TABLE IV

Results of Tests with Castor, Palm, Sperm, and Sesame Oils

Antioxidant[a]	Stability, Hrs. (70 meq. peroxide)			
	Castor	Palm	Sperm	Sesame
None	91	3.0	1.0	4.5
PG	210	3.5	1.0	16.0
BHT	97	4.0	2.0	5.5
BHA	95	4.0	3.5	4.5
R Group of Phenone				
Methyl	139	4.5	3.0	25.0
Propyl	117	4.0	2.5	12.5

[a] Concn. = 0.02% by wt.

TABLE V

Results of Tests with Tallows and Greases

Antioxidant	Stability, Hrs. (20 meq. peroxide)						
	Tallows			Greases			
				Choice white		Yellow	
	Fancy	Choice	Prime	A[a]	B[b]	A[a]	B[b]
None	28	10	23	0.5	1.0	2.0	30.0
BHA	170	>260	83	0.5	46.0	5.0	74.0
PG	89	>260	35	0.5	63.0	3.5	57.0
BHT	95	197	43	0.5	14.0	3.0	32.0
R Group of Phenone							
Methyl	100	>260	31	0.5	10.0	5.5	60.0
Propyl	96	>260	40	0.5	5.0	6.0	71.0

[a] 0.01% antioxidant.
[b] 0.01% antioxidant plus 0.05% citric acid.

metal scavenger, or synergist, the greases were stabilized satisfactorily.

Conclusions

On the basis of AOM tests run to date it appears that 2,4,5-trihydroxyphenones are quite potent antioxidants for many applications. Some of the lower members of the series, such as 2,4,5-trihydroxybutyrophenone, are outstandingly effective in lard, paraffin wax, mineral oil, and peanut oil. In other media, such as cottonseed oil, corn oil, castor oil, sesame oil, and tallows, they are less effective but still fairly active. In greases, palm oil, and sperm oil, they are only moderately effective. Over-all the 2,4,5-trihydroxyphenones compare quite favorably with current commercial products. It would appear that as more testing is done, more applications for these compounds may be found.

Subacute toxicity studies made with 2,4,5-trihydroxyacetophenone and 2,4,5-trihydroxybutyrophenone indicate that they are of a low order of toxicity. Long-term feeding tests on rats and dogs are underway with the butyrophenone, and after four months there are no apparent ill effects.

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Present Status of the Filtration-Extraction Process for Cottonseed[1]

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DEVELOPMENT of the various phases of the filtration-extraction process for cottonseed has been reported in previous papers (1, 2, 3, 4). Since the publication of these papers many important improvements or "process refinements" have been made, and some of these have been applied commercially in the first large-scale plant which was installed in Mississippi. Many of these improvements have been developed on a cooperative basis with the Mississippi Cottonseed Products Company[3] and the Lukenweld Division of Lukens Steel Company.[3]

Improvements or changes in the processing procedures and operating features, which depict the present status of the development of the process for cottonseed, involve the following phases of the process: conditioning of the meats or flakes prior to cooking; extraction temperature; effect of screw conveying both flakes and cooked meats; effect of an open-weave type filter medium; effect of recycling the initial concentrated miscella filtrate; effect of reforming cooked material; effect of cake thickness; and product quality. The following brief discussion of the filtration-extraction process is required better to understand the application of the process refinements.

Essential steps of the process are shown in Figure 1. Prepared cottonseed flakes are cooked in conventional four-to-six-high stack cookers, using lower temperatures and shorter cooking time than normally used for hydraulic cooking. Moisture content of the material is maintained throughout the cooking period at levels higher than for hydraulic cooking. The cooked material is "crisped" by evaporative cooling and by reducing the size of any large agglomerates formed during the cooking operation. The conditioned material is mixed with one of the miscella filtrates to form a slurry which is held for 25 to 40 min. The slurry is filtered, and the resulting cake countercurrently washed three times on a horizontal rotary vacuum filter. Total time on the filter is only 2 to 4 min. The solvent damp extracted meal (marc) is discharged to a conventional desolventizer for meal and solvent recovery. The concentrated miscella is pumped to the oil recovery system for separation of oil and solvent.

