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Agricultural Residue Pulps—Bleaching Studies on Straw Pulps*

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Abstract

1. The present status of the industrial utilization of agricultural residue fibers is discussed briefly.

2. Wheat, oat, rice, barley, and rye straws, flax shives and soybean stalks were analyzed and cooked with sodium hydroxide to yield pulps of varying lignin content, which then were bleached by the single-stage and three-stage processes.

3. The lignin contents, permanganate numbers, and Roe chlorine numbers were determined for the various pulps, and the interrelationships between these characteristics and bleach consumption at a brightness (Hunter reflectometer) of 70% were studied.

4. The data obtained show, in general, that these agricultural residues classify themselves into two groups, with the cereal straws in one group and the flax shives and soybean stalks in the other.

5. Straight-line relationships were obtained for lignin with permanganate number and with Roe chlorine number, and, from these in turn, between permanganate and Roe numbers. Direct relationships were also found for bleach consumption with lignin, with permanganate number, and with Roe chlorine number.

6. Rice straw pulp consumes less chlorine than the other pulps bleached to the same brightness, possibly due to the high silicious ash content of this pulp.

7. Economy in chlorine results when three-stage instead of single-stage bleaching is used, but this is partly offset by the higher loss in pulp substance with the three-stage process.

8. To avoid excessive degradation of alpha-cellulose, single-stage bleaching may be used to obtain pulps with brightness up to 70%, but three-stage bleaching should be used beyond that point.

Economic rather than technological factors have been mainly responsible for the fact that fibrous agricultural residues, such as cereal straws, sugar cane bagasse, cornstalks, etc., have found only very limited use in the commercial manufacture of pulp and paper.

Only in recent years have agricultural residues been used on a large commercial scale as a source for paper pulps in countries poor in forest resources. The Pomilio process has been operated for several years in Italy *(10)*, and more recently, plants using this process for making a wide variety of papers have been built and are operating in South Africa *(11)*, in Chile *(12)*, and in Argentina *(13)*. A pilot plant was using this process in 1941 in the Philippines *(15)*. The Japanese are said to use bagasse for paper manufacture in Formosa *(8)*, and the Dutch in Java were using rice straw *(14)*.

In Europe today, with the exception of the Scandinavian countries, agricultural residues serve to quite an extent to supplement wood as a source for paper and for dissolving pulps. England, particularly, has given considerable attention to the conversion of mills to use cereal straw; partly in an effort to replace esparto and wood pulp, and partly to produce a variety of needed papers *(9)*.

No one can foresee how much further such economic changes may go either during the war or afterwards. It appears that this country is not likely to face any such situation in cellulose supply in the near future as do the European countries and most other world nations, but many shortages have been found unexpectedly in prosecution of the war.

It is certain that the whole world is in a period of rapid and extensive economic change, and that to realize a world peace many of our present ideas and customs require modification. Any lasting basis for peace must take into account a much sounder economic structure for the farmer since food and fiber are necessities of life. Such an agricultural economy will require the utmost dollar return to the farmer for the fruits of his soil and labor. Agricultural residues represent more than one half the annual growth on cultivated lands the world over. While a goodly share of such residues should be returned to the soil, there are many reasons why millions of tons of these wastes, which bring no money value to agriculture, should find industrial utilization. This is a world-wide problem; much effort has been expended on it with but meager results.

In the United States it is estimated that one hundred million tons of such residues are annually available for use by industry *(2, 18)*, but only a little more than 1.25 million tons find use today. Of this amount, three industrial uses account for approximately 1 million tons—e.g., wheat and rye straw for manufacture of corrugating box board, seed flax straw for the manufacture of cigarette paper, and sugarcane bagasse and cornstalks for the manufacture of insulating building material. The products so manufactured are outstanding in their respective fields.

The problem of developing commercial uses for agricultural residues in the United States and possessions was assigned to the Northern Regional Research Laboratory, one of the four such regional laboratories established by Congress and put into operation by the United States Department of Agriculture early in 1941. This problem is being attacked on four fronts: (a) Improvement in the economic factors of collection, transportation, and preservation of these residues, including surveys relating to production, location, and accessibility to industry *(3, 7)*; (b) methods of utilizing the cellulosic constituents of the residues;

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The Northern Regional Research Laboratory is one of four regional laboratories authorized by Congress in the Agricultural Adjustment Act of 1938 for the purpose of conducting research to develop new uses and outlets for agricultural commodities. These laboratories are operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

(c) methods of using the hemicellulose fractions; and (d) methods of using lignin and lignin residues.

Two guiding principles are recognized—first, every process considered must, if possible, secure some money return from each major constituent, e.g., cellulose, hemicellulose, and lignin; and, second, the main product of a commercial process must fill the use requirement better than competitive products.

More study has been given to the use of the cellulosic constituents of agricultural residues than to that of the other components. The patent and technical literature abound with processes and experiments on cellulose production from such sources. Most of these are fragmentary and, in general, the effort has been to develop a paper or dissolving pulp as a substitute for a product prepared from wood. On the other hand, the outstanding commercial products made from the residues mentioned above have for many years been able to compete satisfactorily with substitutes made from wood. Success, therefore, logically falls to the raw material which can produce a superior product. It has long been known that cellulose fibers resulting from the pulping of straws, stalks, bagasse, etc., possessed properties differing from those of wood fibers, and these differences have for the most part been considered detrimental for pulp and paper.

No exhaustive study of the properties of cellulosic fibers from agricultural residues has been made to the end of finding in what respects such fibers may be superior to wood fibers. As a result of extensive developments in the field of paper specialties and of the slowly accepted technique by the paper mill operator of the blending of fibers to produce such special products, a wide field is open for fibers with special properties.

An exhaustive study of agricultural residue fibers as related to industrial uses is under way at this Laboratory.

The first work in this program arose with the war emergency. It was anticipated that pulps made from cereal straws might produce needed properties not completely supplied by pulps made from wood. This goal was realized.

In preparing purified pulps from cereal straws for these special purposes, it was found that a drastic loss in yield occurred in the bleaching and alkaline refining steps. The bleachabilities of these pulps, to the desired brightness determined by the usual jar method, showed that the procedures used for wood pulps could not be applied directly to the cereal straw pulps without some modification. This is also indicated by other recent work *(16, 17)*. A program was initiated to obtain the correlations between bleaching and some of the methods for determining the bleachability of agricultural residue pulps.

Preparation and Analyses of Raw Materials

The materials used in this study were: wheat, oat, rice, barley, and rye straws, flax shives, and soybean stalks. Pulps from some of these straws were on hand from previous work, and the remainder were obtained by cooking with various amounts of caustic soda to yield products with different lignin contents.

The various straws and other raw materials were shredded in an ensilage cutter or in a hammer-mill type shredder and then screened to remove dust and fines. With wheat and rice straws the screening and removal of hulls, weeds, and seeds were carried out by hand on a stationary 4-mesh screen, while a mechanical vibrating screen (4-mesh) was used for the others. The major portion of the cut or shredded cereal straws used for cooking varied from ½ inch to about 3 inches in length. All of the flax shives retained on a 40-mesh screen, and the soybean stalks remaining on a 10-mesh screen, were saved for the experiments. The description of the raw materials and the screening data are given in Table I. Variations in yields of screened materials are due partly to the type of material itself, and partly to the nonuniformity of the methods of shredding and screening used.

