The 4th Crop Reporting District of Mississippi is the south half of the Delta and includes the Counties of Humphreys, Issaquena, Leflore, Sharkey, Sunflower, Washington, and Yazoo. During the season of 1937-38 these counties averaged 450 pounds of lint per acre compared with an average of 433 pounds produced in Poinsett and Mississippi Counties, Arkansas.

The moisture content of only about 13 percent of the seed in the 4th District exceeded 12 percent, but the average f. f. a. content of about 95 percent of the seed was over 10 percent. Compare this with conditions in Poinsett and Mississippi Counties where more than 51 percent of the seed contained an average of 14.3 percent moisture but only 13 percent of the seed exceeded 1.8 percent f. f. a. and this averaged only 3.0 percent. The difference between these two sections is about 2 degrees of latitude, so that f. f. a. control may be a matter of temperature at the time of maturity of the seed. It may be that if cotton is picked promptly after the bolls open, and the seed moved quickly from the field to the oil mill and there chilled before storage, f. f. a. generation will be arrested.

It seems to me that both of these angles of approach to better quality cottonseed are worthy of special study.

Hydrolytic Treatment Of Cottonseed Hulls‡

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THE annual production of cottonseed hulls in the United States amounts to more than one million tons. Some of this material is used for cattle feed, a portion being used directly for roughage, and a portion as a filler in order to control the protein content of cottonseed meal sold for feed.

Since the digestibility of cottonseed hulls is quite low (Henry and Morrison, 1936, show 43.7 percent), any treatment which would increase this factor would enhance the value of such feed as is prepared from the hulls. The present work was undertaken to follow the changes produced in cottonseed hulls by various treatments with acids and alkalies.

Alkaline digestions (1), varying in kind of alkali and conditions of treatment, have been made in order to increase the feed-value of straw and wood. This treatment washes out silica and lignin which presumably act as incrusting materials in the untreated hulls. Archibald (2) extracted cottonseed hulls with cold 1.5 percent sodium hydroxide, but concluded from feeding tests that the results ". . . . . were in the main negative."

Honcamp and Hilgert (3) found that by simply steaming straw a product of improved value for use as a feedstuff was obtained.

The hydrolysis of cottonseed hulls with acids has resulted in the formation of reducing sugars. Hudson and Harding (4) and Hall, Slater and Acree (5) have described methods for the preparation of xylose from cottonseed hulls. Sherrard and Blanco (6) used high temperatures and pressure to form reducing sugars from cottonseed hulls; these sugars, they found, could be only partially fermented. Ivannova and Kuronnova (7) reported improvement in the feeding value of cottonseed hulls after acid hydrolysis.

Experimental

After hydrolysis with either acid or alkali and subsequent neutralization or washing, the wet hulls were dried in a steam-heated oven at a temperature below 30°C. The oven dried samples were spread in a thin layer to establish moisture equilibrium with the air of the laboratory and allowed to remain overnight. One hundred grams of this material were ground to pass through a one mm. sieve and subsequently used for analysis.

The Methods of Analysis — A.O.A.C. — Fourth Edition — was used as a source of methods for determining (a) moisture by 135° oven; (b) ash; (c) pentosans; (d) crude fiber; (e) ether extract; (f) nitrogen; and (g) lignin (without correction for protein).

Cross and Bevan cellulose was determined by the method of Phillips (8) with the exception that no permanganate bleach was used at the end. The method described by Shaffer and Hartmann (9) was used for the determination of reducing sugar which was calculated as xylose.

Methods of Digestion

A. With alkali: — Three one-hundred-gram samples of hulls were weighed into two-liter Erlenmeyer flasks. Eight hundred c.c. of 1.5 percent suspension of calcium oxide was added to each. One flask was stoppered and allowed to remain at room temperature overnight (18 hours); another flask was connected to a reflux condenser and the contents were boiled for one-half hour; the third flask was placed in an aluminum pressure cooker and the pressure was held at 25 pounds for one-half hour. Hulls were treated in a similar manner with 1.3 percent sodium hydroxide and with 1.3 percent sodium carbonate, except that the sodium carbonate treatment was not made under pressure. After cooling, each sample was filtered and washed until the washings were colorless.

