Summary

The authors describe an improvement in their analytical method for determination of the rosin-acids content in mixtures with fatty acids, especially for tall oil products.

Good agreement is obtained for the whole range of rosin acids and fatty acids compositions.

The method is faster, simpler, and less laborious than other methods that have been suggested, but seems to give as good results as these.

The method can therefore advantageously be applied both for research work, sales analysis, and as a routine control analysis.

Acknowledgment

The authors want to express their thanks to Mo och Domsjö AB, Hercules Powder Company, and Central Laboratory of the Cellulose Industry as well as their employees who have given valuable assistance in development of the method.

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Pilot Plant Development of the Alkali Cooking Process for Cottonseed Meats. I. Effect of Flake Thickness and of Time, Temperature, and Moisture Content During Cooking

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IN A PREVIOUS REPORT on the processing of cottonseed (4) it was pointed out that cottonseed meals of low free gossypol content, high nitrogen solubility, and high nutritive value (as determined by short-term chick feeding studies) could be produced by subjecting the flaked meats to a vigorous stirring action in the presence of high moisture content and alkali, followed by mild evaporative dehydration. The extracted oils were also shown to be of high quality. The basic function of this type of treatment is to rupture the pigment glands and inactivate the gossypol by causing it to bind with the meal constituents under conditions which result in high solubility of the meal nitrogen. Under the conditions employed the meats passed through a plastic and doughlike state. Reduction of the moisture content during agitation resulted in crumbling of the plastic mass to discrete particles of meal mixed with oil in such a manner that the oil is readily extracted. A planetary-type mixer, similar to a Hobart food mixer,[2] was found to be convenient for accomplishing the above procedure in the laboratory.

The unique qualities of the materials produced in the laboratory seemed to justify investigation of the process on a larger scale in an effort to determine the equipment requirements. At the same time it was considered desirable to obtain additional data on the effect of flake thickness, cooking moisture content, temperature, and time of cooking in the presence of alkali on the characteristics of the meals and oils produced. Some 27 experiments were selected in accordance with a "Latin square" design (2, 9), as shown in Table I. The combinations of conditions selected for the 27 experiments are indicated by "X" marks.

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

[2] The use of trade names does not constitute an endorsement by the Department of Agriculture of the product named over similar products of other manufacturers.

TABLE I

Experimental Rolling and Cooking Conditions Investigated

Flake thickness............		0.005"			0.009"			0.014"		
Cooking moisture %.........		18	24	31	18	24	31	18	24	31
Cooking tempera- ture °F.	Cooking time (min.)									
180	minimum	X				X				X
180	45		X				X	X		
180	60			X	X				X	
200	minimum		X				X	X		
200	45			X	X				X	
200	60	X				X				X
214	minimum			X	X				X	
214	45	X				X				X
214	60		X				X	X		

Experimental

The jacketed Banbury-type, sigma-blade mixer (Evarts G. Loomis Manufacturing Company) used permitted handling 15.4-lb. batches of flaked meats. This mixer is equipped with rotating blades, which provide thorough agitation, in a jacketed box having a capacity of approximately 2 cu. ft. Either steam or cooling water may be circulated through the jacket and blades. The cover is arranged so that compressed air may be circulated through openings into the chamber, and a thermocouple well extends down from the cover to the middle of the rotating blade area. A diagram of this mixer is shown in Figure 1.

A single lot of prime cottonseed, analytical data for which are given in Table II, was used throughout the investigation. Sufficient seed for each day's cooking operation was adjusted to a moisture content of 9 to 10% and allowed to equilibrate in a closed container for 24 hrs. These seed were hulled through the pilot plant Carver equipment in such a manner as to yield whole and cracked meats which were essen-

TABLE II
Analyses of Seed, Meats, and Flaked Meats

Sample	Nitrogen %	Nitrogen solubility %	Free gossypol %	Total gossypol %	H_2O %	Lipids %	F.F.A. %
Hull free meats	5.98	98.0	0.92	1.04	6.53	32.62	0.33
0.005-in. flakes	5.69	99.1	0.89	1.02	11.3	31.84	—
0.009-in. flakes	5.76	98.5	0.95	1.10	10.4	32.00	—
0.014-in. flakes	5.85	98.2	0.93	1.06	9.1	32.26	—