The screened raw materials, ground in a Wiley-type mill to pass a 3-mm. screen, were analyzed for

TABLE I.—RAW MATERIALS, SCREENING, AND PREPARATION
(All data based on original air-dry raw material)

Material	Source and Condition	Treatment	Original Weight, lb.	Retained on Screen, %	Through Screen, %	Dust and Fines Recovered, %	Loss, %
Rice straw	Crop year 1941, Louisiana; dry and bright; considerable adhered dirt; quite leafy and free from weeds.	Shredded in ensilage cutter; hulls and weeds removed by hand; screened on ¼" stationary screen.	130	82.1	16.2	..	1.7
Barley straw (Ezond)	Crop year 1942, Nebraska; dry and bright; free from weeds; high chaff content, quite leafy; baled from stack.	Shredded in hammer mill; screened on ¼" vibrating screen.	773	74.3	25.9	0.3	+0.5*
Wheat straw (Russian)	Crop year 1941, Illinois; dry, slightly weathered; quite free from weeds; considerable chaff and leaves.	Shredded in ensilage cutter; hulls and weeds removed by hand; screened on ¼" stationary screen.	57	60.2	33.9	..	5.9
Rye straw	Crop year 1939, Iowa; dry, slightly weathered; quite free from weeds; considerable chaff and leaves; baled from stack.	Shredded in hammer mill; screened on ¼" vibrating screen.	99	59.3	37.9	1.0	1.8
Oat straw	Crop year 1939, Iowa; dry, bright; quite free from weeds; considerable chaff and leaves; baled from stack.	Shredded in hammer mill; screened on ¼" vibrating screen.	109	63.1	35.6	0.9	0.4
Flax shives	Crop year 1941, Minnesota; dry, slightly weathered; 6.6% fines and dirt, 5.4% tow.	Shredded in hammer mill; screened on 40-mesh vibrating screen.	89	89.6	7.9	1.7	0.8
Soybean stalks (Chief)	Crop year 1942, Illinois; dry, slightly weathered; 5.2% leaf blades and petioles, 10% pods, 5.4% beans, 2.9% weeds; baled from windrow immediately after combining.	Shredded in hammer mill; screened on 10-mesh vibrating screen.	125	61.2	37.0	1.8	0.6

* Plus value probably due to increase in moisture content during shredding and screening operations.

the following: ash, cold water extractives, hot water extractives, 1% NaOH extractives, benzene-alcohol extractives, lignin, pentosans, Cross and Bevan (C&B) cellulose, pentosans in C&B cellulose, chlorine consumption in C&B cellulose determination, alpha-cellulose, and nitrogen. The official TAPPI methods and those recommended for wood by the Forest Products Laboratory *(1)* were used whenever possible, but some of the methods required modification for use with these agricultural residue materials. The data are given in Table II.

TABLE II.—RAW MATERIALS—PROXIMATE ANALYSIS
(All values except moisture are on basis of moisture-free material)

Constituent	Material						
	Rice Straw	Barley Straw	Wheat Straw	Rye Straw	Oat Straw	Flax Shives	Soy-bean Stalks
Moisture, %	8.0	8.4	6.6	7.4	7.0	8.1	8.3
Ash, %	16.1	6.4	6.6	4.3	7.2	3.5	2.3
Extractives							
Alcohol-benzene, %	4.6	4.7	3.7	3.2	4.4	4.1	3.9
Cold water, %	10.6	16.0	5.8	8.4	13.2	9.7	7.3
Hot water, %	13.3	16.1	7.4	9.4	15.3	11.4	8.8
1% NaOH, %	49.1	47.0	41.0	37.4	41.8	32.0	32.0
Nitrogen, %	0.58	1.10	0.38	0.72	0.46	0.69	0.66
Lignin, %	11.9	14.5	16.7	19.0	17.5	22.3	19.8
Pentosans, %	24.5	24.7	28.2	30.5	27.1	23.6	24.8
Cross and Bevan Cellulose							
Crude, %	49.8	48.2	54.4	54.9	53.6	48.4	50.1
Ash free, %	48.6	47.4	53.6	54.3	53.4	46.2	48.2
Chlorine consumption, %	14.8	15.6	13.9	14.6	14.4	12.4	10.3
Pentosans, %	27.8	30.0	26.8	29.5	28.4	21.6	22.1
Alpha-Cellulose							
In Cross and Bevan cellulose, %	72.7	70.1	73.3	68.5	73.4	72.1	68.7
Basis o.d. straw, %	36.2	33.8	39.9	37.6	39.4	34.9	34.5

Preparation and Analyses of Pulps

A. Cooking

The digestion equipment consisted of steam-jacketed cylindrical, 12-gallon, stainless steel autoclaves, equipped with transmission for tumbling. The bottoms of the autoclaves are conical and are fitted with quick-opening gate valves for "blowing" the digester charge.

Approximately 10 pounds of the air-dry screened straw or stalks were placed in the autoclave and enough alkaline liquor was added to make the ratio of total water to moisture-free material, 8:1. The amount of caustic soda was varied from 9 to 24% on the basis of the moisture-free material. The period of cooking was 2 hours at approximately 100 p.s.i. (165°-170°C.) with approximately 30 minutes to attain the cooking temperature and 10 to 20 minutes to reduce the pressure to about 35 to 40 p.s.i., when the contents were "blown" into a wooden blowpit fitted with a perforated stainless steel false bottom. The pulp was washed in this blowpit by alternate filling with water and draining, the drain liquor passing through a muslin bag to retain any pulp forced through the perforations in the false bottom. When the wash water appeared colorless, the pulp was squeezed in a canvas bag and sampled to determine the overall yield.

B. Screening

The pressed pulp was suspended in water and screened in a laboratory flat screen with 0.004-inch (4-cut) slit openings. The screened pulp was allowed to go over a 100-mesh inclined wire, and the material passing through this wire was collected in a heavy muslin bag and labeled "fines." (A portion of the fines, varying somewhat with the type of material and degree of pulping, was lost through the muslin.) The material remaining on the flat screen was circulated in a small laboratory beater (with sufficient clearance between the roll and bedplate to prevent cutting or extensive beating), to break up some of the cooked fiber bundles not separated by "blowing," and then was rescreened. This additional screened pulp was added to the main portion of the pulp, and the residue on the screen was dried and labeled "screenings."

The screened pulp was pressed, air dried, and sampled for moisture content to obtain yield data.

C. Analyses

The following analyses were made on the screened pulp:

1. *Lignin Content:* The air-dried screened pulp was ground in a Wiley-type cutting mill to pass a screen with openings 1 mm. in diameter and sampled for moisture. Approximately 2 grams of the ground material were weighed accurately and cooled to 15°C. Then 20 ml. of 72% sulphuric acid (15°C.) per gram of the ground material were added, and the mixture stirred thoroughly till fluid, covered, and left in the refrigerator for a total period of 16 hours. Then the solution was diluted to a 3% acid concentration and boiled actively for 4 hours, keeping the volume constant by the occasional addition of distilled water. After standing on a warm plate for a short period, to allow the lignin to coagulate and settle, the solution was filtered in a tared Gooch crucible containing a pad of washed asbestos. After washing in the crucible, the contents were dried, weighed, and ashed in a muffle furnace at 800°C. The lignin content was reported on an ash-free basis.

2. *Permanganate Number:* This value was determined on the ground pulp in accordance with TAPPI Standard T 214 m-37.

3. *Roe Chlorine Number:* A modification of the Roe *(6)* method was used. It was found necessary to increase the moisture content of the sample from the 55% recommended for wood pulp to 75 to 80%, in order to obtain maximum action of the chlorine in the prescribed 15-minute period. The apparatus used was that described by Bray *(1)* for C&B cellulose, employing a sintered glass crucible. The chlorine gas was passed back and forth through the sample for the whole period. A further modification was the addition of about 5 grams of chlorinated, washed sand to the sample, which was found necessary to reduce packing of the wet pulp and to facilitate passage of the gas through the sample, and thus to result in more uniform chlorination.

4. *Ash Content:* The samples were ashed in a muffle furnace at approximately 800°C.

