.60	7.36	1.48	0.26	2.02	0.66	35.10	
32	1.0	750	30	2.0	33.21	8.49	1.43	0.19	1.80	0.64	36.44	
60	1.0	1000	30	2.0	28.10	9.25						
23	2.0	250	30	2.0	30.20	7.53	1.46	0.28	1.78	0.60	33.44	
61	2.0	500	30	2.0	30.08	9.65						
62	2.0	1000	30	2.0	30.50	10.78						

Table VII

stic Concentration on Pulping Fiberous Material

	ANALYSIS OF LIQUORS						Total combustible matter removed	Total Pentosan Removed	Yield of Residue	Analysis of Residue			α-cellulose
	NaOH		Chlorination		Na_2SO_3								
	Combustible Residue	Pentosan	Combustible Residue	Pentosan	Combustible Residue	Pentosan				Ash	Pentosan	Lignin	
	5.82	0.41							83.5		26.10	23.10	55.4
	13.21	1.24							75.5		24.70	17.55	55.2
	20.50	3.68							65.8		20.56	13.07	48.5
	24.60	4.34							62.0		18.52	7.19	45.6
	14.64	1.58	1.77	0.16	2.26	0.91	18.67	2.49	66.5	0.26	18.41	10.79	47.4
	25.90	3.86	1.64	0.24	2.10	0.67	29.64	4.77	60.5	0.26	18.02	4.59	43.7
	28.50	5.83	1.52	0.20	1.95	0.65	31.79	6.68	59.0	0.26	17.18	4.14	42.4
	26.65	5.20							58.4		17.81	3.33	40.6
	24.75	3.61	1.60	0.34	2.30	0.69	28.65	4.64	56.5	0.13	17.90	3.12	40.6
	31.60	7.36	1.48	0.26	2.02	0.66	35.10	8.28	57.4	0.26	16.53	3.96	40.8
	33.21	8.49	1.43	0.19	1.80	0.64	36.44	9.32	55.4	0.25	16.10	3.50	39.0
	28.10	9.25							54.5		16.08	2.23	38.8
	30.20	7.53	1.46	0.28	1.78	0.60	33.44	8.33	51.8	0.15	14.39	2.16	38.2
	30.08	9.65							51.3		13.35	1.94	37.9
	30.50	10.78							49.8		12.41	1.74	37.7

Analysis of Residue			α-cellulose	Combustible matter + yield of Residue	Pentosan removed + pentosan in Residue	Total solids + H_2O soluble material	Remarks
Ash	Pentosan	Lignin					
	26.10	23.10	55.4				Insufficiently Treated
	24.70	17.55	55.2				" "
	20.56	13.07	48.5				" "
	18.52	7.19	45.6				" "
0.26	18.41	10.79	47.45	85.17	20.90	94.37	" "
0.26	18.02	4.59	43.70	90.14	22.79	99.34	" "
0.26	17.18	4.14	42.40	90.97	23.86	100.17	Made fair Pulp
	17.81	3.33	40.60				Made good Pulp
0.13	17.90	3.12	40.60	85.15	22.54	94.35	Made poor Pulp
0.26	16.53	3.96	40.80	92.50	24.81	102.70	Made good Pulp
0.25	16.10	3.50	39.07	91.84	25.42	101.04	Very good Pulp
	16.08	2.23	38.88				" " "
0.15	14.39	2.16	38.20	85.24	22.72	94.44	" " "
	13.35	1.94	37.90				" " "
	12.41	1.74	37.70				" " "