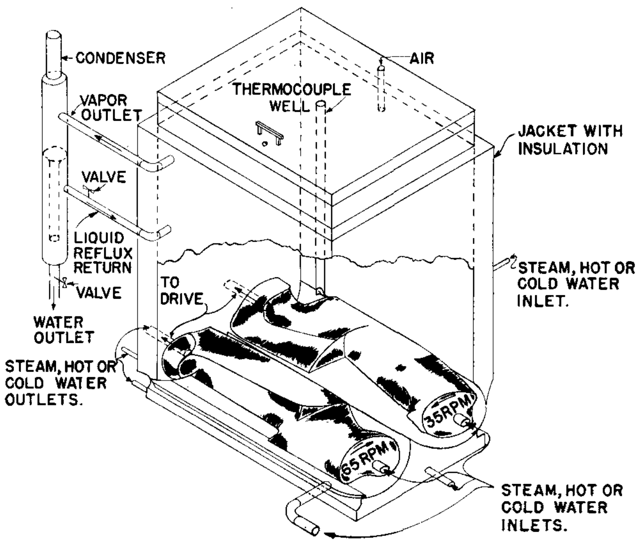

FIG. 1. Schematic view of mixer-cooker.

tially hull-free (less than 2% hulls by weight). All other fractions from the hulling operation were discarded. The meats were then flaked, using the French 5-high rolls after adding sufficient water in the conveyor system to produce flakes of 12–13% moisture content. Roll settings were varied for each of three series of nine experiments to produce flakes of 0.005 in., 0.009 in., and 0.014 in. in thickness. Flakes were placed in covered cans until used with a maximum storage time of 4 hrs. Analyses of the flakes is given in Table II.

In order to adjust the protein content of the final extracted meal to 46%, clean hulls, free of meats, were added to the flakes before charging the cooker. Each charge of 15.4 lbs. was preheated to 135°F. Water, at 135°F., containing dissolved sodium hydroxide in amounts sufficient to adjust the initial cooking moisture to the desired level and the pH to 8.0 to 8.4, was added, and the charge was mixed for 5 min. Following this mixing period the temperature was brought to that specified in Table I as rapidly as possible, usually within 10 min., and held at that maximum for the remainder of the cooking time. After the designated cooking temperature was reached, the cooker was adjusted so that the loss in moisture was evenly distributed over the remaining cooking time. The cooked material was discharged at a moisture content of 11 to 13%. Immediately after discharge it was passed through a ¼-in. square mesh screen and spread on a tray to cool and equilibrate in the air for 15 min. This resulted in a final moisture content after aeration of 8 to 10%.

The cooked meats (usually from 12 to 13 lbs.) were slurried with 19 lbs. of hexane, soaked for 30 min., and then extracted on a filter (3) with three additional 19-lb. washes of hexane.

The resulting extracted meals were desolventized in air, and the total gossypol was determined by the method of Pons, Hoffpauir, and O'Connor (7), free gossypol by the official method of the American Oil Chemists' Society (1), and nitrogen solubility in 0.02 *N* alkali by the method of Lyman *et al.* (6). The pH values of the meal were determined on aqueous slurries (1- to 10-dilution ratio) by use of a glass calomel electrode system. Moisture values during processing were determined with a Steinlite moisture meter. Oven moistures (16 hrs. at 101–105°C.) were obtained after each day's cooking experiments to verify the processing values.

The miscellas were concentrated in a laboratory model, Struthers Wells evaporator and then steam-stripped. Three typical oils were evaluated for refining and bleaching characteristics (Table III). The oils obtained in each experiment were analyzed for gossypol by the method of Pons, Hoffpauir, and O'Connor (8), free fatty acids by the official method of the American Oil Chemists' Society (1), and neutral oil by the method of Linteris and Handschumaker (5). Oil colors were determined by the A.O.C.S. photometric method.