5. *Single-Stage Bleaching:* The pulps were bleached with calcium hypochlorite, using 3, 6, and 9% available chlorine on the basis of the pulp, and the bleaching periods were 1, 2, and 3 hours at 35° to 40°C. The pulp consistency during bleaching was 3%. The strong hypochlorite solutions prepared contained approximately 20 grams available chlorine and 0.1 gram chlorate chlorine per liter.

Ten grams (moisture-free basis) of the pulp were defibered in a small amount of distilled water and placed in a 1-quart jar. Then the required amount of calcium hypochlorite solution, calcium hydroxide solution, and sufficient water to make a 3% pulp suspension at pH 9+ were added. The jar was covered loosely and placed in a water bath at 35° to

40°C. The samples were agitated occasionally and tested with starch-KI test papers. When the chlorine was exhausted or at the end of the period, whichever came first, the contents of the jar were filtered on a Buchner funnel and washed with small amounts of warm distilled water (35°-40°C.) until the washings were neutral to litmus paper. When the chlorine was not exhausted at the end of the bleaching period, the filtrate and washings were combined and analyzed for residual available chlorine. The bleached pulp was treated with dilute hydrochloric acid (5% HCl, basis pulp) for 5 minutes at room temperature, and then filtered, washed free from Cl ion, and made into handsheets, for brightness tests, on a British sheet machine, using fresh blotting paper for each sheet. An aliquot of the sample was filtered, dried, and weighed to determine loss of pulp in bleaching.

6. *Three-Stage Bleaching:* The three stages consisted of (a) treatment with 60% of the total chlorine as chlorine water for 15, 30, and 60 minutes at 20° to 25°C.; (b) heating the residue with 2% sodium hydroxide (basis unbleached pulp) for 1 hour at 50°C.; and (c) treatment of the residue from (b) with the remaining chlorine as calcium hypochlorite for 1, 2, and 3 hours at 35° to 40° C. The pulp consistency was kept at 3% throughout these treatments, and the total chlorine added to the samples amounted to 3, 6, and 9% on the basis of moisture-free unbleached pulp. In a few instances larger amounts of chlorine were necessary.

(a) Ten grams (moisture-free basis) of the unbleached pulp were defibered in a small amount ot distilled water and placed in a 1-quart jar. The calculated amount of chlorine water and sufficient distilled water were added to make a pulp consistency of 3%, and the jar and contents were kept at 20° to 25° C. for the required period, testing frequently with starch-KI test paper. When the chlorine was exhausted or at the end of the period, whichever came first, the jar contents were filtered on a Buchner funnel and washed with small amounts of cold distilled water until the washings had no effect on the starch-KI test paper. The filtrate and washings were combined and analyzed for available chlorine.

(b) The washed residue from (a) was suspended in distilled water, sufficient alkali was added to equal 2% on the basis of the dry unbleached pulp, and the mixture was diluted with distilled water at 50°C. to a 3% consistency, held at this temperature for 1 hour, with occasional stirring, filtered on a Buchner funnel, and washed with distilled water at 50°C. until the wash water was neutral to litmus paper.

(c) The pulp from (b) was treated as in single-stage bleaching with the remaining chlorine as calcium hypochlorite, and the bleached pulp was made into handsheets on a British sheet machine.

7. *Brightness:* The brightness, or percentage reflectance through a blue filter, was determined on the bleached handsheets with a Hunter factory-control reflectometer. This instrument is a simplified modification of the multipurpose reflectometer (*4*).

8. *Alpha-Cellulose:* The alpha-cellulose contents of the bleached and unbleached pulps were determined in accordance with TAPPI Standard T 203 m-40.

TABLE III.—YIELDS, CHARACTERISTICS AND BLEACHABILITIES OF AGRICULTURAL RESIDUE PULPS

Cook number	Material	NaOH used for cooking[1] %	Yields[1]: Crude pulp %	Yields[1]: Screened pulp %	Yields[1]: Screenings %	Pulp Characteristics[2]: Ash %	Pulp Characteristics[2]: Lignin %	Pulp Characteristics[2]: Permanganate number	Pulp Characteristics[2]: Roe chlorine number	Bleached Pulp—70% Brightness (Hunter Reflectometer), Single-Stage: Chlorine consumption[2] %	Single-Stage: Pulp loss in bleaching[2] %	Three-Stage: Chlorine consumption[2] %	Three-Stage: Pulp loss in bleaching[2] %
17	Rice straw	9	52.4*	35.6	6.5	16.1	6.9	21.4	3.8	14.0	14.0	8.1	18.4
14, 15, 16, 18, 20, 22	Rice straw	12	48.2*	35.7	2.2	15.8	3.5	10.6	2.3	4.9	10.8	3.0	10.2
12	Rice straw	18	43.0*	33.9	0.7	7.1	2.7	7.0	2.1	3.6	7.2	2.7	8.6
11	Rice straw	24	38.8*	30.1	0.2	6.4	2.2	6.5	2.0	3.5	10.7	2.6	10.8
30	Wbeat straw...	9	55.4*	30.8	18.6	5.8	8.5	29.3	7.6	21.1	13.0	16.0	8.4
31	Wheat straw...	12	53.8*	34.5	11.0	2.9	5.1	17.7	4.5	12.1	7.0	8.8	7.6
27	Wheat straw...	18	46.4*	38.2	1.6	2.6	2.2	8.9	1.7	6.0	6.2	3.5	12.8
32	Wheat straw...	24	44.5*	37.5	0.6	2.0	1.4	7.9	1.0	3.5	4.7	2.8	4.2
85	Barley straw...	9	51.4	27.7	11.0	6.6	8.3	22.5	7.4	20.9	13.6	14.8	16.6
86	Barley straw...	12	46.1	29.4	5.1	4.3	5.4	16.7	4.6	15.0	12.5	10.5	15.5
87	Barley straw...	15	44.2	31.6	1.2	3.9	4.0	12.3	3.1	10.0	15.0	6.0	17.6
88	Barley straw...	18	42.9	31.7	0.4	4.3	2.8	8.9	2.1	7.6	8.1	4.4	14.3
89	Barley straw...	24	40.7	30.9	0.1	5.5	2.1	7.9	2.0	5.6	5.1	3.6	12.2
164	Rye straw	9	56.3	29.9	12.9	2.3	7.0	24.2	6.4	17.6	7.4	10.6	9.9
161	Rye straw	12	53.1	33.6	5.8	2.8	3.8	14.7	3.1	10.1	12.1	6.0	7.8
162	Rye straw	15	52.0	36.7	1.4	2.8	2.5	10.6	1.5	6.3	9.1	4.3	7.1
163	Rye straw	24	46.8	32.7	0.8	3.4	1.8	8.7	1.2	4.6	5.6	2.9	5.3
165	Oat straw	9	52.7	40.9	2.0	2.3	6.0	17.4	5.5	15.2	7.4	8.7	8.5
172	Oat straw	12	52.4	39.1	2.7	2.7	3.9	13.1	3.4	9.7	8.4	6.1	10.2
167	Oat straw	15	51.0	40.9	0.6	3.1	2.5	9.9	1.8	6.3	4.9	3.9	6.1
168	Oat straw	18	48.0	38.6	0.6	3.4	2.0	8.1	1.6	4.1	3.5	3.1	5.2
169	Oat straw	24	44.0	35.7	0.2	3.7	1.9	7.9	1.4	3.5	3.3	2.7	4.9
170	Seed flax shives	9	69.6	8.8	48.1	4.7	14.2	28.1	10.7	...	...	...	...
171	Seed flax shives	12	64.7	7.7	47.6	4.4	10.6	25.5	8.7	...	...	...	...
173	Seed flax shives	15	55.7	8.1	39.7	5.2	8.2	25.3	7.6	...	...	20.9	20.9
174	Seed flax shives	18	54.4	9.2	36.2	4.9	7.4	22.6	6.1	27.1	12.9	14.6	19.4
175	Seed flax sbives	24	47.6	12.7	27.0	4.9	6.7	23.5	4.3	21.1	12.2	12.5	16.0
176	Seed flax shives	30	42.2	25.6	8.7	4.1	7.7	25.4	4.5	17.7	10.8	10.3	14.2
177	Seed flax shives	40	35.6	23.6	2.0	3.8	2.5	12.3	2.3	6.5	7.5	4.5	7.7
178	Soybean stalks.	9	69.8	10.7	48.3	2.4	19.0	33.0	16.5	...	...	...	...
179	Soybean stalks.	15	62.4	13.0	39.9	2.7	14.7	33.4	13.8	...	...	29.3	20.0
182	Soybean stalks.	18	57.5	15.0	33.7	3.6	10.9	26.9	8.0	30.0	15.5	17.2	17.9
180	Soybean stalks.	24	48.9	16.3	26.8	4.5	6.8	20.6	3.8	21.6	13.1	10.3	15.0
181	Soybean stalks.	30	45.7	26.6	8.8	4.0	5.1	18.3	2.5	13.8	12.1	7.8	12.5
183	Soybean stalks.	40	42.5	30.9	1.1	3.7	3.4	14.7	1.5	7.8	9.4	5.4	10.2