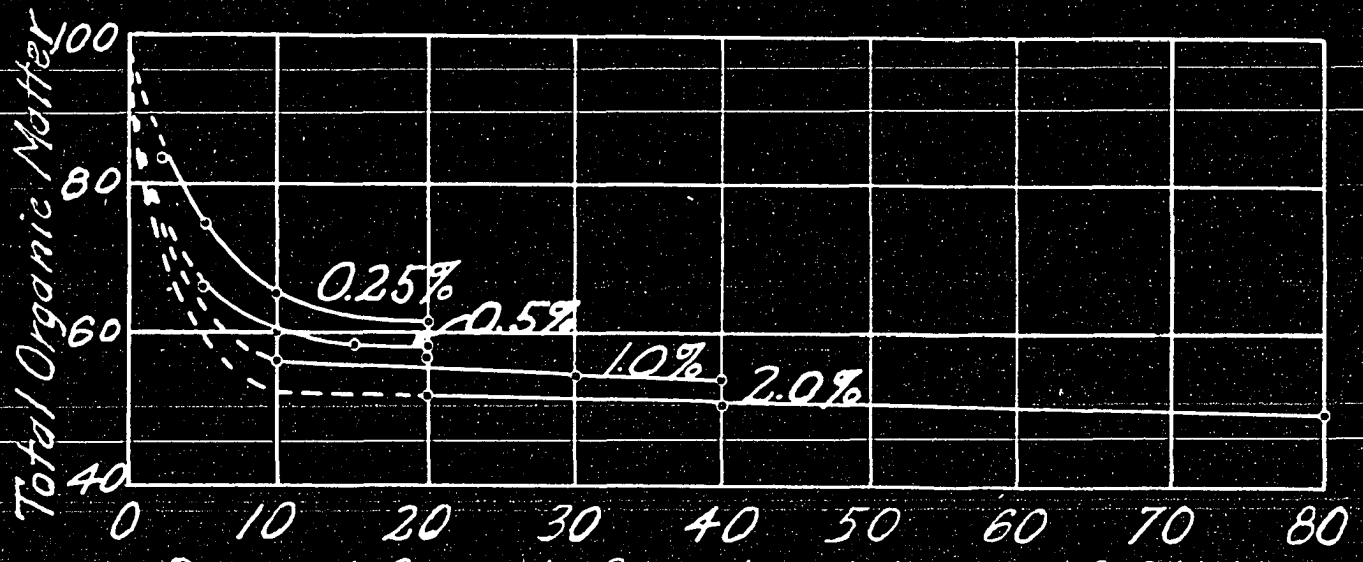


Fig 4 Effect of Caustic on Organic Matter Removal

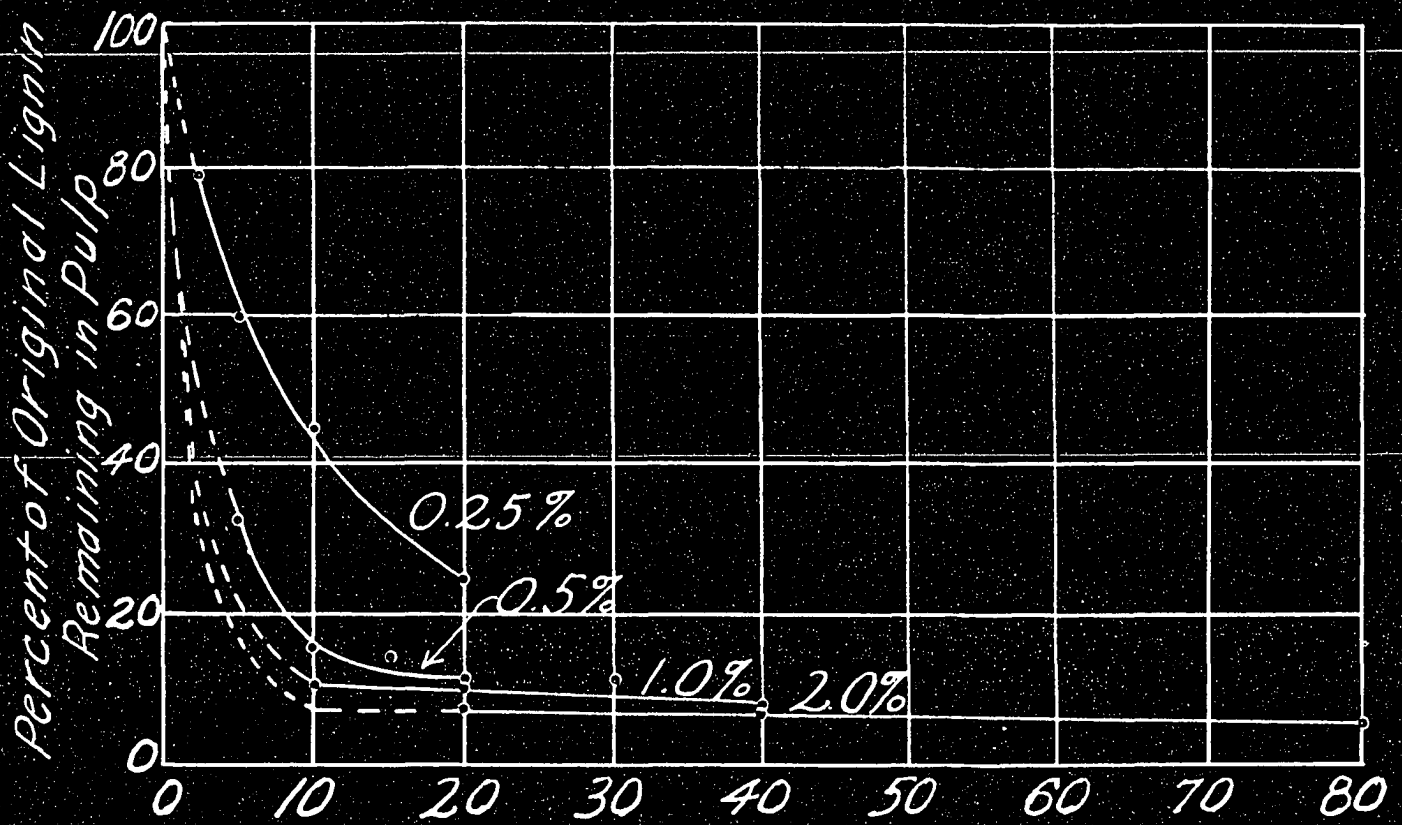


Fig 5 Effect of Caustic on Lignin Removal

Fig 6 Effect of Caustic on Pentosan Removal

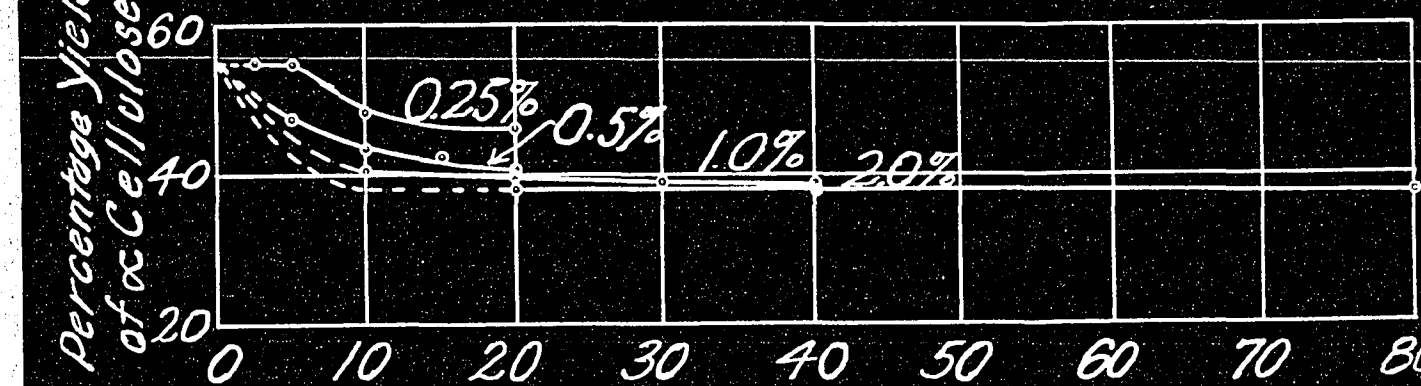


Fig 7 Yield of ∝ Cellulose

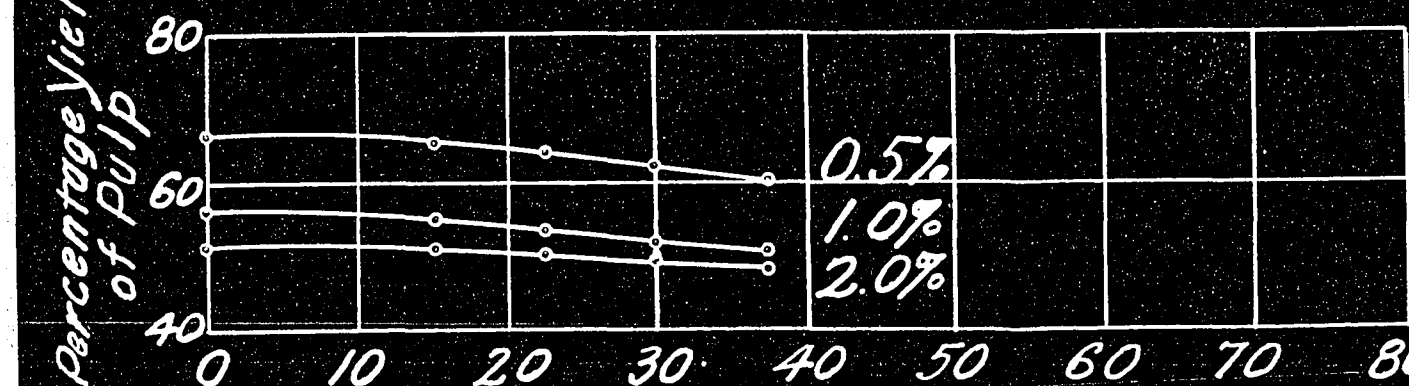


Fig 8 Effect of Pressure on Pulping

Table VIII

Effect of Pressure on Pulping Fiberous Material

Sample No.	Treatment: Conc. NaOH in cc	Vol. NaOH in cc	Chlorination time in Mins.	Conc. Na_2SO_3 in %	Pressure of cook in #/	Yield of Residue	Remarks
5	0.5	250	30	2.0	atm.	66.5	
48	0.5	250	30	2.0	15.0	65.8	Insufficiently Treated
49	0.5	250	30	2.0	22.5	64.3	" "
50	0.5	250	30	2.0	30.0	63.4	" "
51	0.5	250	30	2.0	37.5	60.8	" "
14	1.0	250	30	2.0	atm.	56.6	
52.	1.0	250	30	2.0	15.0	56.0	Made fair pulp
53	1.0	250	30	2.0	27.5	54.1	" " "
54	1.0	250	30	2.0	30.0	52.2	" " "
55	1.0	250	30	2.0	37.5	51.5	Made good pulp
23	2.0	250	30	2.0	atm.	51.8	
56	2.0	250	30	2.0	15.0	51.7	Very good pulp.
57	2.0	250	30	2.0	22.5	50.9	" " "
58	2.0	250	30	2.0	30.0	50.0	" " "
59	2.0	250	30	2.0	37.5	48.9	" " "

pulp is produced is from 35 to 40% of the total stalk and that this value tends to approach a constant minimum value.

The effect of pressure upon pulping is shown in Table VIII and in Fig.VIII. These curves indicate that at low pressure the effect is inappreciable, however, as the pressure becomes greater the effect tends to increase.

SUMMARY

The cornstalk can be mechanically separated into a pith tissue and a fibrous tissue, yielding 63% fibrous and 26% pith based on the weight of the original stalk.

In the de Vains process, when applied to the pulping of cornstalks, the initial caustic treatment is the only variable which has any appreciable effect on the chemical composition of the pulp.

Isolated pentosan material is destroyed by pulping processes, the destruction being greater the greater the caustic concentration of the cook.

The percentage of α-cellulose as well as lignin in the pulp tends to approach a constant minimum value. However the removal of lignin is in no case complete.

PART III

THE PARTITION OF THE CONSTITUENTS OF THE CORNSTALK BY THE USE OF A VOLATILE ALKALI

INTRODUCTION

During the process of converting plant tissues into cellulosic pulp, about forty to fifty per cent of the original tissue is dissolved. In the alkali process, no satisfactory method of isolation of the dissolved substances has been found which will at the same time permit the recovery of the caustic. The purpose of the following investigation is to provide a process which will reduce plant tissue to a cellulosic pulp, which will permit the recovery of the caustic as well as the fermentation or other utilization of the hemi-celluloses removed from the tissue and which will leave the lignin material in a form easily isolated.

Pulping of Tissue

The material used in these studies consisted of the fibrous tissue of the cornstalk as described on page 26. The fibrous tissue was used since it is so much more difficult to pulp than the pith tissue that any pulping process which would pulp the fiber would also pulp the pith.

The chemical treatment reported for the tissue consists essentially of a modification of the de Vains process. The de Vains process consists of three distinct steps:

1. Preliminary treatment with dilute alkali to partially delignify the tissue.
2. Chlorination of the pulp from the alkali treatment to convert the residual lignin into soluble compounds.
3. Extraction of the chlorinated lignin with either sodium sulfite or caustic solutions.

In this investigation the first step of the process has been modified so that a volatile alkali, such as ammonia, is used instead of a non-volatile alkali, as NaOH.

The cornstalk tissue was used in the air dry condition in the same state as it came from the separator. The material had a moisture content of 5.63 per cent on an oven-dry basis of 105°C. The dry tissue ran 1.44 per cent ash.

The oat straw tissue was used in the air dry condition in the same state as it came from the bales. The material had a moisture content of 6.80 per cent on an oven-dry basis of 105°C. The dry tissue ran 3.77 per cent ash.

A special laboratory type of digestor was used for this investigation. A schematic diagram is shown in Figure IX. The four heat units made it possible to get practically any desired temperature since they could be connected in series or in parallel, and also cut out entirely when necessary. The digestor was lead lined in order that it might be used for sulfite cooks. When sulfite cooks were made, the iron head was replaced by a silver plated head. The lead lining also made it possible to get a tight joint at the top.