For purposes of comparison, oil and meal were obtained from 0.009-in. flakes of the same lot of seed, using the normal hydraulic cooking and pressing procedures in the pilot-plant equipment. These oils were evaluated in the same manner.

Discussion of Results

Figures 2 and 3 show the effects of the processing variables on the properties of the meals and oils. Each point in each graph represents the average of nine values of one of the properties of the oil or meal for each level of one of the major variables studied. Although not identical as to individual combinations, these nine values in each case contain the same interaction of the remaining three variables. In this manner 27 experiments suffice; otherwise 81 would be required.

Effect of Flake Thickness

Free gossypol and residual oil in the meal, after extraction, and gossypol content of the oil decrease with decreased initial flake thickness. Flake thickness, in the range studied, had no significant effect on nitrogen solubility of the meal, F.F.A., or neutral oil content of the crude oil, or mass velocity (3), or percentage of solvent in the marc.

Effect of Maximum Temperature and Cooking Time

It will be noted that the net effect of increased cooking temperature, as well as increased cooking time, is to lower the free gossypol content and the nitrogen solubility of the meal. The only effect on the oil was to slightly increase the F.F.A. content.

Effect of Initial Cooking Moisture Content

It was noted in previous experimental work that the amount of alkali required to regulate the pH of

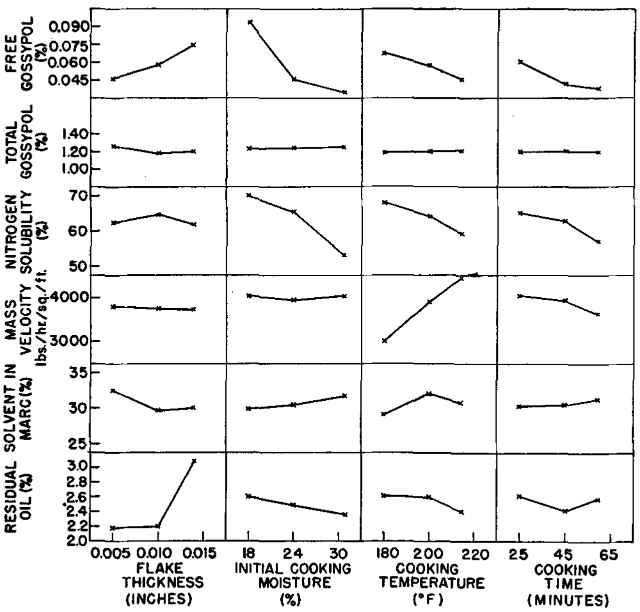

FIG. 2. Effects of processing variables on properties of meals.

the finished meal in a 1- to 10- aqueous slurry varied with the conditions during cooking. The data show that the amount of alkali necessary to achieve pH values of 8.0 to 8.4 is directly related to the maximum initial moisture content during cooking. The other variables studied had very little effect upon the alkali requirements.

Free gossypol in the meal and gossypol and F.F.A. in the oil decrease with increased initial cooking moisture content. None of the other properties except nitrogen solubility of the finished meal appeared to be affected by the initial cooking moisture content. All of the cooked meats exhibited satisfactory mass velocity and solvent-in-marc properties since the high initial moistures used (18 to 31%) in combination with the alkali tended to produce friable, discrete particles after emergence from the plastic state.

When combined with high temperature, as in the case of the present experiments, the rate of reduction of nitrogen solubility of the meal is increased with increased moisture content. The laboratory alkali cooking method (4) yielded meals having nitrogen solubilities of 85–92% when cooking was carried out at 30–40% initial moisture content and pH 8.2. In the present study on alkali cooking the highest nitrogen solubility achieved at 31% initial moisture content during cooking was 64%. One fundamental difference between the cooking procedures used in the present experiments and those used in the laboratory procedure is the relationship between moisture content and temperature (Figure 4). In these later experiments the temperature of the meats was raised to the specified maximum temperature as soon as possible with the cooker closed and moisture loss, prior to reaching this temperature, kept at a minimum. On the other hand, in the laboratory procedure reduction in moisture content began immediately, even in the prestirring period (by agitation in an open bowl, use of warm-air fans, and adjustment of the flake temperature to 110°F.). When heat was applied, the temperature of the charge was kept from rising by evaporation of the moisture and did not reach the maximum (212°F.) until just before the end of the cooking period after the greatest portion of the moisture had been removed.