* Obtained by summation of screened pulp, screenings and recovered fines. Does not include fines lost in screening.
[1] Basis moisture-free raw material.
[2] Basis moisture-free screened pulp.

Results and Discussion

Raw Materials

The data in Table II show that these raw materials resolve themselves into two classes—one, including all of the cereal straws, and the other, the flax shives and soybean stalks. The cereal straws generally show higher 1% alkali solubility, pentosan, and C & B cellulose contents and lower lignin contents than the flax shives or soybean stalks. The sums of the alpha-cellulose and pentosans in the C & B cellulose of the cereal straws are practically equal to 100%. In the case of the flax shives and soybean stalks, however, these constituents add up to only 91 and 94%. With the exception of the barley straw, the cereal straws have higher alpha-cellulose contents than the flax shives or soybean stalks.

All of the C & B pulps contained 22 to 30% pentosans. This is of interest in that it shows that approximately half of the pentosan contents of these agricultural residues are resistant to the mild alternate acid and alkaline treatments involved in this method of isolation. The difference between the two classes of residues is again apparent, since nearly 60% of the flax shive and soybean straw pentosans are eliminated, as against 44 to 49% of the cereal straw pentosans.

Pulp Yields

The yields of crude pulp, screened pulp, and screenings are given in Table III. The calculated crude pulp yields from the rice and wheat straws are low because they do not take into account the considerable portion of the fines lost during screening. The total fines produced in the other cooks may be obtained by subtracting the sums of the yields of screened pulps and screenings from the yields of crude pulp.

Fair yields of usable screened pulp were obtained from the cereal straws with the lower alkali concentrations, but considerably higher concentrations of chemical were required to obtain flax and soybean pulps. The irregularity in screened pulp yields from

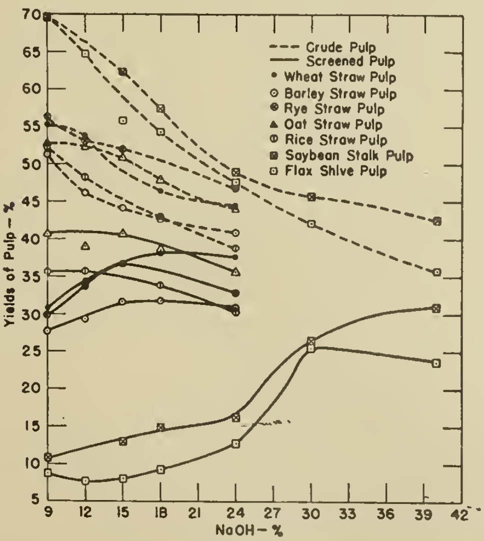

Fig. 1

Yields of Crude and Screened Pulps from Agricultural Residues Cooked with Varying Amounts of Caustic Soda

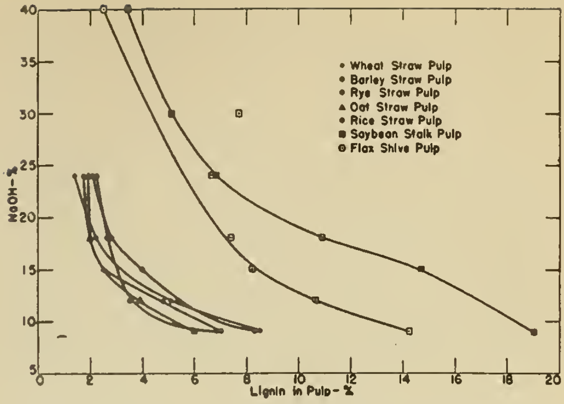

Fig. 2

Variation of Lignin Content of Agricultural Residue Pulps with Concentration of Alkali Used for Cooking

flax shives and soybean stalks is probably due to the rawness of these pulps.

The yields of screened pulp increased somewhat in the order: barley, rice, rye, wheat, and oat, in the case of the cereal straws, as shown in Fig. 1. Larger yields of screened pulp were obtained from the soybean stalks than from the flax shives under comparable cooking conditions. The amounts of screenings obtained from the flax shives and soybean stalks were practically identical for the cooks made with equal alkali concentrations. For the cereal straws the screenings increased at the lower alkali concentrations in the order: oat, rice, barley, rye, and wheat; but at the higher concentrations the screenings were all low.

The fines (obtained by subtracting the screened pulp and screenings from the crude pulp, and including the material lost through the muslin bag) averaged 11.2% for barley, 13.6% for rye, 9.4% for oat, 9.0% for flax shives, and 9.2% for soybean stalks. The figures for wheat and rice pulp fines are not included due to the fact that the fines lost through the muslin bag were not determined.

Ash in Pulps

The ash contents of the pulps, shown in Table III, varied from about 2 to 5% with the exception of the rice straw pulp. The increasing concentration of alkali used for cooking resulted in increasing ash contents of the rye, oat, barley, and soybean pulps; in practically no change in the flax shive pulp; and in decreasing ash contents of the rice and wheat pulps.

Lignin in Pulps

Lignin determinations made on the screened pulps are shown in Table III. The variations in lignin content of the screened pulps with the concentration of alkali used for cooking are shown in Fig. 2. Here, also, the agricultural residue pulps fall into two groups, cereal straw pulps and those from flax shives and soybean stalks. It is difficult to explain the lignin content of the flax shive pulp obtained by cooking with 30% caustic soda. It is possible that a large portion of the screenings from this cook was broken up in the beater to pass the 4-cut screen. This high-lignin material, added to the bulk of the screened pulp, would probably raise the lignin content of the mixture above that of the original screened pulp. It must be noted that the lignin and other determinations were checked repeatedly, particularly in cases like this where the first results obtained appeared questionable.

Bleach Consumption of Pulps

In order to compare the bleachability of the pulps with lignin and other pulp characteristics, the necessary bleach consumption for each pulp to give a brightness of 70% on the Hunter reflectometer was chosen. The data on the bleach consumptions and pulp losses for the various pulps at this brightness are given in Table III. (Individual bleaching data for three sample cooks are shown in Table VII, and will be discussed later in connection with the effect of bleaching on the alpha-cellulose contents of the pulps.)