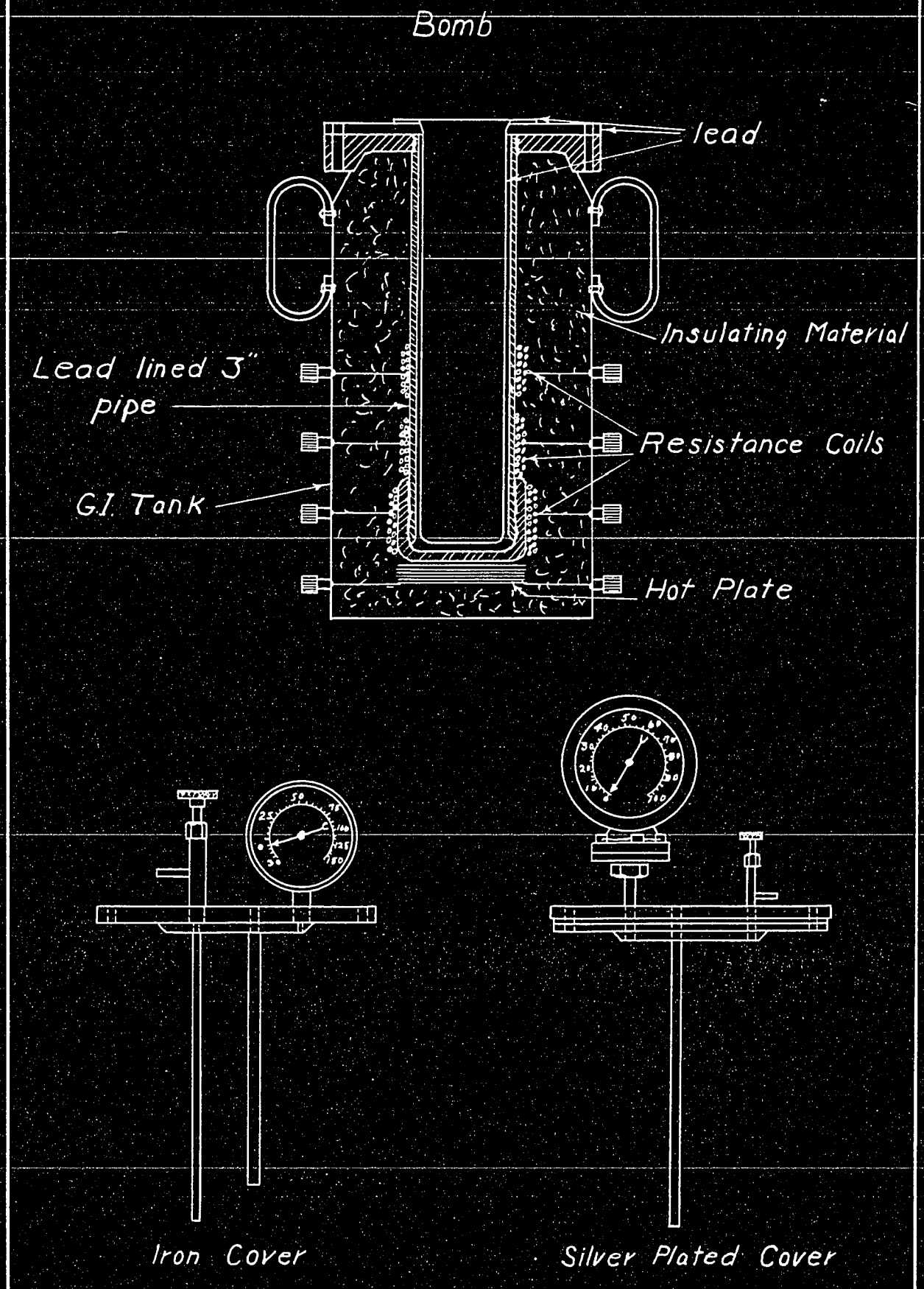

Bomb
lead
Insulating Material
Lead lined 3" pipe
Resistance Coils
G.I. Tank
Hot Plate
Iron Cover
Silver Plated Cover

Fig. 9

Table IX

Pulping Cornstalk Fibers with Ammonia

Sample No.	Treatment					Analysis of Liquor		
	Conc. NaOH in %	Vol. NH_4OH in cc	Pressure in # /	Temperature in cc. °C.	Time of cook in hours	Combustible Residue	Pentosan	N in
1	28.5	1000	100	115	15	32.31	7.08	6
2	28.5	1000	100	115	15	29.90	6.98	6
3	28.5	1000	100	115	15	30.00	7.10	1
4	28.5	1000	100	115	15	31.00	7.20	0
5	28.5	1000	100	115	15	30.50	7.18	0
6	14.25	1000	100	145	15	28.71	6.91	5
7	14.25	1000	100	145	15	29.36	6.97	2
8	14.25	1000	100	145	15	29.09	6.81	0
9	14.25	1000	100	145	15	28.97	7.01	0
10	14.25	1000	100	145	15	---	---	-
	14.25	1000	100	145	15	---	----	-
11	14.25	1000	100	145	15			
	14.25	1000	100	145	15	---	----	-
de Vains	---	--	---	---	--	33.77	8.40	-
de Vains	---	--	---	---	--	33.44	8.33	-

Table X

Pulping Oat Straw with Ammonia

1	28.5	1000	100	115	15	31.40	8.48
2	28.5	1000	100	115	15	32.10	8.21
3	28.5	1000	100	115	15	33.30	8152
4	28.5	1000	100	115	15	32.90	9.31
	28.5	4000	100	115	8	-----	----
	28.5	4000	100	115	15	-----	----
	28.5	4000	100	115	15	-----	----
de Vains	----	----	---	---	-	33.85	9.21
de Vains	----	----	---	---	--	34.92	8.95

The data for the digestion of cornstalk material with NH_4OH are given and compared with do Vains cooks in Table IX.

The data for the digestion of oat straw with NH_4OH are given and compared with oat straw cooks by the de Vains process in Table X. This table also shows data on the pulping of a few samples of wheat straw by the use of NH_4OH on a semi-commercial scale in which 400 gram samples were used. This work was done in the Chemical Engineering laboratories.

LABORATORY PROCEDURE

One hundred gram samples were used. The material was placed in the digestor and the smallest volume of aqueous ammonia of the indicated concentration sufficient to cover the sample was added. This amounted to about 1000 CC in all cases. The digestor head was put in place and bolted down. The pressure in the digestor was slowly brought to 90# to 110# and held at this pressure for from 8 to 15 hours by use of the electric heat units. The pressure was decreased to some 15 to 25# by letting the digestor cool. This pressure was decreased to atmospheric by opening the blow off valve. This served to drain off practically all the liquor from the digestor and the expansion served to set free practically all of the ammonia. What little ammonia was not set free by the expansion was easily removed by boiling the black liquor with the simultaneous passage of air through it. This gave a muddy liquid containing a large amount of brown material in suspension.

The digestor was now opened, the pulp removed and washed well with water by filtering with the aid of suction, through a cloth filter.

The tissue was transferred to a laboratory sized paper beater and beaten until a good pulp was obtained. The time of beating varied with the concentration of the ammonia and the duration of the cook.

The tissue, after beating, was subjected to the action of chlorine gas for about 20 minutes or until the tissue lost the brown color and became a faint yellow. After chlorination, the liquor was filtered off and the tissue washed until free from chlorine.

The tissue was finally treated with enough 2 per cent sodium sulfite to make a heavy suspension. This was slowly brought to a boil and boiled for five minutes. The hot sodium sulfite extract was filtered off and the residue washed until the washings came through colorless.

The tissue resulting from these treatments was bleached with permanganate solution followed by sulfurous acid solution. A portion was dried in a vacuum oven at 60°C. and analyzed for ash, pentosan, lignin and cellulose content. Another portion was made into paper. This paper was of such a quality as to compare with any of the de Vains process or soda process paper.

Attempts to Utilize Waste Liquors

It is known that pentosan material extracted from corn-

stalks by 5 per cent NaOH is very rapidly attacked by thermophilic organisms, also that the digestor liquors from ammonia pulping contain about 25 per cent pentosan on the basis of total solids. It should, therefore, be possible to ferment the pentosan material of this liquor by the use of thermophilic organisms, leaving a pure lignin. Accordingly, the liquor from the ammonia digestion, after removal of the excess ammonia by evaporation, was made into a fermentation medium composed of 10 grams peptone, 1 gram K_2HPO_4, 00.2 gram $CaCO_3$, a quantity of concentrated digestor liquor equivalent to 25 grams of solids, and 1000 CC of water. After sterilization, this medium was inoculated with thermophilic type bacteria and incubated at 61°C. The results of this investigation were of no practical value since the material was not attacked by the thermophilic organisms to any noticeable extent. Since no fermentation took place, there must have been something in the digestor liquor which was toxic to the organisms or the pentosan must have been different. By separation and purification of a quantity of pentosan from the digestor liquor by the process described on page 17 and comparing with the pentosan from the 5 per cent NaOH extraction of stalks, it was found that the two were identical in both chemical and biochemical properties. Therefore the substance prohibiting fermentation of the digestor liquor must be the lignin or some other material in the liquor which is removed when the pentosan is separated and purified.