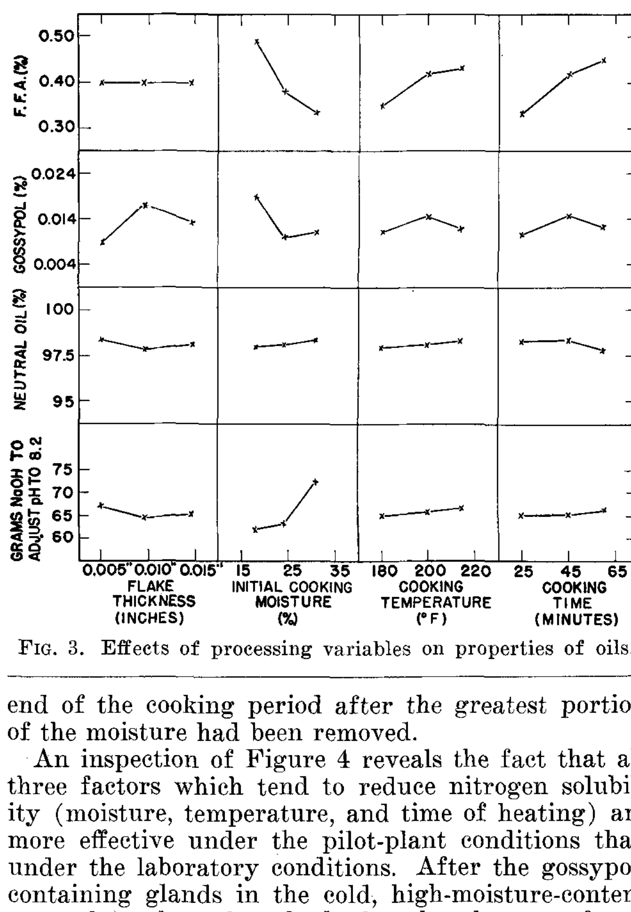

FIG. 3. Effects of processing variables on properties of oils.

An inspection of Figure 4 reveals the fact that all three factors which tend to reduce nitrogen solubility (moisture, temperature, and time of heating) are more effective under the pilot-plant conditions than under the laboratory conditions. After the gossypol-containing glands in the cold, high-moisture-content meats have been largely broken by the use of mechanical agitation, the indications are that a reduction in time or temperature for the cooking operation is desirable, or the desired effects may be accomplished by removal of much of the moisture before the higher cooking temperatures are reached. It is apparent

TABLE III
Oil Evaluation

Cooking conditions					Analytical results			Refining data						
Run no.	Flake thick. (in.)	H_2O initial %	Temp. °F.	Time (min.)	Gossypol %	Neutral oil %	FFA %	Method	NAOH Bé	NAOH G[c]	Loss %	Color refined	Bleached	Flavor
33	0.014	18	180	45	0.021	98.58	0.45	D.C.[a]	12	6.2	6.7	4.8	1.8	Prime[d]
40	0.005	31	180	60	0.004	98.69	0.33	D.C.[a]	12 12	6.0 4.5	5.1 4.1	4.2 4.7	1.3 1.3	Prime
44	0.005	18	214	45	0.013	97.97	0.57	D.C.[a]	12	6.6	6.8	5.1	1.8	Prime
Hyd.	0.009	13	222	60	0.030	97.98	0.86	CUP S.B.[b]	12 14	7.1 6.0	4.4 4.7	5.9 5.2	2.5 2.6	Prime[e] Prime

[a] DeLaval centrifuge. [b] Slow break. [c] G. soln./100-g. sample. [d] Trace solvent. [e] Trace incipient rancidity. Hyd.—Meats from same seed subjected to typical hydraulic cooking and pressing procedure in pilot plant.

