The Effects of Alkali Cooking on the Yields of Crude and Neutral Oil from Cottonseed Meats[1]

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THE FULL POTENTIAL of cottonseed as a source of edible oils and of meals for animal nutrition has not been realized by the conventional commercial methods of preparing cottonseed for extraction or expression of the oil. Severe cooking conditions, while tending to yield oils of satisfactory quality and meals low in free-gossypol content, also denature the meal proteins and reduce the nutritional value of the meals (13). Mild cooking conditions, while causing less protein denaturation, invariably result in meals high in free gossypol and often in oils which are difficult to decolorize (4).

A number of researchers have investigated the use of chemical additives to cottonseed meats in conjunction with modifications of the conventional, commercial cooking methods as a possible means of accomplishing results not obtainable by varying cooking conditions alone. Cavanagh (3) has reported that, on a commercial-scale operation, the addition of sodium carbonate to cooked cottonseed meats prior to extraction of the oil resulted in improved meal and oil products. King, Wolford, Thurber, *et al.* (7) investigated the effect of varying the pH of cottonseed meats undergoing cooking and found that significant improvements in the quality of both the meals and oils produced were obtained when the pH of the meats was maintained at about 8.2 while cooking. More recently King, Knoepfler, *et al.* (8, 10) have reported the results of a series of studies in which the pH of the meats undergoing cooking was kept essentially constant while the degree of comminution of the meats, the cooking time, temperature, and moisture content were varied. The amount of alkali required to result in a pH of 8.2 to 8.4 in the final meals was dissolved in the water added for moisture adjustment in the initial cooking stage. The results of these studies substantiated those obtained in the earlier studies (7) and indicated that an initial cooking moisture content of 31% yielded the best-quality oils. No data on the yields of oils were presented.

The heating of cottonseed meats in intimate admixture with sodium hydroxide solution could possibly result in saponification and loss of neutral oil. As the oil of cottonseed exceeds the meal in value, it appears that obtaining improved meal quality at the expense of oil yield might well be uneconomical, especially in view of the fact that present trading practices do not provide any premiums for meals of improved quality. This paper presents the results of a study conducted primarily to determine the yields of crude and neutral oil from cottonseed meats prepared by the alkali cooking procedures found to yield the best-quality oil. The composition of the crude oils and meals obtained are also presented.

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Experimental

Equipment. Cooking was conducted in a bench-scale, stainless-steel cooker (5), designed to simulate the operation of the conventional type of stack cooker employed by most oil mills but permitting close control of cooking conditions and quantitative recovery of all materials. Extractions were carried out in a modified Soxhlet [3] type of extractors fitted with glass-wool filter pads.

Materials. Three lots of cottonseed flakes, containing 35.4%, 36.1%, and 39.7% of oil (as determined by the conventional analytical method), respectively, were used in the tests. Each lot of flakes was prepared from essentially hull-free, whole meats at the time used. The thickness range of the flakes was 0.005 to 0.007 in.

Distilled water was used for the control cooks. The solutions used for the alkali cooks were prepared from reagent-grade, sodium hydroxide pellets and distilled water. The extraction solvent employed was commercial hexane, boiling range 67°C. to 70°C., and contained no residue which was not volatile at steam-bath temperatures.

Procedure. Each batch of meats was flaked, thoroughly mixed, and reduced to 1,200 g. by quartering, then divided into four portions of virtually identical composition. One portion was reserved for analysis, one was extracted "as is," one was cooked at 31% moisture content using distilled water, and one was cooked at the 31% moisture level with 3.2 g. of sodium hydroxide pellets dissolved in the water. The amount of sodium hydroxide used was that which had been determined to result in a pH of from 8.2 to 8.4 for the final air-dried meals (9).