When the digestor liquor is evaporated to dryness, a dark brittle residue is formed which can be ground to a fine powder. By mixing this material with phenol in the ratio of 2 to 1 or 20 grams of residue with 10 grams, of phenol and adding a small amount of concentrated HCl, about 1 c.c., then placing this material in a glass tube and sealing off and heating the tube at 100°C. for four hours, a black tough plastic material is formed. The explanation for this may be due to the fact that during the heating, the pentosan material is dehydrated by the HCl to furfural which condenses with the phenol to form a plastic, also the lignin material condenses with the phenol to form a jet black plastic called phenollignin.

DISCUSSION OF RESULTS

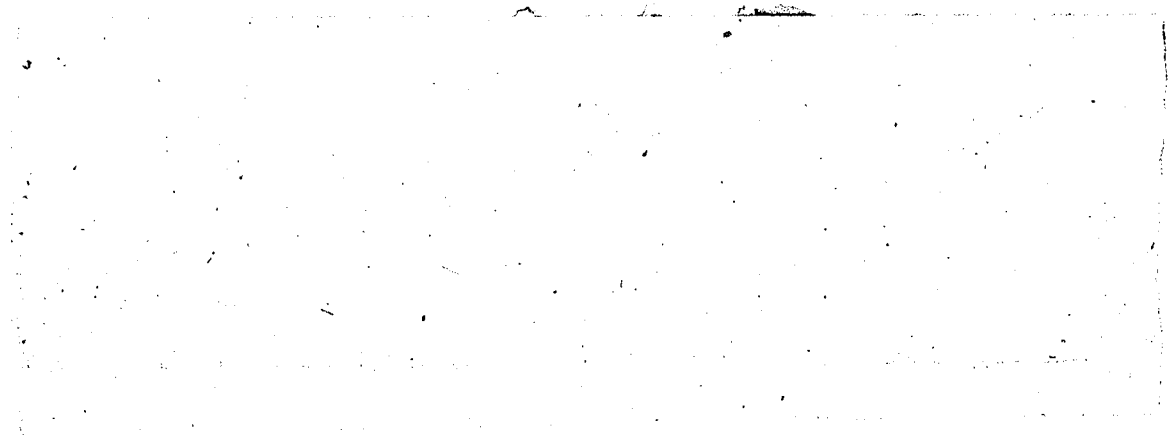
From the results of Table IX and a comparison of the paper shown on page 51 , it is seen that a paper pulp of very good quality may be obtained from cornstalk material by a modification of the de Vains process in which the NaOH is replaced by a volatile alkali, such as NH_4OH. When commercial concentrated NH_4OH is used a good pulp is obtained with one cook while when a cook liquors of one part concentrated NH_4OH to one part H_2O is used it is necessary to give the material two cooks before a good pulp is obtained. The solid material obtained by the evaporation of the digestor liquor contains about 25 per cent pentosan, the remainder is considered to be lignin. The NH_3 content in samples

Samples of Cornstalk Paper made by

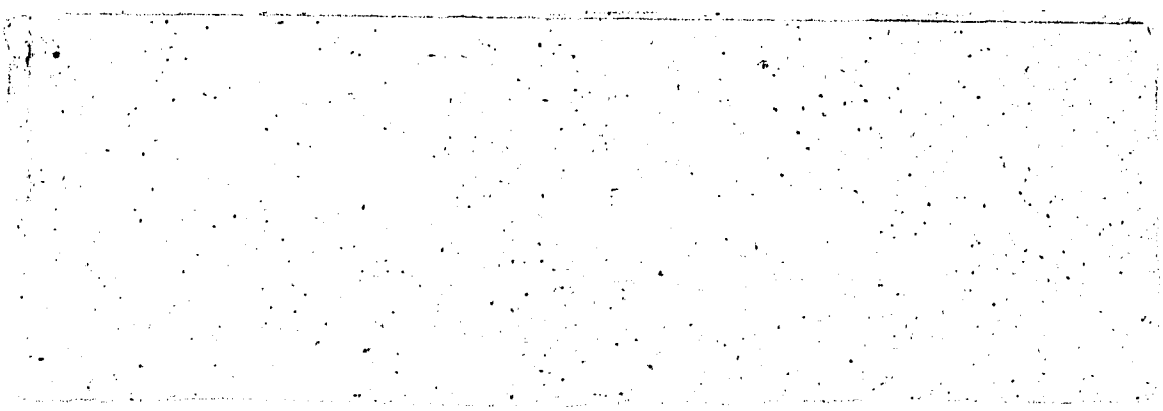
Ammonia process

de Vains process

Samples of Oat Straw Paper made by



Ammonia process



de Vains process

1 and 2 is seen to be about 6.6 per cent while in sample 3 it is only 2 per cent and in sample 4 and 5 the NH_3 content is about 0.5 per cent. This difference is due to the fact that in the samples 1 and 2 the liquor was evaporated without the passage of air through it, while air was passed through sample 3 as it was evaporated. The NH_3 content of samples 4 and 5 is low, due to the fact that a small amount of NaOH was added to the liquor before evaporation liberating the NH_3 from its salts. Air was also passed through the liquor during the evaporation. This indicates that the NH_3 can be almost quantitatively recovered. The yield of cellulosic pulp by this process is somewhat higher than it is in the case of the de Vains process. The analysis of the pulp indicates that the cellulose content of the two are about the same, while the pentosan content is somewhat higher in the case of the ammonia pulp.

Table X and the samples of paper on page 52 indicate that a very good cellulose pulp may be obtained by the use of ammonia as a pulping agent when applied to oat straw. The yield of pulp is higher by the use of NH_4OH then by the use of NaOH. The reason for this higher yield is possibly due to the fact that the action of NaOH, which is known to destroy and weaken a portion of the cellulose in the production of pulp by its use.

Attempts to ferment the residue left after evaporation of the digestor liquor have proved unsuccessful by the use of thermophilic organisms. This is possibly due to the fact that

the lignins in the residue, which are phenolic type bodies, may act as a poison to the organism, or there might be some other constituent in the liquor which is toxic to the organisms.

It has been shown that a plastic may be obtained by treating the dry residue with phenol and HCl at 100°C. for several hours. The formation of this plastic is probably due to the generally accepted explanation of the formation of a phenollignin and also due to the *in situ* formation of a phenol furfural condensation product, since at a high temperature the HCl would attack the pentosan tending to dehydrate it to furfural. This furfural then reacts with the phenol to form a plastic.

SUMMARY

A process is described by which ligno-celluloses may be pulped by the use of a volatile alkali, such as NH_4OH.

Attempts to ferment the digestor liquors from ammonia pulping have been unsuccessful.

The residue from ammonia pulping may be made into a plastic material by the addition of phenol and processing for the production of such characteristic condensation products.

PART IV

DECOMPOSITION OF THE CORNSTALK TISSUE BY THE USE OF THERMOPHILIC BACTERIA

INTRODUCTION

It has been known for sometime that certain bacteria attack cellulose and pentosans decomposing them into soluble products; it is also stated in the literature that during this fermentation any lignin which might be present is unattacked[1]. The thermophilic type organisms attack cellulose more rapidly[2] than any of the other organisms. The products of the thermophilic fermentation of cellulose are principally acetic and formic acids[3]. Since it is possible to commercially prepare acetic and formic acids from cellulose by the thermophilic fermentation, it should be possible to commercially utilize cornstalks and other cellulosic waste materials by fermenting them into valuable acids and other products. Due to the fact that during these fermentations the lignin is presumably unattacked it should be possible to prepare a pure lignin by this process. The purpose of the following investigation was to commercially ferment the cellulose and pentosan materials of the cornstalk into valuable products as well as to prepare a lignin material more nearly the natural product than can be prepared by any of the chemical

1. Lymn and Langwell, J. Soc. Chem. Ind. 42, 280T, (1923)
2. Pringsheim, Z. Physiol. Chem. 78, 266 (1922).
3. Pringsheim, Centr. Bakt. Parasitenk, II, Abt. 38, 513 (1913).

processees.

HISTORICAL REVIEW
Cellulose Fermentation

That cellulose is decomposed by thermophilic organisms was first noted by Macfayden and Blaxall[1] in 1899. These investigators inoculated a medium containing broth, nutriet salts and swedish filter paper with manure, and noticed the production of acetic and formic acids at 55 to 65°C. They attributed the production of the acids to a symbiotic action of unknown species of bacteria, since they failed to isolate a pure culture which would produce the characteristic fermentation. They found the optimum temperature to be from 55 to 65°C, but that fermentation would take place as low as 37°C.

Pringsheim[2] in 1912, classified the cellulose fermenting bacteria into four groups:

Group	Products of Fermentation
1. Methane bacteria...	CH_4, CO_2 and lower fatty acids to butyric acid.
2. Hydrogen bacteria...	H_2, CO_2, and lower fatty acids to butyric acids.
3. Thermophilic bacteria...	CH_4, H_2, CO_2, formic and acetic acids.
4. Denitrifying bacteria...	N_2 and CO_2.