The hulls which had been treated with sodium hydroxide were given a more thorough washing in order to reduce the amount of ash in the residue. After filtering, the hulls

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were washed with water until the washings were no longer alkaline to litmus. The residue thus obtained was then soaked in 800 c.c. of distilled water for five days. It was again filtered, washed and soaked overnight in another 800 c.c. of water. The next day it was once more filtered, washed, dried and prepared for analysis.

B. With steam: — Five hundred grams of hulls were placed in an oil jacketed autoclave fitted with a device for mechanical stirring. After the addition of one liter of water, heating was continued until 15 pounds pressure had been reached and was maintained at that point for one hour. At the end of this time the pressure was released and the residue in the autoclave was dried without further treatment.

C. With acid: — Quantities of hulls weighing 500 to 1,000 grams were heated in the autoclave with twice their weight of sulfuric acid of varying concentration (See Table II). The pressure was held at 15 pounds for one-half hour with constant stirring. After releasing the pressure, calcium carbonate was added in quantity calculated to neutralize the acid used.

TABLE I.
Analyses of Cottonseed Hulls and Bran.

Sample	Moisture	On a Moisture Free Basis. Ash	Ether extract	Protein	Crude fiber	Pentosan	Reducing Sugar	Cellulose Cross & Bevan	Lignin
	%	%	%	%	%	%	%	%	%
1. Cottonseed Hulls	9.52	2.32	0.65	3.30	49.18	30.65	<1	52.30	—
2. Cottonseed Hull Bran	8.43	2.44	0.45	3.59	45.81	34.30	<1	48.60	18.95
3. Cottonseed Hull Bran	10.52	2.68	0.51	3.75	42.80	36.70	<1	48.30	19.20

The samples were then dried and prepared for analysis.

Two other samples (17 and 18 of Tables II and III) were boiled under reflux at atmospheric pressure with constant stirring for one-half hour, then neutralized and treated as the others had been.

After hydrolysis with hydrochloric acid in the autoclave, samples 19 and 20 (Tables II and III) were washed, dried and prepared as previously noted.

Discussion

The proximate analysis of cottonseed hulls (Table I) shows that they are low in protein and in ether extract. Pentosan, cellulose and lignin make up the major portion of the composition of the hulls. It is upon these components that interest is centered.

In Table II are listed briefly the treatments to which hulls have been subjected and the analyses of the resulting products calculated to the moisture-free basis.

Table III, showing the absolute values for the original and final products, has been included to show changes in the individual constituents which have resulted from the treatment of the hulls. The figures here given have been calculated on the basis of material derived from 100 grams of moisture-free original hulls, while those of Table II have been calculated to the basis of 100 grams of moisture-free products.

The summation of analytical figures is not equal to the theoretical value because of overlappings; for example, xylose will show up as

TABLE II.
Analyses of Treated Hulls.
(oven-dry)