In all cooks the temperature of the flakes was

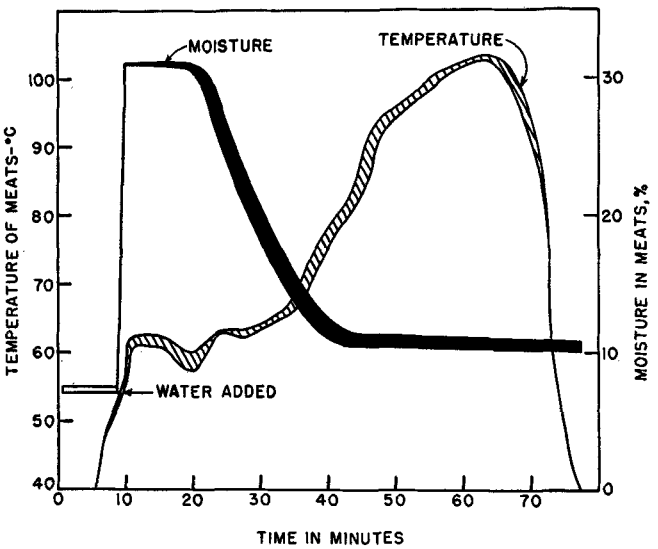

FIG. 1. Cooking conditions.

[3] It is not the policy of the Department to recommend the products of one company over those of any others engaged in the same business.

TABLE I
Material Balance [a]

Expt. No.	Preparation of flakes for extraction	Input			Output				Recovery of input material
		Flakes	Sodium (of NaOH) [b]	Total	Meal		Crude oil	Total	
					Solids	Residual oil			
		g.	g.	g.	g.	g.	g.	g.	%
1	None, extracted "as is"	279.0	—	279.0	178.5	0.5	100.0	279.0	100.0
	Cooked with water only	279.0	—	279.0	182.8	0.8	96.4	280.0	100.4
	Cooked with alkali	279.0	1.9	280.9	184.7	0.6	96.3	281.6	100.2
2	None, extracted "as is"	279.3	—	279.3	176.3	0.3	102.9	279.5	100.1
	Cooked with water only	279.3	—	279.3	179.6	0.5	99.2	279.3	100.0
	Cooked with alkali	279.3	1.9	281.2	182.4	0.4	98.2	281.0	99.9
3	None, extracted "as is"	282.3	—	282.3	169.8	0.5	111.2	281.5	99.7
	Cooked with water only	282.3	—	282.3	173.2	1.1	107.2	281.4	99.7
	Cooked with alkali	282.3	1.9	284.2	176.0	0.9	107.0	283.9	99.9

[a] All data on a moisture- and volatiles-free basis.
[b] Sodium content of 3.2 g. of sodium hydroxide.

brought to 55°C. at the time of moisture adjustment. The water was added as a fine spray while the flakes were being agitated.

The cooking procedures and conditions were comparable to those previously described by King, Knoepfler, *et al.* (8, 10); an important difference was the use of a different type of cooking-mixing equipment. The temperature, time, and moisture-content relationships while cooking are shown in Figure 1. The moisture content of the meats at various stages of cooking was determined by calculations based on the initial moisture of the wetted flakes and on the amount of water removed from the flakes and collected while cooking.

After cooking, the flakes were transferred quantitatively to the extractors (no sampling for moisture determinations was required as the moisture content of the cooked flakes was determined by weighing the entire batch of flakes) and exhaustively extracted with commercial hexane. The temperature of extraction was approximately 50°C., and each batch was subjected to 30 separate extractions.

The miscellas were collected, desolventized, and weighed in the same flasks to avoid loss. The major portion of the solvent was removed from the miscellas by evaporation under about 360 mm. Hg. absolute pressure. Traces of solvent were stripped from the oils with nitrogen under low absolute pressure.

The wet marcs were quantitatively transferred from the extractors to tared sheets of aluminum foil, equilibrated over-night under a gentle stream of air, weighed, thoroughly mixed, and sampled for analyses. The first moistures of the equilibrated meals were determined when the meals were weighed.

Analytical Methods. The raw cottonseed flakes were analyzed for moisture, oil, free fatty acids of the oil, free gossypol, total gossypol, and total phosphorus. The air-dried meals were similarly analyzed with the exception that the pH determination was included (8) and that the free fatty acids of the residual oils were not determined. The crude oils were analyzed for moisture and volatiles, free fatty acids, neutral oil, oxidized fatty acids, gossypol, phosphorus, unsaponifiables, and sodium.