1. Macfayden and Blaxall, Trans. Jenner. Inst. II, (1899), 182.
2. Pringsheim, Z. Physiol. Chem. 78, 266, (1912)

He was able to show that all the cellulose fermenting organisms produced an enzyme which hydrolized the cellulose to cellobiose as well as an enzyme which hydrolized the cellobiose to glucose. The cellobiose producing enzyme was active at low temperatures while the glucose producing enzyme was more active at higher temperatures.

Kelleman and McBeth[1] (1912) described three organisms capable of fermenting cellulose, and in addition, reported isolating 11 other cellulose destroying species, one of which was thermophilic.

Kroulik[2] fermented cellulose at 60 to 65° by using fecal material from ruminants as inoculum. Yellow flakes appeared on the filter paper, which was used as a medium, in two or three days. Soon the entire surface of the paper turned yellow, many bubbles arose, and the fermentation proceeded rapidly. 12 to 18 hours after the appearance of the yellow flakes, the paper became full of holes, the solution became turbid, and finally the paper was changed to a yellow gelatinous mass. It was found that small amounts of iron salts ($FeCl_3$) were very good catalysts, however, large concentrations of these materials were destructive to the organisms.

All attempts to isolate a pure culture of a thermophilic cellulose fermenting organism were fruitless. However, it was possible to isolate the same two different aerobic bacilli from

1. Kelleman and McBeth, Centr. Bakt. Parasitenk, II, Abt. 34, 485, (1912)
2. Kroulik, Centr. Bakt. Parasitenk, 36, 339, (1913)

each of the fermentations.

The products from the aerobic fermentations were: CO_2, small amounts of hydrogen, acetic acid, and small amounts of formic and butyric acid. About 70% of the cellulose was fermented in the aerobic cultures. The anaerobic fermentation gave CO_2, hydrogen, and some H_2S (likely from the reduction of sulphates). Methane was not produced. Complete fermentation, 90% or more, took place in the anaerobic cultures. Kroulik did not identify the acids produced during the anaerobic fermentation.

Pringsheim[1] confirmed Kroulik's results, and in addition, quantitatively measured the end products. He was able to recover about 45% of the decomposed cellulose as fatty acids. About 18% of this acid material was identified as formic acid, the remainder being acetic. The other products of the fermentation were: CO_2, H_2 and traces of lactic acid. He was unable to show the presence of methane. Pringsheim was unable to isolate a pure culture of the thermophilic fermenting organisms.

Fowler and Ganski[2] (1920) suggested the use of fermentation gases from cellulose as a fuel. The fermentation was found to be most active with hemicellulose, less active with lignocellulose and least with pure cellulose. Septic tank sludge was used as inoculum. Thefineness of the cellulose has a great effect upon the rate of fermentation, the best results being obtained

1. Pringsheim, Centr. Bakt. Parasitenk, II Abt., 38, 513 (1913)
2. Fowler and Ganski, J. Indian Inst. Sci., 3, pt. 4, 39, (1920) See C.A. 15, 3720, (1921)

from a pulp. The rate of fermentation was greatly accelerated by removal of the acid products as fast as formed by neutralization. The gaseous products of the fermentation were found to be 81% CH_4 and 14.5% H_2, the remainder being CO_2. Acetic acid was the principal acid formed. The optimum temperature of this fermentation was 30°.

Lynn and Langwell[1] (1923) found a bacillus which would attack any kind of cellulose under either aerobic or anaerobic conditions. However, these organisms attacked ligno-and cutocelluloses quite slowly unless they were first hydrolized. The organism is procured from steaming stable manure, and is a thermophilic, its optimum being 60° to 68°C. They found two types of organisms present. However after isolation neither of the organisms retained their cellulose fermenting power. The products of the fermentation were acetic, butyric and lactic acid, ethyl alcohol, CO_2, hydrogen, and CH_4. The percentage of these compounds varies with the material fermented as well as the conditions. To ferment lignocelluloses, the material must first be treated to remove the lignin as by a pulping process. Langwell has covered all phases of this process by patents,[2] in which he states, among other things, that the alcohol content may be increased by a complete aerobiosis while under complete anaerobiosis,

1. Lynn and Langwell, J. Soc. Chem. Ind., 42, 280T, (1923)
2. Langwell. U.S. Patent 1,443,881, Jan 30, (1923)
   U.S. Patent 1,639,571, Aug. 16, (1927)
   U.S. Patent 1,602,306, Oct. 5, (1926)
   Numerous British and Canadian Patents.

the per cent of alcohol is decidedly decreased with a material increase in acetic acid content. His patents claims the process of distilling off the alcohol as fast as formed by placing the fermentation tanks under a vacuum which would cause the alcohol to distill at 60°C. He also states that the rate of fermentation as well as the degree of fermentation is materially increased by fine grinding of the cellulosic material to be fermented. He has patented the pH range from pH 9 to pH 5.

Madame Khouvine[1] (1923) isolated a cellulose destroying organism from human feces to which she gave the name Bacillus cellulose dissolvens. This organism fermented cellulose at temperatures from 35 to 51°, more rapid fermentation taking place at the higher temperature. She found that the rate of decomposition of cellulose by this organism was increased five fold when it was associated with other organisms. The main products of the fermentation were acetic acid, ethyl alcohol, CO_2, H_2, and a small amount of butyric acid.

Viljoen, Fred and Peterson[2] (1926) report the isolation of a pure culture of a thermophilic cellulose fermenting organism. They state that organic nitrogen is necessary for its growth, peptone being the best. The products from this fermentation are acetic and butyric acids, ethyl alcohol, CO_2 and hydrogen. It was not possible to show the presence of methane. About 70 to 95% of the cellulose was fermented with 50 to 60% being recovered as

1. Khouvine, Ann. Inst. Pasteur, 37, 711, (1923)
2. Viljoen, Fred and Peterson, J. Agri. Sci., 16, 1, (1926)
   See also Abst. Bact. 8, 11, (1924)

acetic acid, 5 to 25% as ethyl alcohol and the rest as butyric acid, CO_2 and H_2. Its optimum temperature was found to be 65°. It was found that the alcohol content reached a maximum at the end of 3 days, then began to decrease and was practically zero at the end of 7 days. The amount of butyric acid produced was about 6.25 per cent of the total volatile acids.

Coolhaas[1] has made an extensive study of the thermophilic organisms. He found that the salts of the fatty acids were changed into methane and CO_2, by this fermentation. Especially was it active towards the salts of acetic and formic acids, causing quantitative fermentation of them. In his work with the action of the thermophilic organisms upon cellulose he used filter paper as a source of cellulose and mud and fecal material as sources of his organisms. He found that when the fermentation was first started large quantities of CO_2 and CH_4 but practically no hydrogen was given off. However, as the organism was transferred to new medium the methane fermentation was lost. The third transfer still gave methane while the fourth transfer gave nothing but CO_2 and H_2. Coolhaas interprets this as a purification of the culture. He states that the true thermophilic fermentation is a hydrogen fermentation, the methane being produced at the beginning by contaminating organisms which are killed off by overgrowth. As evidence of this he cites the facts that at the

1. Coolhaas, Centr. Bakt. Parasitenk., II, Abt. 75, 161, (1928)
2. Coolhaas, Centr. Bakt. Parasitenk., II, Abt. 76, 38, (1928)

beginning, the products of the fermentation are principally CO_2 and methane, with only small amounts of acids, there being no formic acids, but as the fermentation becomes older, the production of formic acid increases considerably while the production of methane ceases entirely. Since the salts of formic and acetic acids are quantitatively fermented to methane and CO_2, the presence of these acids in the products would mean that the methane fermentator had been destroyed. Coolhaas isolated pure cultures of the organism but after isolation the organism lost its power to ferment cellulose.

Pentosan and Lignin Fermentations

The fermentation of pentosan with a pure culture, like the fermentation of cellulose, seems to be a rather difficult procedure. Schmidt, Peterson and Fred[1] have been able to ferment this material quite successfully with pure culture of molds but not with bacteria. However, the hydrolysis products of this material, xylose and arabinose, are quite easily fermented, as has been shown by Fred, Peterson and Anderson[2], Burkey[3] and others. The principal products of these fermentations are acetic and lactic acids in a 1 to 1 ratio. The organisms used were not thermophilic. Patrick[4] has been able to get slow fermentation of xylan with pure cultures isolated from soil and various other sources.

1. Schmidt, Peterson and Fred, Soil Sci., 15, 479 (1923).
2. Fred, Peterson and Anderson, J. Biol. Chem., 48, 385 (1921).
3. Burkey, Iowa State College, J. Sci. 3, 57 (1928).
4. Patrick, M.S. Thesis, Iowa State College Library (1929). (In manuscript)

Lignin, until quite recently has been classed as a compound which could not be fermented. Schrader[1] (1921) makes the statement that in a series of fermentation experiments the lignin showed no trace of fermentation, while all the other materials, cellulose, etc. fermented.