The bleach consumption of the various pulps plotted against the lignin contents of these pulps are illustrated in Fig. 3 for single-stage and 3-stage bleaching. The linear relationship between these two characteristics is expressed by the factor, 2.51:1 as the ratio of bleach consumption to lignin content for single-stage bleaching, and of 1.66:1 for 3-stage bleaching. Most of the individual experimental values fall closely to the line expressing the average values, particularly in the region of lower lignin contents. This indicates that irrespective of the type of agricultural raw materals used in these studies, with the exception of rice straw, the bleach consumption is a direct function of the lignin content of pulps produced under similar conditions of soda pulping.

The bleach consumption-lignin ratio for rice straw pulp was considerably lower than the average ratio for the other pulps as shown in Fig. 3, varying from 54 to 81% of the average values obtained for the other pulps of similar lignin content in single-stage hypochlorite bleaching. Even greater economy of chlorine was obtained in 3-stage bleaching. This difference in the behavior of rice straw pulp in bleaching may be due to the high silicious ash content of this material. The silica content of the ash from rice straw and rice straw pulp was 60 to 90%. This relatively high amount of silica in the pulp may function similarly to sodium silicate, cited by Jeglum

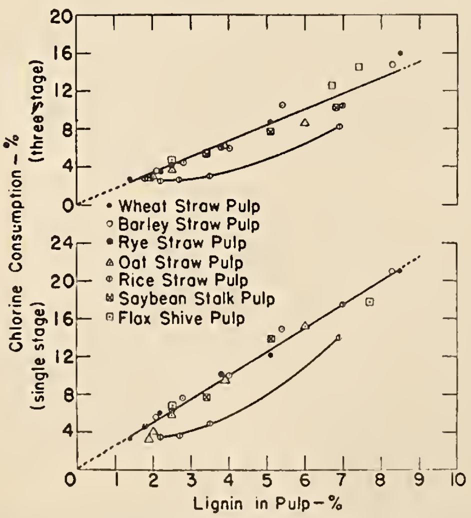

Fig. 3

Relation of Lignin Contents of Agricultural Residue Pulps to Bleach Consumption in Single- and Three-Stage Bleaching to 70% Brightness (Hunter Reflectometer)

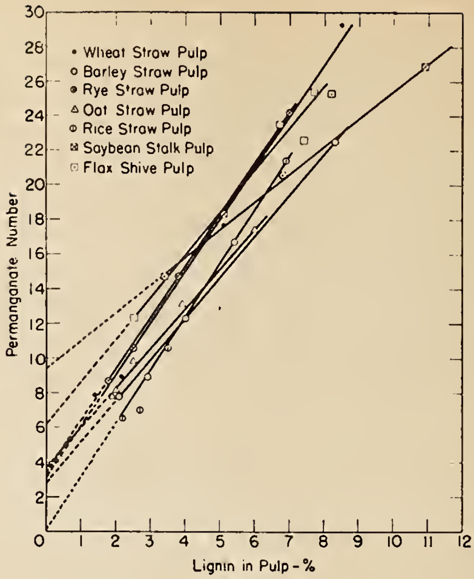

Fig. 4

Relation of Permanganate Number to Lignin Content of Various Agricultural Residue Pulps. (Note the Different Slopes of the Lines and Their Intercepts on the Vertical Axis)

(5), in reducing the chlorine consumption of the pulp.

The losses of pulp substance in bleaching to 70% brightness generally decrease with increasing degree of pulping, as shown in Table III. Some of the irregularities in these values, as indicated in Cooks 12, 27, 87, and 172, may be due to errors in sampling the small amounts of bleached pulps.

Permanganate Number of Pulps

The permanganate number of the pulps is given in Table III. These values decrease regularly with increasing concentration of chemical or degree of cooking, except in the case of the flax shive pulps. With the latter material there is no such correlation until 30% caustic soda was used for pulping.

The relationship of the permanganate number with lignin and with bleach consumption of the various pulps is illustrated in Figs. 4 and 5. The relationship between lignin and permanganate number is rectilinear and different for each type of raw material, as indicated by the slopes of the various lines (Fig. 4). The broken lines extending from the lowest experimental values to the vertical axis intercept the latter above the zero point in all cases except rice straw pulp. The intercepts on the vertical axis for the various pulps are: rice, 0; barley, 2.8; wheat, 3.2; rye, 3.3; oat, 3.7; flax shive, 6.2; and soybean stalk, 9.4. These intercepts are measures of the permanganate demands of the various pulps in the lignin-free, or almost lignin-free, condition. Note that the cereal straw pulps, with the exception of rice straw pulp, all have intercepts in the narrow range of 2.8 to 3.7. This range also covers the permanganate values of highly purified commercial pulps of very low lignin content; for example, a commercial spruce alpha pulp had a permanganate number of 3.5 and bleached filter paper had a value of 1.9.

Here again there seems to be a distinct classification of the pulps into two groups.

The slopes of the lines plotted from experimental data in Fig. 4 may be expressed by the equation:

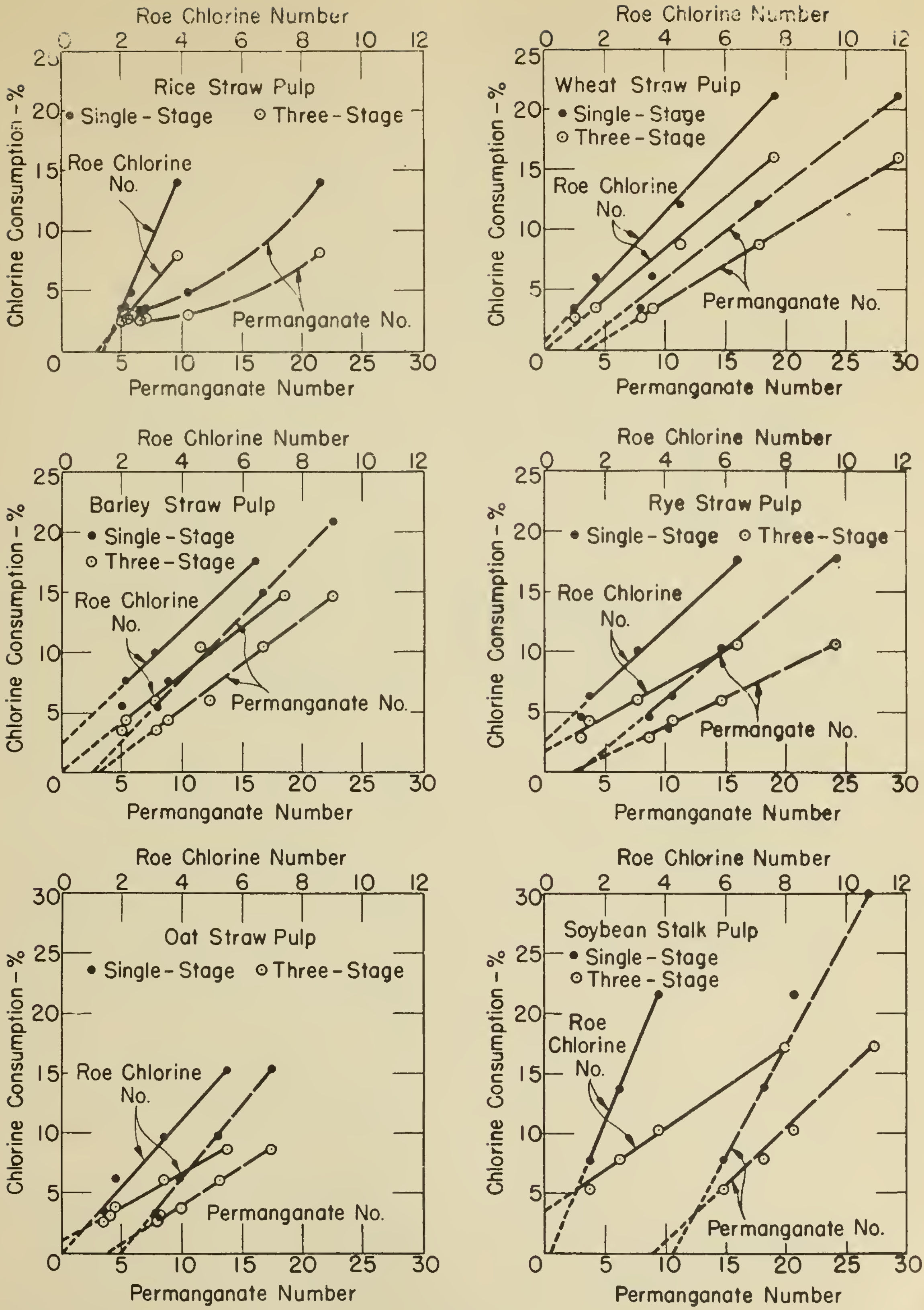

FIG. 5
Relation of Permanganate Number and Roe Chlorine Number to Bleach Consumption (Single- and Three-Stage) of Agricultural Residue Pulps Required to 70% Brightness (Hunter Reflectometer)