Neutral oil in the crudes was determined by the chromatographic method of Linteris and Handschumacher (11), which was adopted as a tentative method at the 1957 meeting of the American Oil Chemists' Society. The crude oils were analyzed for gossypol and gossypol-like materials by the method of Pons, Hoffpauir, and O'Connor (14). Phosphorus determinations were by the methods of Pons, Stansbury, and Hoffpauir (15).

Sodium in the crude oils was determined by flame photometry, using the method of O'Connor and associates (12). All other analyses were done in accordance with the pertinent methods of the American Oil Chemists' Society (1).

Results and Discussion

The material balance data are given in Table I. For the purposes of the balance it was assumed that the sodium hydroxide used in the alkali cooks (3.2 g.) had reacted completely with components of the meats with the formation of molar equivalents of water as one reaction-product. As the balances were calculated to a moisture- and volatiles-free basis, only the metallic sodium was considered in the calculation of the balances for the alkali cooks. Of the six individual test balances shown, only one, a test in which the meats were cooked with water (Experiment 1), failed to balance within the limits of analytical accuracy. The consistently low material-recoveries for Experiment 3 are attributable to slightly deteriorated meats. While stripping these crude oils (Experiment 3), it was observed that a small amount of unidentified, volatile material other than solvent was removed near the end of the operation.

The analyses of the raw flakes and of the meals produced are given in Table II.

Alkali cooking did not have any greater effect on the free gossypol of the meals than did cooking with water; variations between the free gossypol contents of the water-cooked and alkali-cooked meals were within the limits of variation of the methods of analysis. There was however a definite effect on the total gossypol of the meals. The alkali-cooked meals contained about 13% less total gossypol than the meals from the flakes cooked with water. In view of some recently reported nutritional studies (2, 6), reduction in total gossypol content may be of greater significance than reduction in free gossypol content.

Neither the total phosphorus nor the nitrogen contents of the meals were significantly affected by alkali cooking as compared to cooking with water. The alkali-cooked meals analyzed lower in nitrogen throughout than did the water-cooked meals. Calculation of nitrogen balances on the basis of moisture, lipide, and sodium-free meal weight showed that there was no appreciable difference in the total nitrogen content of the comparable meals. The meals were not analyzed for sodium; however the crude oils were, and it was assumed that the sodium not accounted for

TABLE II
Analyses of Cottonseed Flakes and Meals [a]

Expt. No.	Material	Oil	Gossypol		Nitrogen	Phosphorus	pH value
			Total	Free			
		%	%	%	%	%	
1	Flakes, uncooked	35.40	1.02	0.76	6.52	1.03	—
	Meal from uncooked flakes	0.15	0.89	0.66	10.20	1.62	—
	Meal from flakes cooked with water only	0.44	1.27	0.073	9.97	1.53	6.5
	Meal from flakes cooked with alkali	0.32	1.11	0.072	9.75	1.58	8.4
2	Flakes, uncooked	36.12	1.08	0.92	6.49	1.12	—
	Meal from uncooked flakes	0.14	1.12	0.77	10.16	1.74	—
	Meal from flakes cooked with water only	0.27	1.56	0.081	10.01	1.72	6.6
	Meal from flakes cooked with alkali	0.20	1.34	0.061	9.74	1.71	—
3	Flakes, uncooked	39.74	1.07	0.90	6.00	0.99	—
	Meal from uncooked flakes	0.31	1.22	0.83	9.84	1.60	—
	Meal from flakes cooked with water only	0.62	1.55	0.107	9.74	1.61	6.3
	Meal from flakes cooked with alkali	0.53	1.36	0.110	9.50	1.58	8.2

[a] All analyses on a moisture-free basis.

in the extracted crude oils remained in the meals. When calculated on the foregoing basis, it was found that the sodium in the alkali-cooked meals which was derived from the added sodium hydroxide was 1.02%, 1.04%, and 1.07% of the moisture-free weight of the respective meals.