Conditioning of Meats or Flakes. Cottonseed used in the earlier pilot-plant runs had a normal average moisture content of 9 to 11%. The moisture of the resulting flakes was increased to the required 16 to 22% in the first or second ring of the cooker. In some of the recent runs the use of cottonseed having a moisture content of 6 to 8% showed the preferability of altering the method of adding the water. The drier meats from this seed tended to produce more fines when flaked to 0.008 to 0.010 in.; and the resulting flakes required the addition of more water to at-

[1] Presented at the 45th annual meeting of the American Oil Chemists' Society, San Antonio, Tex., April 11-14, 1954.

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

[3] The Agricultural Research Service has memorandum of understanding with this Company.

tain a cooking moisture comparable to that used for the wetter seed. It was found that better results were obtained by adding part of the required cooking moisture to either or both the meats and flakes prior to cooking. Sufficient water is added to increase the moisture content of the flakes going to the cooker to 11 to 13%. By this procedure the diffusion of the water and agglomeration of fines begins before the cooking step, and a more uniform intermixing of water and flakes is attained in the cooker.

Effect of Screw Conveying on Prepared Material. In designing the first commercial filtration-extraction plant (installed in Greenwood, Mississippi), the problem arose of transferring the cooked material a distance of over 450 feet from the cooker to the solvent building due to the location of existing equipment. The use of screw conveyers was desired by both the manufacturer and the oil mill because of the lower cost of screw conveyers as compared to other conveying equipment, such as belt conveyers. But it was conceivable that screw-conveying cooked material for that distance might undo the desirable agglomeration and particle size distribution attained during the cooking and crisping steps. Physical degradation might actually be sufficient to hamper the filtration operation.

A test was conducted in the pilot plant in which cooked cottonseed material, prepared as is normally done for filtration-extraction, was repassed through a 17-ft. conveyer, 6 in. diameter, until the total conveying distance was 500 ft. Periodic samples were taken for filtration-extraction tests. These tests showed an appreciable decrease in mass velocity (lbs. of filtrate per hour per sq. ft. of filtering area) with distance of conveying. For example, in a test in which the screw conveyor turned at 37.5 r.p.m., a sample taken at 34 ft. had a mass velocity of 4,570 as compared to 1,000 for the sample taken at 510 ft. For practical operation the prepared material for extraction should have a mass velocity above 2,000.

Method of Crisping. The original method of crisping the cooked material was another phase of the process that was considered impractical for commercial use. The cooked material was spread in thin layers on open trays for 10 to 20 min. to attain an evaporative cooling effect which would decrease the moisture content by 2 to 4% and decrease the temperature to 130 to 150°F. Large lumps were broken up by hand. The later method developed for the crisping operation was to discharge the cooked material from the cooker to a screw conveyer, the top of which was opened for the first half and hooded for the last half to permit the movement of air over the material by aspiration. Large agglomerates were broken up by the screw conveyer. The conveyed material was discharged on a shaker screen as discussed below. The combination of screw conveying, movement of air over the material, and screening effected the desired continuous crisping action considered practical for commercial operation.

Screening versus "Reforming" Cooked Material. For the early test runs cooked material was "reformed" by passing the material through a set of smooth rolls to break up large agglomerates formed in the cooker and to reduce size of hull enclosed meat particles. To re-roll the warm, cooked material did not appear commercially practical either economically