Fringsheim and Fuchs[2] studied the fermentation of ammonium lignate, containing some 5.35% pentosan. This material was made by treating sawdust with 5% NaOH, filtering off the liquor and then precipitating the lignic acid with HCl. This was made into the ammonium salt. Inoculation of a medium made from this material with soil and incubation at 37°C caused a slight amount of gas to be produced the first day. The material was incubated 8 days. By making repeated transfers the impurities of the soil were reduced to a minimum. The lignic acid remaining after fermentation was obtained by precipitation with HCl 60% of the original was obtained. Analysis of this indicated that all the pentosan had been fermented and that the lignic acid had become more soluble in alcohol as well as having a higher carbon content. The original contained 62.02% carbon while the fermentation product contained 65.75% carbon.

Waksman and Tenney[3] report that during the decomposition of plant material in the soil the substances decompose in the follow-

1. Schrader, Chem. Zentr., III, 1649, (1923).
2. Fringsheim and Fuchs, Ber. 56B, 2095 (1923)
3. Waksman and Tenney, Soil Sci., 24, 317, (1924)

ing order: soluble organic matter, pentosan, and cellulose. The lignins are very resistant to decomposition and these together with microbial nitrogen complexes are important constituents of humus.

Rogozinski and Starzewska[1] report that lignin prepared by the Bechmann method was not digested to any noticeable extent by ruminants. The ruminant used was sheep.

Falck and Haag[2] report that woods are attached by certain white rot fungi leaving a white residue in which is thought to be cellulose, the lignin haveing been decomposed.

Fisher and Lieshe[3] report that in the natural decomposition of plants the lignin component tends to increase, due to its stability and to the removal of the other constituents.

Boruff and Buswell[4] (1929) have reported a process by which cellulose and cellulosic materials are fermented by a sewage inoculation. They state that the cellulose and probably the pentosan material is fermented to CO_2 and CH_4 in a 1 to 1 ratio or

$$(C_6H_{10}O_5)_x + x\,H_2O \longrightarrow 3CO_2 + 3CH_4$$

In the case of cornstalk material about 35 to 50% of the stalk is fermented. The pith and fine fiber being fermented

1. Rogozinski and Starzewska, Chem. Abst. 23, 3012, (1929)
2. Falck and Haag, Ber. 60, 225, (1927).
3. Fisher and Lieshe, Biochem. Z., 203, 351, (1928).
4. Boruff and Buswell, Ind. Eng. Chem. 21, 1181, (1929).

first with the long fiber and outer shell left behind. They do not state what the acid products are, if any. The fibrous material which is unfermented may be used for the preparation of paper and pulp. There are no data given on the change of composition of the material but it is thought that only the cellulose and pentosans are fermented, thereby leaving the lignin.

A very interesting piece of work from an industrial standpoint is that of Beckman[1] in which he uses thermophilic organisms, Bacillus delbrueckia, obtained from brewer's malt, for the purpose of decomposing the protein and cellulose walls around the fat cells in the cocoanut. The oil thus liberated comes to the top and may be filtered or skimmed off. He states that the product of fermentation from the cellulose is lactic and that the proteins are hydrolized to amino acids.

Falck[2] in a study of the decomposition of straw reports that by thermophilic fermentation the lignin is not decomposed but that by a nitrate and humic forming bacterial action is somewhat similar to the action of fungi.

Tenney and Waksman[3] report that in the decomposition of organic matter in soil, the lignins are more resistant to decomposition and tend, therefore, to accumulate. However, under aerobic conditions, there is a decided reduction in the total

1. Beckman, Ind. Eng. Chem., 22, 117, (~~1920~~ 1930).
2. Falck, Cellulose Chemie, 9, 1, (1928).
3. Tenney and Waksman, Soil Sci., 28, 55, (1929).

lignin content, indicating that, although it is attacked less readily than the cellulose and pentosan, its resistance to decomposition is only relative.

The products of the fermentations of lignin were not given in any of the above studies.

EXPERIMENTAL

The material used for this investigation consisted of cornstalks ground in a Wiley mill to pass a 12 mesh screen, mechanically separated cornstalk pith approximately 12 mesh, mechanically separated cornstalk fibers ground to pass a 12 mesh screen, mechanically separated fibers ground in a colloid mill, and mechanically separated fibers ground in a ball mill to pass a 100 mesh screen. These materials were all used in the air dry condition.

The medium employed consisted of 25 grams of cornstalk material, 1 gram K_2HPO_4, 10 grams (Bacto) peptone, and 0.2 gram $CaCl_2$ in a liter of tap water. This medium was sterilized at 20 pounds pressure for 20 minutes, in order to insure the destruction of any contaminating thermophilic spores.

The organisms were obtained by inoculating flasks of the medium with goat feces[1], incubating for 24 to 48 hours, at a constant temperature of 61°C., then transferring to a second flask and again incubating for the same period. After the

1. Carter, M.S. Thesis, Iowa State College Library (1929). (In manuscript)

third transfer, no organisms other than the two which are characteristic of this fermentation were present. The cultures were then propagated b y meking transfers from actively fermenting medium.

The method of procedure was essentially to prepare flasks of sterile medium, adjust the pH to 8.5 to 9.0 or just alkaline to phenolphthalein, inoculate with 50 cc. of the inoculum and incubate at 61°C. The acid produced was neutralized daily with 1 N. KOH by adjusting the pH to 8.5 to 9.0. The fermentation was quite active for from 5 to 10 days, after which the medium became very dark in color and ceased to produce acid and gas. This was taken as a criterion of complete fermentation. The contents of the flasks were filtered, using closely woven cloth as a filter medium, and the residue washed with water.

The residue was dried in a vacuum oven at 60°C and weighed. The loss in weight was taken as a criterion of the amount of material fermented. This dry residue was ground in a Wiley mill to pass a 60 mesh screen and used for pentosan and lignin analyses. The lignin was determined by the cold 72 per cent sulfuric acid method[1] and the pentosan was determined by the 12 per cent HCl distillation method.[2]

The filtrate from above was steam distilled for the recovery of any alcohols or other neutral volatile products which might

1. See page 9.
2. Schorger, "Chemistry of Cellulose and Wood," p. 534, McGraw-Hill Book Co. (1926).

TABLE XI

Effect of Transfers on Acid Production

Transfer No.	Dry weight Cornstalk pith used in gms.	Duration of fermentation in days	Total Vol. in KOH used to Neutralize acid produced	gms. acid produced calculated as acetic	Material unfermented in gms.	Material fermented in gms.	Per cent of fermented material accounted for as acids	Per cent original cornstalk material accounted for as
Original tissue								
Original inoculatin	23.45	11	90	5.4	7.8	15.65	34.8	23.
1	23.45	9	96	5.76	10.3	13.15	43.8	24.
2	23.45	8	110	6.6	10.9	12.55	52.6	28.
3	23.45	7	130	7.8	10.5	12.95	60.5	33.
4	23.45	6	115	6.9	14.8	8.65	79.7	29.
5	23.45	5	120	7.2	14.7	8.75	82.2	30.
6	23.45	5	100	6.0	16.0	7.45	80.5	25.

TABLE XI

rs on Acid Production

erial rment- in gms.	Material fermented in gms.	Per cent of fermented material accounted for as acids	Per cent of original cornstalk material accounted for as acids	Analysis of Acid Distillate		Analysis of Residue		
				Formic Acid in %	Acetic Acid in %	Lignin cold 72% H_2SO_4 method in %	Lignin R.T. 72% H_2SO_4 method in %	Pentosan in %
						20.2	32.0	27.7
.8	15.65	34.8	23.0	8.4	91.6	28.7	29.8	19.6
.3	13.15	43.8	24.6	9.7	92.3	28.3	30.6	20.7
.9	12.55	52.6	28.2	10.3	89.7	26.7	31.9	18.4
.5	12.95	60.5	33.2	12.1	87.9	24.2	32.1	15.7
.8	8.65	79.7	29.4	14.0	86.0	22.8	31.8	11.7
.7	8.75	82.2	30.7	13.9	86.1	21.1	31.2	10.0
.0	7.45	80.5	25.6	14.1	85.9	21.9	33.8	11.4

have been formed during the fermentation. Qualitative organic analysis of this distillation indicated the presence of only small amounts of ethyl alcohol.

The residue from this distillation was made strongly acid with H_2SO_4 and again steam distilled. The distillate was strongly acid and had the odor of acetic acid; the odor of butyric acid could not be detected. This distillate was titrated with standard NaOH. Qualitiative analysis of this acid distillate indicated the pressure of only acetic and formic acids.

The residue from this second distillation was extracted with ether and the ether evaporated. A very small amount of an oily acid substance was left. This was most probably lactic acid since Pringsheim[1] reports that traces of this acid are formed in the thermophilic cellulose fermentation.