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII
										C. & B. Cellulose		
Sample No.	Orig. Hulls used	Reagent used	Ratio reagent to hulls	Temp. or Pressure	Time (hr.)	Final Treatment before drying	Ash %	Pentosan %	Reducing sugar as xylose %	Crude %	Ash & Pentosan Free %	Lignin %
4	2	1.5%CaO	8 : 1	R. T.[2]	18	Washed	13.0	32.2	<1	48.2	22.8	15.3
5	2	1.5%CaO	8 : 1	A. P.[3]	½	Washed	8.5	34.2	<1	50.4	25.9	16.2
6	2	1.5%CaO	8 : 1	25 lbs.[4]	½	Washed	7.5	32.2	<1	49.5	26.9	17.3
7	2	1.3%Na_2CO_3	8 : 1	R. T.	18	Washed	2.6	36.4	<1	56.6	29.6	19.6
8	2	1.3%Na_2CO_3	8 : 1	A. P.	1	Washed	3.2	39.4	<1	62.2	29.9	16.6
9	2	1.3%NaOH	8 : 1	R. T.	18	Washed	4.1	39.7	—	63.3	32.6	15.2
10	2	1.3%NaOH	8 : 1	A. P.	½	Washed	3.3	41.5	—	68.4	34.3	14.4
11	2	1.3%NaOH	8 : 1	25 lbs.	½	Washed	2.5	42.5	—	80.9	40.1	11.6
12	2	Water	2 : 1	15 lbs.[5]	1	None	2.7	32.9	1.0	42.9	25.9	20.2
13	2	3%H_2SO_4	2 : 1	15 lbs.[5]	½	Neutralized with $CaCO_3$	15.3	26.5	17.5	31.9	25.1	19.8
14	2	3%H_2SO_4	2 : 1	15 lbs.[5]	½	with $CaCO_3$	10.5	29.2	20.1	32.3	24.6	23.1
15	2	4%H_2SO_4	2 : 1	15 lbs.[5]	½	with $CaCO_3$	13.1	26.9	21.9	29.7	23.6	20.8
16	3	3%H_2SO_4	2 : 1	15 lbs.[5]	½	with $CaCO_3$	12.0	26.2	20.4	32.8	24.6	24.1
17	2	3%H_2SO_4	3 : 1	A. P.	½	with $CaCO_3$	16.4	29.7	5.6	37.3	25.5	20.5
18	3	3%H_2SO_4	3 : 1	A. P.	½	with $CaCO_3$	15.6	32.4	5.3	33.2	23.7	18.8
19	2	0.5%HCl	2 : 1	15 lbs.	1	Washed	1.3	26.1	—	42.8	29.9	23.0
20	2	3%HCl	2 : 1	15 lbs.	½	Washed	0.8	17.3	—	47.1	38.6	31.0

1. Column II — 2 & 3 refer to samples listed in Table I.
2. Column V — R. T.-Allowed to stand at room temperature — 18 hrs.
3. Column V — A. P.-Boiled under reflux at atmospheric pressure.
4. Column V — 25 lbs.-In aluminum pressure cooking without stirrer.
5. Column V — 15 lbs.-Oil-jacketed autoclave — continually stirred.

both reducing sugar and as pentosans, and this is especially true in samples 13, 14, 15 and 16.

A study of the data (Table III) shows that digestion with alkali removed from 7 to more than 50 percent of the lignin. Sodium hydroxide solutions removed more lignin than did either sodium carbonate or calcium oxide. Except with calcium oxde where temperature and presure made little difference, the effect of increased temperature is to bring about the removal of more lignin.

In the case of pentosans there is apparently a tendency toward a slight decrease as a result of the treatment. After digesting with alkali the amount of Cross and Bevan cellulose is increased, due in large part to the increase of pentosans in this cellulose. Some of this increase may be an indirect result of the removal of lignin by the alkali, since fewer chlorinations are necessary to prepare a white sample of cellulose if alkaline extraction has been used before chlorination.

There was some difficulty in obtaining products of low ash content from those samples which had been treated with alkali. Even after the extensive washing of the samples which had been digested with sodium hydroxide some of the samples (e.g., No. 9, Table III) still showed an increase in ash over the original. This is in agreement with data published by Hall, Slater and Acree (5).

Steam at 15 pounds pressure produces little change in the composition of the cottonseed hulls (See No. 12, Tables II and III).

Treatment with sulfuric acid at 15 pounds pressure, under the conditions of these experiments, forms reducing sugars amounting to 20 percent of the original hulls. That this is mostly at the expense of pentosans is shown by the relatively small decrease in the Cross and Bevan cellulose which had been corrected for ash and pentosans. The apparent lignin content of samples treated with sulfuric acid shows an increase. The high ash content found is the result of neutralization of the acid with calcium carbonate.