$S = K\text{-}I_k/L$, where S is the slope, K is the observed permanganate number, I_k is the intercept value for the particular pulp, and L is the lignin content of the pulp in percentage. The experimental values for the slopes obtained for the various pulps are: rice, 3.1; barley, 2.4; wheat, 3.0; rye, 3.0; oat, 2.3; flax shive, 2.4; and soybean stalk, 1.6. It will be noted that these slopes segregate the pulps into three groups, consisting of: rice, wheat, and rye in one; barley, oat, and flax shive in another; and soybean stalk in the third.

This equation presents some interesting possibilities. For instance, given the permanganate number of a known pulp of the above groups produced by the soda process, it may be possible to calculate its lignin content within reasonably close limits. These data applied to relatively large (10-20 pound) batches of rice and barley straw pulps, prepared and bleached in connection with another problem, gave the results shown in Table IV.

TABLE IV.—RELATIONSHIP OF PERMANGANATE NUMBER AND LIGNIN CONTENT OF PULPS

Pulp	Observed $KMnO_4$ Number	Observed Lignin Content	Calculated Lignin Content $\left(L = \frac{K - I_k}{S}\right)$
Rice	7.68	2.56	2.48
	7.51	2.67	2.42
	7.55	2.48	2.44
	7.27	2.42	2.35
	6.29	2.15	2.03
	6.85	2.38	2.21
Barley	11.96	3.49	3.81
	11.79	3.76	3.75
	11.94	3.47	3.81

The differences between the observed and calculated values for lignin are practically within the experimental error of the analytical methods used.

The relationships of the various pulps between the permanganate number and chlorine consumption (brightness 70%) are also rectilinear, with the exception of that for the rice pulp, as shown in Fig. 5. The

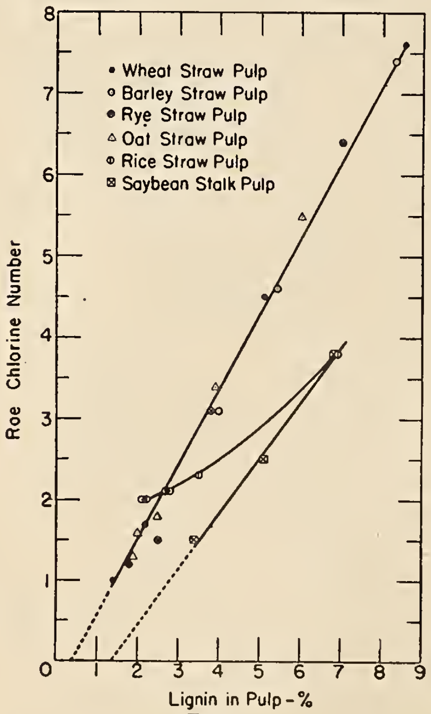

FIG. 6

Relation of Lignin Content to Roe Chlorine Number of Agricultural Residue Pulps

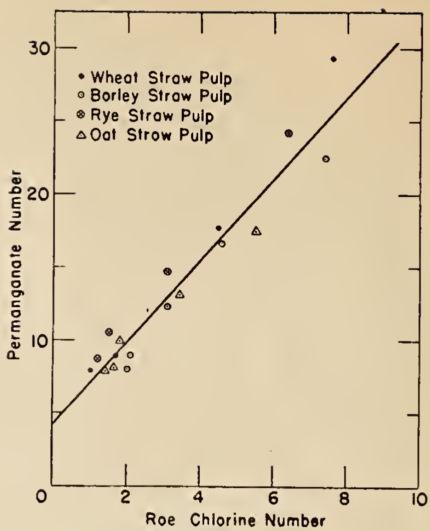

FIG. 7

Relation of Roe Chlorine Number to Permanganate Number of Agricultural Residue Pulps

data for the flax shive pulps were not included due to the relatively small quantities of uniformly cooked pulp obtained. Again, as in Fig. 3, the chlorine consumption-permanganate number relationship for rice straw pulp is definitely curvilinear, due perhaps to the high silicious ash contents of the rice pulps.

The intercepts and slopes of the lines for the other straw pulps and soybean stalks are given in Table V.

TABLE V.—RELATIONSHIP OF CHLORINE CONSUMPTION TO PERMANGANATE NUMBER ($S_1 = C/K - I_k$)

	Single-Stage Bleaching		Three-Stage Bleaching	
Pulp	Intercept on $KMnO_4$ Axis (I_k)	Ratio Cl:$KMnO_4$ No. (S_1)	Intercept on $KMnO_4$ Axis (I_k)	Ratio Cl:$KMnO_4$ No. (S_1)
Barley	2.8	1.04	3.2	0.77
Wheat	2.5	0.77	3.5	0.62
Rye	3.3	0.86	3.0	0.50
Oat	4.8	1.22	3.4	0.64
Soybean stalk	10.4	1.83	10.0	1.00

The intercepts of these lines on the permanganate axis are approximately the same as those obtained for the lignin-permanganate number relationships. However, the slopes of these lines, obtained by the equation $S = C/K\text{-}I_k$, where C is the chlorine consumption required to reach a brightness of 70%, apparently do not group themselves in the same manner as in the case of the lignin-permanganate number relationships. Examination of the data in Table V reveals the raw material individuality. The ratio of chlorine consumption to permanganate number for oat straw pulp in single-stage bleaching is nearly double that for three-stage bleaching, while in the case of wheat straw pulp this ration is only about 25% higher. The corresponding ratio increases for the other pulps are: barley, 35%; rye, 72%; and soybean, 83%.

Roe Chlorine Number of Pulps

The Roe chlorine number of the pulps is given in Table III, and the relationships of their values to the lignin contents of the pulps are shown in Fig. 6. The wheat, barley, rye, and oat pulps fall into one group; whereas the rice and soybean pulps give lines with quite different slopes. The line for all of the cereal straw pulps, except for rice, cuts the lignin axis, but so closely to the origin that the small deviation may or may not be significant. The slope of this line (ex-