During the preparation of the culture it was observed that as the fermentation became older the amount of acid produced, based upon the amount of material fermented, became greater and that the time of fermentation was decidely decreased. The data is given in Table XI and shown in Fig. X . All values in the Table are averages of at least 2 samples. The material used for this study was cornstalk pith material only. No gas analyses were made during this investigation.

The results of investigation to determine the effect of the degree of subdivision of the tissue on the fermentation are shown in Table XII. Gas analyses made at this time indicated only CO_2 and H_2 as gasious products of the fermentation.

1. Pringsheim, Centr. Bakt. Parasitent II abt. 38, 513, (1913)

Fig. 10 Effect of Age of Fermentation On Acid Production

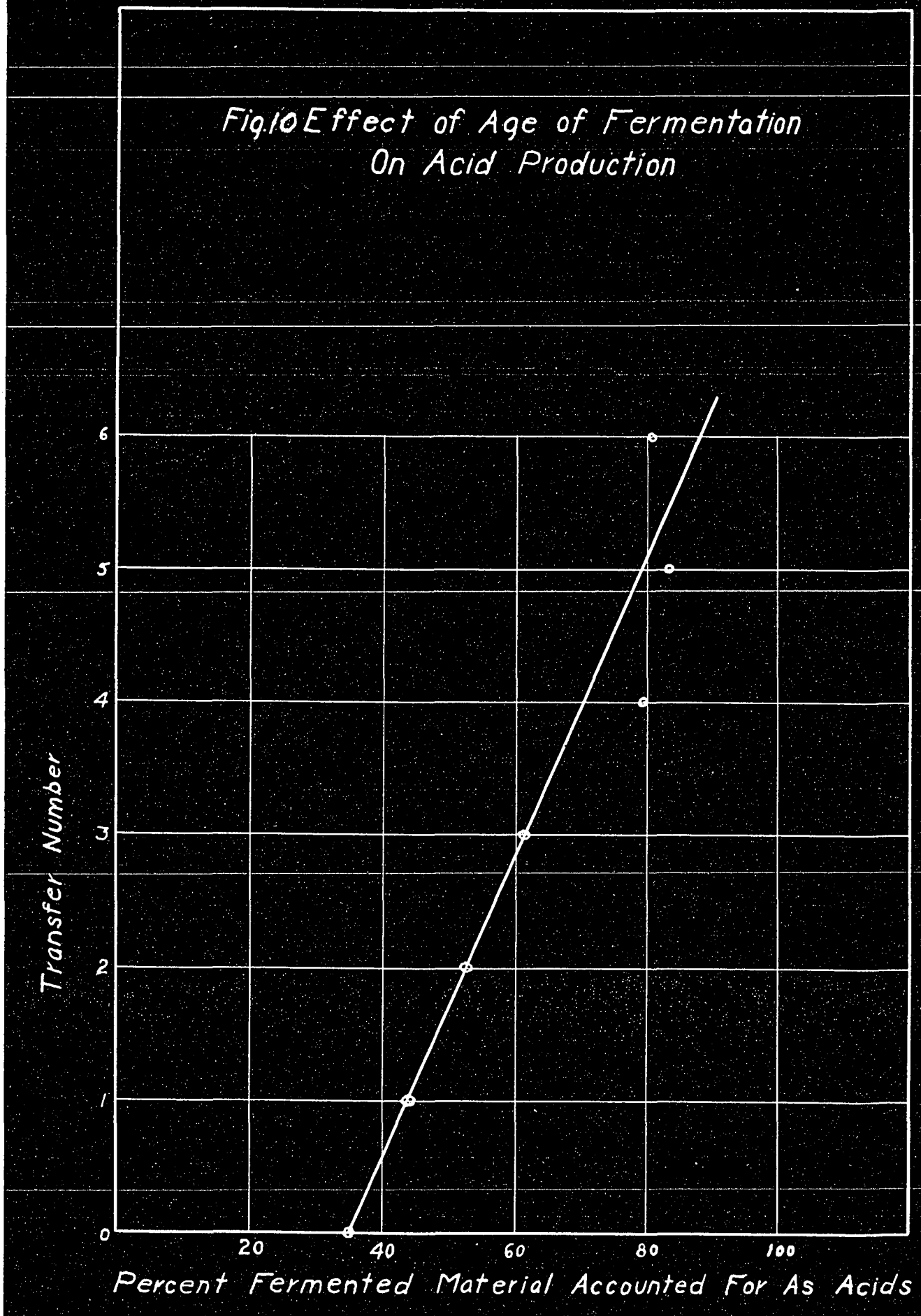


TABLE XII

Effect of Degree of Subdivision on Fermentation

Material Fermented	Dry weight material used in gms.	Duration of fermentation in days	Total Vol. in KOH used to Neutralize acid produced	gms. acid produced calculated as acetic	Material unfermented in gms.	Material fermented in gms.	Per cent of fermented material accounted for as acids	Per cent original material accounted for as a
Total stalk 12 mesh	23.00	8	81	4.86	15.3	7.7	63.2	21.2
Cornstalk pith	23.45	5	130	7.8	14.1	9.35	83.4	33.2
Cornstalk fibers 12 mesh	23.35	8	60	3.6	18.15	5.20	69.3	15.4
Cornstalk fibers Collodial	23.35	6	115	6.9	14.05	9.30	74.2	29.6
Cornstalk fibers 100 mesh	23.35	5	125	7.5	13.15	10.20	73.8	32.1
Cornstalk Pentosan	24.20	5	177	9.96	9.5	14.7	68.0	41.2

TABLE XII

ct of Degree of Subdivision on Fermentation

ms. acid produced alculated s acetic	Material unfermented in gms.	Material fermented in gms.	Per cent of fermented material accounted for as acids	Per cent of original material accounted for as acids	Analysis of Acid Distillate		Analysis of Residue		
					Formic Acid in %	Acetic Acid in %	Lignin cold 72% H_2SO_4 method in %	Lignin R.T. 72 % H_2SO_4 method in %	Pento in %
4.86	15.3	7.7	63.2	21.2	14.0	86.0	23.56	26.5	20.
7.8	14.1	9.35	83.4	33.2	14.2	85.8	22.2	31.3	10.
3.6	18.15	5.20	69.3	15.4	13.7	86.3	24.7	32.1	21.
6.9	14.05	9.30	74.2	29.6	14.1	85.9	25.1	30.3	15.
7.5	13.15	10.20	73.8	32.1	14.0	86.0	27.4	30.9	11.
9.96	9.5	14.7	68.0	41.2	12.2	87.8	4.7	----	86.

cent of iginal terial counted as acids	Analysis of Acid Distillate		Analysis of Residue			Analysis of original material		
	Formic Acid in %	Acetic Acid in %	Lignin cold 72% H_2SO_4 method in %	Lignin R.T. 72 % H_2SO_4 method in %	Pentosan in %	Lignin cold 72% H SO method in %	Lignin cold 72% H SO method in %	Pentosan in %
21.2	14.0	86.0	23.56	26.5	20.45	23.7	34.3	27.6
33.2	14.2	85.8	22.2	31.3	10.3	20.2	32.0	27.7
15.4	13.7	86.3	24.7	32.1	21.6	23.7	34.2	26.3
29.6	14.1	85.9	25.1	30.3	15.4	23.7	34.2	26.3
32.1	14.0	86.0	27.4	30.9	11.3	23.7	34.2	26.3
41.2	12.2	87.8	4.7	----	86.1	2.25	----	88.0

The results of attempted complete fermentation of the cornstalk tissue are shown in Table XIII and Fig. XI. In this part of the investigation the material used consisted of mechanically separated cornstalk pith only. After the first fermentation the small fibers which had gone through the separator appeared in much greater prominence than before. After the second fermentation the pith cells were in the minority and in order to get the fermentation to proceed with any degree of rapidity the third time it was necessary to grind the fibrous residue.

DISCUSSION OF RESULTS

From TableXIand Fig.X it is seen that the amount of acid produced from a given amount of fermented material is greatly increased as the culture becomes older. Also the time of fermentation is decreased by about half. These results might possibly be explained, according to the work of Coolhaas[1], by the fact that in the original inoculum there are present, bacteria which cause a methane fermentation of acetic and formic acid salts. These bacteria would tend to destroy these acids and therefore cut down the yield of acids and also increase the time of fermentation, for it is quite apparent that the fermentation does not cease until the concentration of salts reach a certain limit or the available food supply is used up.