TABLE III

YIELD OF CONSTITUENTS FROM 100 GMS. OVEN-DRY ORIGINAL HULLS.

Sample No.		Yield Total gm.	Ash gm.	Pento-san gm.	Reducing Sugar gm.	C. & B. Cellulose Crude gm.	C. & B. Cellulose Corr. for Ash & Pent. gm.	Lignin Corr. for Ash gm.
2	Table I	100	2.4	34.3	<1.0	48.6	30.2	19.0
3	Table I	100	2.7	36.7	<1.0	48.3	29.3	19.2
4	Table II	110.3	14.3	35.5	<1.1	53.2	25.2	16.9
5	Table II	101.0	8.6	34.5	<1.0	50.9	26.2	16.4
6	Table II	97.7	7.3	31.5	<1.0	48.4	26.3	16.9
7	Table II	90.4	2.4	32.9	<0.9	51.2	26.8	17.7
8	Table II	81.5	2.6	32.1	<0.8	50.7	24.4	13.5
9	Table II	86.8	3.6	34.5	—	54.9	28.3	13.2
10	Table II	77.2	2.6	32.0	—	52.8	26.5	11.1
11	Table II	72.0	1.8	30.6	—	58.2	28.9	8.4
12	Table II	99.0	2.7	32.6	0.9	42.5	25.6	20.0
13	Table II	117.9	18.0	31.3	20.6	37.6	29.6	23.4
14	Table II	109.1	11.5	31.9	21.9	35.2	26.8	25.2
15	Table II	115.2	15.1	31.0	25.2	34.2	27.2	24.0
16	Table II	106.6	12.8	27.9	21.8	35.0	26.2	25.7
17	Table II	112.2	18.4	33.3	6.3	41.9	28.6	23.0
18	Table II	116.0	18.1	37.6	6.2	38.5	27.5	21.8
19	Table II	88.5	1.2	23.1	a	37.8	26.4	20.3
20	Table II	67.8	0.5	11.7	b	31.9	26.2	21.0

a—About 2.5 grams xylose in washings.
b—About 20 grams xylose in washings.

At a decreased temperature sulfuric acid formed only slightly more than one-fourth of the quantity of reducing sugars produced at 15 pounds pressure (Nos. 17 and 18 in Tables II and III).

Hydrochloric acid acting on cottonseed hulls also produced free sugars from the pentosans. Three-percent hydrochloric acid (Number 20 in Table III) at 15 pounds pressure gave a yield of reducing sugar in the washings comparable to that given by three-percent sulfuric acid. (See Nos. 19 and 20, Tables II and III).

Conclusion

1. Alkaline solutions under the conditions of these experiments extracted from 7 to 50 percent of the lignin, depending upon the conditions of temperature and pressure.

2. Steam under pressure had little effect upon the composition of cottonseed hulls.

3. Dilute acids hydrolyzed more or less of the pentosans, depending upon temperature and pressure.

4. During both the steam and acid treatments there was a slight increase in the apparent lignin content.

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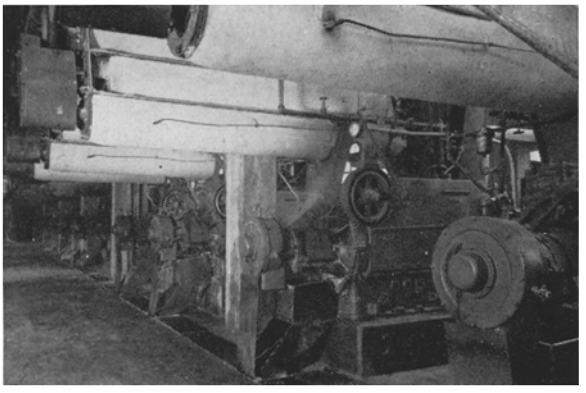

Four new expellers added in winter of 1939 to Central Soya Co. plant at Decatur, Indiana, making a total of 16.