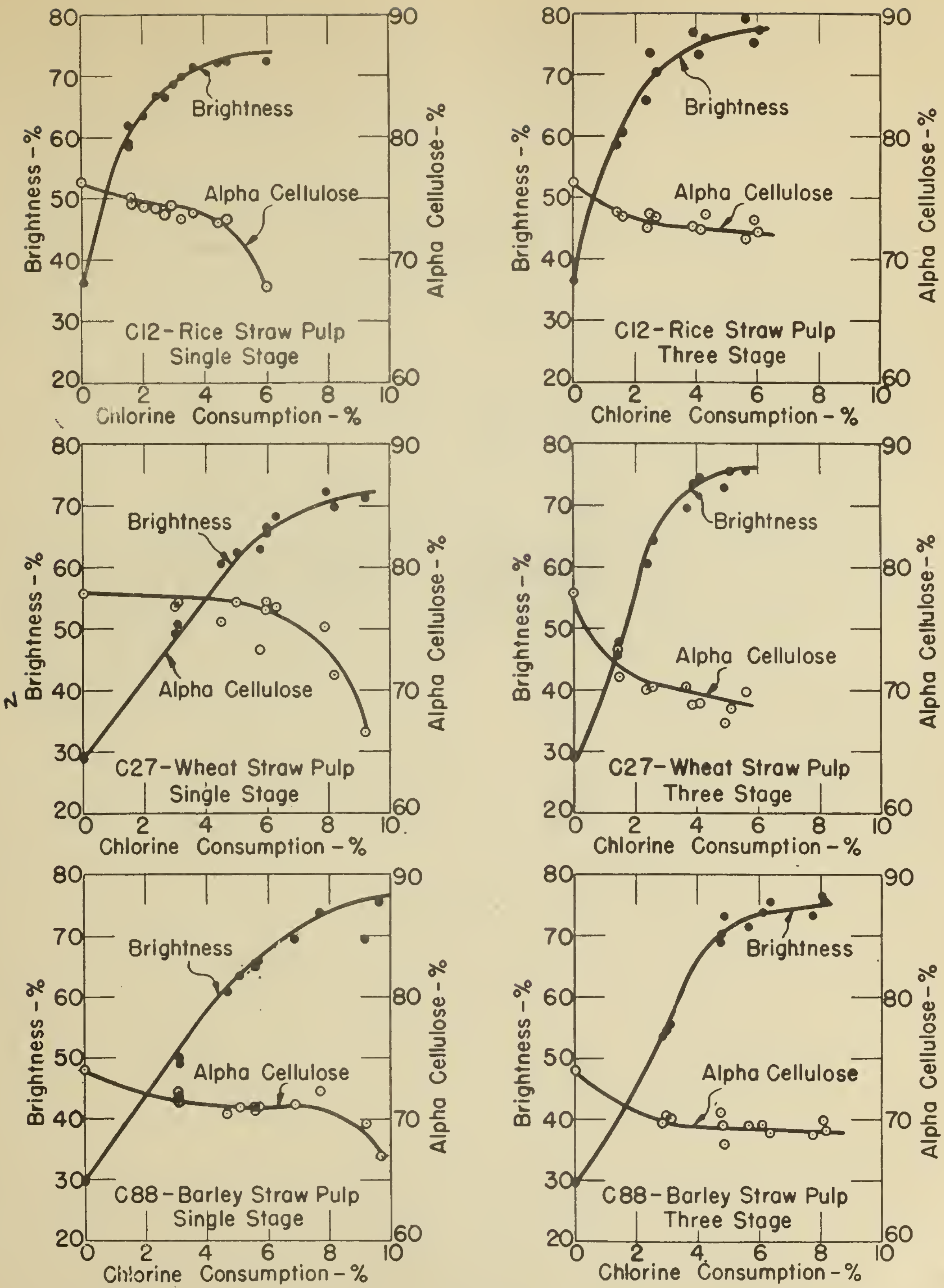

FIG. 8
Relationship of Brightness and Alpha-Cellulose Content of Bleached Pulp with Bleach Consumption in Single- and Three-Stage Bleaching

TABLE VI.—RELATIONSHIP OF CHLORINE CONSUMPTION TO ROE CHLORINE NUMBER ($S_2 = C - I_v/R - I_h$)

Pulp	Single-Stage Bleaching: Intercept on Vertical Axis (I_v)	Single-Stage Bleaching: Intercept on Horizontal Axis (I_h)	Single-Stage Bleaching: Ratio Cl Consumption to Roe Number (S_2)	Three-Stage Bleaching: Intercept on Vertical Axis (I_v)	Three-Stage Bleaching: Intercept on Horizontal Axis (I_h)	Three-Stage Bleaching: Ratio Cl Consumption to Roe Number (S_2)
Barley	1.5	..	2.6	..	..	2.0
Wheat	1.0	..	2.7	..	..	2.1
Rye	2.5	..	2.3	1.5	..	1.5
Oat	..	..	3.0	..	..	1.6
Rice	..	3.5	6.2	..	3.0	3.1
Soybean	..	0.5	6.0	2.0	...	2.2

perimental ratio, Roe chlorine number: lignin content) is 0.94, and the intercept on the lignin axis is 0.4. The lignin content of the pulp may thus be estimated directly from the Roe chlorine value by the equation: $L = R/0.94 + 0.4$, where L is the lignin content, and R is the chlorine number of the pulp. The slope of the line for soybean pulp is 0.68 and the intercept of this line with the lignin axis is 1.3.

A curvilinear relationship between the lignin content and Roe chlorine number was obtained for rice straw pulp, as shown in Fig. 6. Apparently the action of chlorine, as well as that of hypochlorite, is affected by the same factor, possibly the high silicious ash of the rice straw.

The relationship between the Roe chlorine number and chlorine consumption of the various pulps for attaining a brightness of 70% are shown in Fig. 5. In this case, some of the lines depicting these relationships cut the vertical as well as the horizontal axis. The intercepts of these lines on both axes and the slopes of the lines are given in Table VI.

These slopes may be expressed by the equation: $S_2 = C\text{-}I_v/R\text{-}I_h$, where R is the Roe chlorine number, I_v is the intercept on the vertical (chlorine consumption) axis, and I_h the intercept on the horizontal (Roe chlorine number) axis.

The Roe chlorine number may also be expressed in terms of the permanganate number and vice versa. From the Roe chlorine number-lignin relationship, the value for lignin L is expressed by the equation: $L = R/0.94 + 0.4$, where R is the Roe chlorine number. The same value from the permanganate number-lignin relationship may be derived from the equation: $L = K\text{-}I_k/S$, where K is the permanganate number, I_k the intercept on the permanganate axis, and S the slope of the permanganate number-lignin line.

$$L = \frac{R}{0.94} + 0.4 = \frac{K - I_k}{S} \quad (1)$$

$$R = 0.94\,\frac{(K - I_k)}{S} - 0.4 \quad (2)$$

$$K = S\left(\frac{R}{0.94} + 0.4\right) + I_k \quad (3)$$

Substituting arbitrary values for permanganate number K in Equation 2 for oat, wheat, rye, and barley pulps, and solving for Roe chlorine number gave average values, R, of 0.23, 2.0, 5.6, and 9.1 for the permanganate numbers of 5, 10, 20, and 30, re-

TABLE VII.—EFFECT OF SINGLE-STAGE AND THREE-STAGE BLEACHING ON LOSS OF PULP SUBSTANCE, AND ON BRIGHTNESS AND ALPHA-CELLULOSE CONTENT OF BLEACHED AGRICULTURAL RESIDUE PULPS