1. Coolhaas, Centr. Bakt. Parasitenk II Abt., 76, 38, (1928)

Fig. 11 Amount of Cornstalk Fermented by Repeated Fermentations

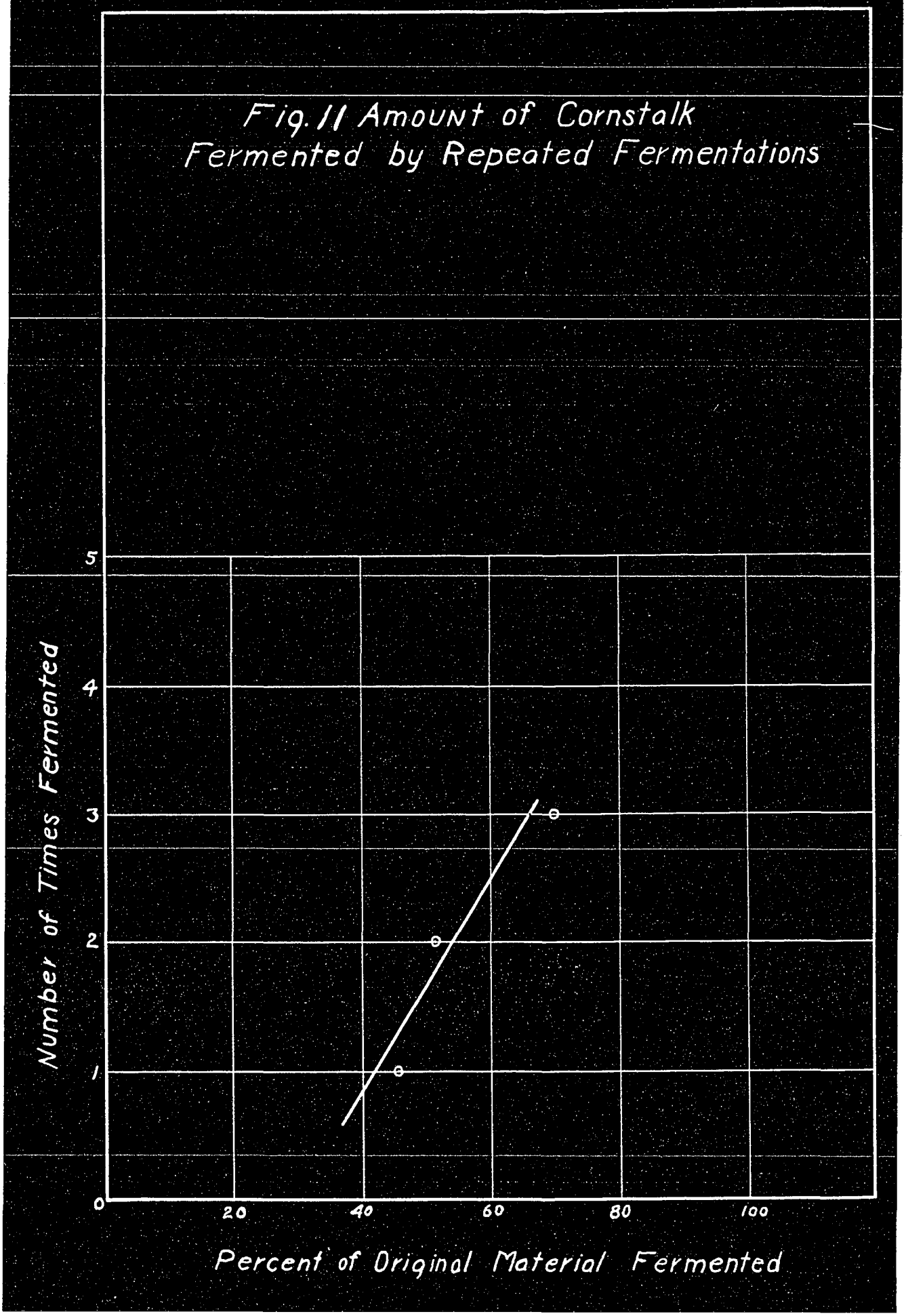


TABLE XIII

Attempts to Completely Ferment Cornstalks Material

No. of times Fermented:	Dry weight material used in gms:	Duration of fermentation in days	Total Vol. in KOH used to Neutralize: acid produced	gms. acid produced calculated: as acetic	Material unfermented in gms.	Material fermented in gms.:	Per cent of fermented material accounted for as acids:	Per ce origi mater accou for as
Original tissue								
1	46.9	5	265	15.9	26.9	20.0	79.5	33.9
2	26.9	5	43	2.6	21.0	5.9	44.1	9.6
3	21.0	5	75	4.5	15.0	6.0	75.0	21.4
1	23.45	5	100	6.0	16.0	7.45	80.5	25.6
2	16.0	5	140	8.4	5.7	10.3	81.5	52.5

TABLE XIII

mpletely Ferment Cornstalks Material

Material unfermented in gms.	Material fermented in gms.	Per cent of fermented material accounted for as acids	Per cent of original material accounted for as acids	Per cent of original material fermented	Analysis of Acid Distillate		Analysis of Residue	
					Formic Acid in %	Acetic Acid in %	Lignin Cold 72% SO Method in %	Pentosan in %
							20.2	27.7
26.9	20.0	79.5	33.9	42.7	13.8	86.2	24.2	15.7
21.0	5.9	44.1	9.6	55.2	12.1	87.9	26.8	13.1
15.0	6.0	75.0	21.4	68.1	14.4	85.6	33.2	10.8
16.0	7.45	80.5	25.6	31.7	14.1	85.9	18.03	10.53
5.7	10.3	81.5	52.5	75.6	13.7	86.3	38.25	11.57

The data would indicate that the methane producing organisms were lost between the third and fourth transfer. This is in harmony with Coolhaas[1] results which indicate that the methane producer is destroyed at about this period. He explains the destruction of the methane producing organism as due to overgrowth by the hydrogen producing organisms.

The percentage of acid produced from a given amount of fermented material reaches a maximum of about 80 per cent after the fourth transfer and continues constant thereafter. This is somewhat of a contradiction to the work of Fred, Peterson and Viljoen[2] which indicates that the fermentation becomes less active with age. The percentage of formic acid in the acid distillate increases with the number of transfers up to the fourth in which it reaches a maximum of about 14 per cent and remains approximately constant thereafter.

The data of TableXIIIindicate that as the degree of subdivision is increased, the amount of acid produced and the rate of fermentation is increased. This is in harmony with the results of Fowler and Ganski[3] which indicate that, in the production of gases from cellulosic material, the finer the material, the more rapid the fermentation. This is probably due entirely to a surface phenomenon, that is, the greater exposed surface the greater

1. Coolhaas, Centr. Bakt. Parasitenk II Abt. 76, 38. (1928)
2. Fred, Peterson and Viljoen, J. Agri. Sci., 16, 1. (1926)
3. Fowler and Ganski, J. Indian Inst. Sci., 3, Pt.4, 39, (1920)
   See Chem. Abt. 15, 2780 (1921)

the activity of the fermentation.

This table also indicates that of the three materials, the pith, the fiber and the total stalk of the cornstalk, the pith material is most rapidly fermented, the total stalk next and the fiber most slowly of all. The reason for this is undoubtedly due to the light and porous nature of the pith with the accompanying large surface exposure in comparison to the fibers. After the fermentation of the total stalk it is rather difficult to distinguish the pith cells while the fibrous cells are present in a seemingly undiminished quantity. If this was true, the thermophilic fermentation would be a very good means of separating the pith from the fibers of the cornstalk. This is somewhat in harmony with the results obtained by Buswell[1] during the fermentation of the cornstalk at lower temperatures.

It is also shown by this table that cornstalk pentosan is very rapidly attacked by the thermophilic organism.

Table XIII and Fig XI indicate that cornstalk material may be fermented completely or practically so. The only requisite is the removal of the salts, so that the concentration does not become too high and the disintegration of the material to be fermented to such a degree that a relatively large surface is exposed.

From the data on the analysis of residue of each Table, it may be seen that the composition of the material left after fermentation, except in two cases in Table XIII, is not materially changed from the original tissue in regard to lignin content.

1. Buruff and Buswell, Ind. Eng. Chem. 21, 1181, (1929)

This would certainly indicate that the lignin has been used in the fermentation or has been changed to a soluble material. In the two cases to Table XIII where the lignin content rise considerably above the normal, it need only be remembered that in one case 68.1 per cent of the original material has been decomposed while in the other, 75.6 per cent has been decomposed. Therefore if no lignin had been fermented, the lignin values should be 63.4 per cent and 82.8 per cent respectively, which are much higher than the values found. This is in harmony with the results reported by Waksman[1] in his work on plant decomposition in the soil, which indicate that although lignin is somewhat more resistant to fermentation than the cellulose and pentosam bodies, its resistance to fermentation is only relative.

As would be expected from the results of the investigation with cornstalk pentosan as shown in Table VI, the pentosan material in the stalk is very rapidly fermented, but tends to reach a constant minimum value. This result is in harmony with that of Waksman[1].

SUMMARY

A process is described in which acetic and formic acids may be produced commercially from agricultural wastes by the use of thermophilic organisms.

It is indicated that the fermentation proceeds more rapidly and more completely when the material to be fermented is finely ground.

1. Tenney and Waksman, Soil Sci., 28, 55, (1929)

It is also indicated that agricultural waste materials may be completely fermented if the fermentation products are removed before the concentration becomes too great.

It is pointed out that during the fermentation of cornstalk material by the thermophilic organism the lignin is fermented or at least decomposed in some manner.