The analyses of the crude oils extracted from the raw, the water-cooked, and the alkali-cooked flakes are shown in Table III. The analyses of the crude oils indicate that the cooking, with or without alkali present, had the effect of drastically reducing the impurities content of the crude oils. As a consequence the neutral oil content of the oils from both types of cooked meats was from 2 to 3% greater than that of the oils from the uncooked meats. Comparison of the analyses of the crudes from the alkali-cooked meats with those from the water-cooked meats shows that they did not differ significantly in their content of neutral oil, oxidized fatty acids, and unsaponifiable matter. The analyses did show appreciable differences with respect to free fatty acids, gossypol, and phosphorus. The oils from alkali-cooked meats contained less of the material determined as free fatty acids than did the oils from the meats cooked with water but were significantly higher in phosphorus content. Perhaps the most important effect of alkali cooking, when compared to cooking with water, is the magnitude of the difference in the gossypol content of the crude oils. The oil from the alkali-cooked meats contained only 0.01% to 0.02% gossypol while the oils from water-cooked meats contained about five times this amount.

The quantity of sodium found in the crude oils obtained from the raw "as is" flakes was surprisingly high, ranging from 0.0019 to 0.0058%. It is interesting to note that the sodium content of the oils obtained from the water-cooked flakes was lower than that of those from the raw flakes. Sodium in the crude oils from the alkali-cooked flakes was not as high as anticipated, ranging from about 0.007 to 0.016%. The amount of sodium in the oils from the alkali-cooked flakes, when corrected for that found in the crudes from the water-cooked flakes, indicated that the crude oils from the alkali-cooked meats contained about 0.11%, 0.07%, and 0.19% soaps.

The products-yield data are shown in Table IV.

TABLE IV
Yields of Meal, Crude Oil, and Neutral Oil [a]

Expt. No	Source material	Meal [b]	Crude oil [c]	Neutral oil [d]
		%	%	%
1	Uncooked flakes	63.98	36.02	34.44
	Flakes cooked with water only	65.52	34.84	34.39
	Flakes cooked with alkali	65.52	34.73	34.18
2	Uncooked flakes	63.12	36.95	35.40
	Flakes cooked with water only	64.30	35.70	35.34
	Flakes cooked with alkali	64.63	35.30	34.88
3	Uncooked flakes	60.15	39.57	37.87
	Flakes cooked with water only	61.35	38.36	37.56
	Flakes cooked with alkali	61.67	38.22	37.42

[a] Yields based on the respective moisture-free weights of input flakes.
[b] Corrected to an oil-free basis; yields from alkali-cooked flakes were also corrected for sodium content.
[c] Based on the weights of crude oil actually recovered plus the weight of oil determined in the respective meals.
[d] Calculated from analyses and weight of crude oils.

Yields are given in the table as percentages of the moisture-free weights of uncooked, "as is" flakes used as starting materials for each of the respective tests. Crude and neutral oil yields were based on the weights of crude oil actually recovered plus the weight of oil remaining in the meals. The yields of meal from the alkali-cooked meats were corrected to an oil- and sodium-free basis.

The yields of crude oil from the flakes cooked with water averaged 96.77% of that obtained from the uncooked flakes while the yields from the flakes cooked with alkali were lower, averaging 96.18% or 0.6% less. The yields of meal increased proportionately as the yields of crude oil decreased.

TABLE III
Analyses of Crude Oils [a]

Expt. No.	Source material	FFA (as oleic)	Neutral oil	Oxidized fatty acids	Gossypol	Phosphorus	Unsaponifiable matter	Sodium
		%	%	%	%	%	%	%
1	Uncooked flakes	0.98	95.6	1.37	0.42	0.079	0.52	0.0027
	Flakes cooked with water only	0.75	98.7	0.38	0.050	0.013	0.55	0.0019
	Flakes cooked with alkali	0.53	98.4	0.34	0.013	0.029	0.50	0.0105
2	Uncooked flakes	1.26	95.8	1.07	0.77	0.074	0.53	0.0058
	Flakes cooked with water only	0.58	99.0	0.19	0.085	0.008	0.53	0.0016
	Flakes cooked with alkali	0.37	98.8	0.25	0.020	0.021	0.45	0.0069
3	Uncooked flakes	1.71	95.7	0.90	0.52	0.074	0.50	0.0019
	Flakes cooked with water only	1.27	97.9	0.12	0.084	0.021	0.73	0.0018
	Flakes cooked with alkali	0.91	97.9	0.20	0.014	0.041	0.74	0.0161

[a] All analyses on a moisture- and volatiles-free basis.