Material	Single-Stage Bleach: Ca (OCl)₂ Time of bleach, hr.	Single-Stage: Ca (OCl)₂ Chlorine added, %[1]	Single-Stage: Total chlorine* consumption, %	Single-Stage: Pulp loss in bleaching, %[1]	Single-Stage: Alpha-Cellulose Basis bleached pulp, %	Single-Stage: Alpha-Cellulose Basis screened pulp, %	Single-Stage: Brightness, %	Three-Stage Bleach: Chlorine Water Time of bleach, min.	Three-Stage: Chlorine Water Chlorine added, %[1]	Three-Stage: Ca (OCl)₂ Time of bleach, hr.	Three-Stage: Ca (OCl)₂ Chlorine added, %[1]	Three-Stage: Total chlorine* consumption, %	Three-Stage: Pulp loss in bleaching, %[1]	Three-Stage: Alpha-Cellulose Basis bleached pulp, %	Three-Stage: Alpha-Cellulose Basis screened pulp, %	Three-Stage: Brightness, %
Rice Straw Cook 12	.	..	..	..	...	76.3	36.5	..	..	.	..	..	...	...	76.3	36.5
	1	1.5	1.6	4.5	78.5	75.0	58.4	15	0.9	1	0.6	1.4	7.9	80.1	73.8	58.9
	2	1.5	1.6	4.7	78.4	74.6	58.3	30	0.9	2	0.6	1.6	8.0	79.9	73.5	60.6
	3	1.5	1.6	5.5	78.8	74.5	61.9	..	..	.	..	..	...	...	...	...
	1	3.0	2.0	5.9	79.1	74.4	63.8	15	1.8	1	1.2	2.4	9.2	80.1	72.7	66.0
	2	3.0	2.4	5.7	78.7	74.2	66.4	30	1.8	2	1.2	2.7	8.6	80.5	73.5	70.4
	3	3.0	2.9	5.5	78.8	74.5	68.3	60	1.8	3	1.2	2.5	8.9	80.9	73.7	73.7
	1	6.0	2.7	6.4	78.7	73.7	66.8	15	3.6	1	2.4	4.1	10.4	80.9	72.5	73.2
	2	6.0	3.6	5.7	78.4	73.9	71.3	30	3.6	2	2.4	4.3	10.0	81.9	73.7	75.9
	3	6.0	4.7	7.2	79.1	73.3	72.5	60	3.6	3	2.4	3.9	11.5	82.1	72.6	77.4
	1	9.0	3.2	7.4	79.3	73.4	70.0	15	5.4	1	3.6	5.9	10.2	81.8	73.4	75.3
	2	9.0	4.4	6.5	78.3	73.2	72.4	30	5.4	2	3.6	6.0	11.7	82.0	72.3	77.2
	3	9.0	6.0	9.9	75.4	67.9	72.2	60	5.4	3	3.6	5.6	11.7	81.2	71.7	79.0
Wheat Straw Cook 27	..	..	..	..	...	77.9	29.0	..	..	.	..	..	...	.	77.9	29.0
	..	..	..	..	...	...	...	15	0.9	1	0.6	1.4	9.1	80.6	73.3	45.7
	..	..	..	..	...	...	...	30	0.9	2	0.6	1.5	12.0	80.7	71.1	47.9
	1	3.0	3.0	5.0	81.0	76.9	49.8	15	1.8	1	1.2	2.4	12.7	80.3	70.1	60.5
	2	3.0	3.1	4.5	80.8	77.1	50.8	30	1.8	2	1.2	2.6	12.5	80.3	70.3	64.4
	1	6.0	4.5	4.9	79.5	75.6	60.7	15	3.6	1	2.4	3.7	12.8	80.6	70.3	69.6
	2	6.0	5.8	7.9	79.6	73.3	62.9	30	3.6	2	2.4	3.9	13.3	79.5	68.9	73.5
	3	6.0	6.0	4.5	80.8	77.2	66.5	60	3.6	3	2.4	4.1	13.3	79.5	68.9	74.6
	1	9.0	5.0	4.5	80.9	77.3	62.5	15	5.4	1	3.6	4.9	15.1	79.4	67.4	72.9
	2	9.0	6.3	4.7	80.6	76.8	68.4	30	5.4	2	3.6	5.1	13.7	79.4	68.5	75.6
	3	9.0	7.9	5.1	79.1	75.1	72.2	60	5.4	3	3.6	5.6	14.2	81.5	69.9	75.8
	1	12.0	6.0	5.8	81.2	76.5	65.5	..	..	.	..	..	...	...	...	...
	2	12.0	8.2	7.0	76.7	71.3	69.9	..	..	.	..	..	...	...	...	...
	3	12.0	9.2	7.7	72.2	66.6	70.6	..	..	.	..	..	...	...	...	...
Barley Straw Cook 88	..	..	..	..	...	74.7	29.8	..	..	.	..	..	...	...	74.7	29.8
	1	3.0	3.1	7.6	77.4	71.5	49.3	15	1.8	1	1.2	2.9	9.4	77.1	69.8	53.8
	2	3.0	3.1	7.4	77.7	72.0	49.7	30	1.8	2	1.2	3.0	9.0	77.3	70.4	54.4
	3	3.0	3.1	7.4	77.9	72.2	49.4	60	1.8	3	1.2	3.1	9.6	77.6	70.1	55.2
	1	6.0	4.7	8.7	77.3	70.5	60.9	15	3.6	1	2.4	4.8	10.4	77.7	69.5	68.9
	2	6.0	5.6	7.7	76.9	71.0	65.8	30	3.6	2	2.4	4.8	9.6	78.2	70.6	70.1
	3	6.0	5.7	8.4	77.5	71.0	66.0	60	3.6	3	2.4	4.9	13.0	78.2	68.0	73.2
	1	9.0	5.1	8.4	77.6	71.1	63.4	15	5.4	1	3.6	5.7	10.9	78.0	69.6	71.6
	2	9.0	6.9	8.1	77.4	71.1	69.4	30	5.4	2	3.6	6.1	11.1	78.4	69.6	73.9
	3	9.0	7.7	7.5	78.2	72.4	74.0	60	5.4	3	3.6	6.4	11.6	78.1	69.0	75.8
	1	12.0	5.6	8.7	77.6	70.8	65.1	15	7.2	1	4.8	7.8	11.2	77.5	68.8	73.3
	2	12.0	9.2	8.7	76.4	69.7	69.4	30	7.2	2	4.8	8.2	11.9	78 4	69.1	75.3
	3	12.0	9.7	9.7	74.3	67.0	75.2	60	7.2	3	4.8	8.1	11.5	77.1	70.0	76.5

* Chlorine consumption calculated on basis of ash-free screened pulp.
[1] Basis moisture-free screened pulp.

spectively. The straight line obtained from these values is shown in Fig. 7. The actual experimental values are seen to fall very close to the calculated line.

It should be stated at this point that, while the formulas appear to be valid for the lignin-permanganate number—Roe number—bleach consumption relationships of the soda pulps used in this study, they are based on an insufficient amount of data to permit of their general application. They are included in this paper because they fit the data obtained under the controlled laboratory and pilot plant conditions for soda pulping used in this work, and because, if substantiated by further work, they open up interesting possibilities for general use for evaluating pulp relationships.

Bleach Consumption and Alpha-Cellulose

In order to determine the effect of the bleaching on the alpha-cellulose in the pulp, determinations were made on rice, wheat, and barley pulps bleached to various degrees by the two types of bleaching. Complete data are given in Table VII. The bleach consumption-brightness-alpha-cellulose relationships are illustrated in Fig. 8. These data show that the pulp brightness increases rapidly with chlorine consumption until a brightness of about 70% is attained. The rate of increase in brightness is greater in three-stage than in single-stage bleaching. Beyond about 70%, the brightness increases but little or not at all with increasing chlorine consumption. The loss of pulp substance increases somewhat with increased bleach consumption.

The larger losses shown for three-stage bleaching are probably due to the action of the caustic in the intermediate stage.

It may be readily seen from Fig. 8 that three-stage bleaching results in considerable economy of chlorine, particularly in the wheat and barley straw pulps. It is also apparent that rice straw pulp consumes less chlorine than the other pulps for attaining a given brightness, especially in single-stage bleaching.

Single-stage bleaching degrades the alpha-cellulose to a lesser extent than three-stage bleaching up to a bleached pulp brightness of about 70%. It is evident, however, from the data in Fig. 8 that, in order to prevent undue degradation of the alpha-cellulose, the multistage methods of bleaching should be used for obtaining brightness higher than 70% with agricultural residue soda pulps.

Acknowledgment

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