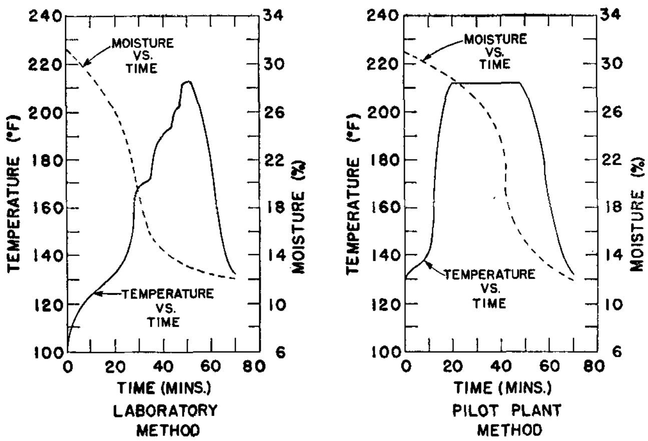

FIG. 4. Comparison of moisture-temperature relationship in laboratory and pilot plant cooking operations.

that the conditions of processing must be carefully selected and carefully controlled if cottonseed meals of the highest nutritive value are to be produced.

None of the variables studied had any significant effect on the neutral oil content of the extracted crude oils. Only three of the 27 oils produced had neutral oil content below 97%. Lower refined and bleached colors were obtained with the oils from the alkali cooks than with the hydraulic type of cooking. Raising the moisture content in the alkali cooks resulted in improved refined and bleached color as well as a lower refining loss by the DeLaval centrifuge refining method.

Summary and Conclusions

Results obtained from alkaline cooking experiments show that all of the four variables studied—cooking moisture content, temperature, time and flake thickness—influenced the properties of the resultant meals in varying degrees. Under the experimental conditions used a high initial moisture content, above 18%, is necessary to lower the free gossypol content in the finished meal to less than 0.04%. When this amount of moisture is used, a plastic mass results at the beginning of the process which requires special equipment to supply the mechanical action necessary to break the pigment glands at a low temperature. In the presence of high moisture content and alkali the gossypol, which is released when the glands are ruptured, is bound to the meal. When sufficient initial moisture is present (24–31%), only traces of gossypol (0.010% or less) are found in the extracted crude oil.

High temperatures in the presence of high moisture content reduce the solubility of the meal protein (in 0.02 N NaOH). Under the conditions of moisture, temperature, and time of cooking used in the experiments the maximum nitrogen solubility obtained under conditions necessary to produce low free gossypol content was 64%. This differs from results obtained in previous work performed under different conditions. A probable reason for the difference is given based on the interrelationship of the three variables.

The results demonstrated further that finer comminution of the raw meats by rolling to 0.005-in. thick flakes results in lower free gossypol content in the finished meal and lower gossypol content of the oils as well as more complete removal of the oil by the filtration-extraction procedure used.

TABLE IV
Chemical Properties of Typical Meals

Run no.	Moisture content %	Residual oil %	Nitrogen solubility %	Free gossypol %	Total gossypol[b] %
33	9.0	2.86	74.8	0.127	1.18
40	8.7	2.66	63.7	0.024	1.20
44	8.8	2.51	61.7	0.068	1.23
Hydraulic[a]	9.1	6.43	76.3	0.103	1.28

[a] Pilot-plant processing.
[b] 46% protein basis.

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Dilatometric Errors and an Application to Volume Changes For the Solid State of Methyl Stearate[1,2]

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A PREVIOUS PUBLICATION from this laboratory dealt with the volume changes associated with the heating and cooling cycles for the solid state of methyl esters of fatty acids (1). These data showed a difference in the shape of curves representing the heating and cooling cycles although the same volume change occurred on both cycles between —38°C. and a temperature a few degrees below the melting point of the particular ester.

The present work involves the establishing of standard errors in dilatometric measurements and the use of these error figures to test the validity of differences found in specific volumes for the solid state of methyl stearate. The effect of past history on

[1] Presented at the fall meeting, American Oil Chemists' Society, Philadelphia, Pa., Oct. 10–12, 1955.
[2] Issued as N.R.C. No. 4178.