The data indicate that both water cooking and alkali cooking had an adverse effect on the neutral oil yields. The losses resulting from water cooking were of a low order while those resulting from alkali cooking were sufficiently high as to be significant.

The flakes cooked with water only yielded 99.85%, 99.84%, and 99.18% as much neutral oil, respectively, as the corresponding uncooked flakes while the yields of neutral oil from the flakes cooked with alkali were 99.24%, 98.54%, and 98.81%.

If the yields of neutral oil from the water-cooked flakes are taken as 100% and the yields from water- and alkali-cooked flakes are compared on this basis, it is found that the yields from the three batches of alkali-cooked flakes were 0.61%, 1.30%, and 0.37% lower than those from the corresponding water-cooked flakes. This is an average loss of 0.76% by alkali cooking.

The amounts of alkali used and the conditions of its use were not necessarily optimum with respect to oil yields since no oil-yield data on which to base the studies were available. The conditions were selected on the basis of the data on oil quality. The relatively small losses of neutral oil found to result from the use of the alkali-cooking method would probably be compensated by the lower refining losses of the oils since for each 1% of refining loss below 9% there is an increase of 0.75% in the value of the oil. The improvement in meal quality resulting from alkali cooking, while unquestionably a contribution of great potential value, cannot presently be evaluated since the existing trading rules of the industry fix the value of a meal as a function of its protein content, with no consideration of the quality of the protein.

Summary

Equal quantities of flaked cottonseed meats of identical composition were similarly cooked at high moisture conditions with and without alkali present. The cooked flakes were exhaustively extracted with commercial hexane, and the yields of crude oil, neutral oil, and meal were determined. The yields from an equal quantity of uncooked flakes were similarly determined, chiefly to serve as a neutral oil control. Analyses of the crude oils and meals were compared to determine the effects of the presence of alkali while cooking on the composition of the products.

These experiments show that there was a reduction in the yields of both crude and neutral oil resulting from the admixture of alkali with cottonseed flakes while cooking. Assuming yields from flakes cooked with water as 100%, and average of 0.6% less crude oil was obtained from alkali-cooked than from water-cooked flakes. A similar comparison of the yields of neutral oil shows that those from the alkali-cooked flakes averaged about 0.75% less than from the flakes cooked with water.

The crude oils from alkali-cooked flakes contained only about one-fifth as much gossypol as those from the water-cooked flakes and were appreciably lower in free fatty acids. The crude oils from alkali-cooked flakes were significantly higher in phosphorus. The sodium content of the oils from alkali-cooked flakes indicated that their content of soaps ranged from 0.07% to 0.19%.

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Effect of Long-Term Storage on Acute Oral Toxicity and Gossypol Content of Cottonseed Pigment Glands

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COTTONSEED PIGMENT GLANDS, distinct structures made available in essentially unaltered condition from cottonseed kernels by a flotation process (1, 2), contain gossypol, a polyphenolic yellow pigment, as their principal component. Although gossypol has been regarded as the sole toxic principle of cottonseed for more than 40 years, some investigators have questioned the analyzed gossypol content as a true indicator of toxicity of cottonseed products. This subject has been reviewed by Eagle *et al.* (3). During the past 10 years we have studied numerous samples of cottonseed pigment glands and of pure gossypol for their acute oral toxicity (4, 5, 6, 7). Since some of these samples were available after storage periods lasting as long as nine years, re-evaluations were made to determine the effect of prolonged storage on the oral, median, lethal dose in the rat and on the analyzed gossypol content.