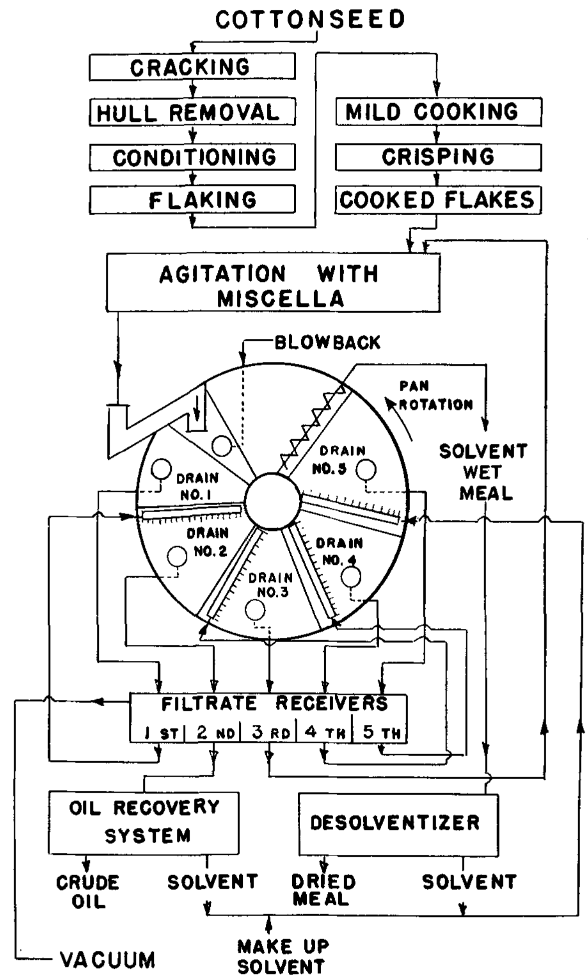

FIG. 1. Flow diagram for the filtration-extraction process.

(cost of expensive rolls) or from the operational viewpoint. A procedure was devised in which the cooked material was screened over an 8-mesh screen, and the overs, amounting to about 10% of the total material, were put through a hammer mill to break up the large agglomerates. This appeared to be a satisfactory procedure and was used in the recent pilot-plant runs.

Effect of Temperature. Recent pilot-plant runs have shown that slurrying (extraction) and filtration steps can be conducted at temperatures of 110-130°F. Reduced pressures of up to about 10 in. Hg. can be used at these temperatures without any appreciable effect upon filtration characteristics. Extraction efficiency is improved as shown in a pilot-plant test run in which the extraction temperature was increased from room temperature (about 76°F.) to 110°F. Residual lipids decreased from 1.13 to 0.73%.

Effect of Filter Media. Several filter media have been tried since undertaking the developmental work for the filtration-extraction process. In the pre-pilot-plant study (4) a 20 x 250 twilled Dutch wire filter cloth proved much more satisfactory than canvas duck material. In the early pilot-plant runs the 20 x 250 twilled Dutch wire filter cloth was replaced with a 24 x 110 plain Dutch weave wire filter cloth (4), which was more sturdy, gave better filtration rates, was less expensive, and yet permitted satisfactory fines retention.

As the process showed commercial possibilities, a more open-weave filter medium was desired. The purpose was to insure the maintenance of a clean filter medium, with the filter blowback arrangement, for continuous 24-hr.-per-day operation. Investigation of filter media showed that No. 942 Saran [4] and a 60 x 60 mesh plain weave stainless steel wire cloth gave satisfactory results although the latter was considered more sturdy. The 60 x 60 mesh medium was consequently used in two 24-hr. pilot-plant runs conducted with rice bran and cottonseed. No sign of plugging was evident at the end of these runs, nor at the end of the recent pilot-plant runs, all of which were conducted with the same filter medium.

The fines in the first filtrate increased from an average of 0.20 to 0.50% in changing from the 24 x 110 mesh screen to the 60 x 60 mesh screen. The increase in fines however was more than overcome by the development of a method of recycling the first filtrate.

Effect of Recycling the First Filtrate. The filter was altered to permit an additional "wash" space on the filter as shown in the flow diagram. The first miscella filtrate, obtained from the initial filtration of the slurry deposited onto the filter, is pumped back onto the filter at a point immediately after the cake is formed. The cake acts as a filtering medium to remove the bulk of the fines from the first filtrate. This second filtrate then becomes the product miscella, which is pumped to the oil recovery system. This recycling procedure reduces the fines content to about 0.03 to 0.05%.

Effect of Cake Thickness. Although the early pilot-plant runs were conducted with a 1-in. cake on the filter, a 2-in. cake was used in most of the later pilot-plant runs. Tests with other oil-bearing materials, as well as with cottonseed, had shown that the 2-in. cake gave the best results with prepared material having the desired filtration-extraction characteristics. Increasing the cake thickness from 1 to 2 in. tended to decrease residual lipids in the cake without any appreciable decrease in mass velocity. The thicker cake also improved the fines retention and minimized the effect of any unevenness in the cake surface.

Product Quality. Crude cottonseed oils produced from cooked cottonseed meats by the filtration-extraction process, using five different lots of seed, were evaluated for color stability under severe storage conditions. Comparison was made with oils produced from the same lots of seed by hydraulic pressing of cooked and uncooked flaked meats and by direct solvent extraction of uncooked flaked meats. Changes in the quantity of gossypol-like materials in the crude oil occurring during storage have been studied to determine any relationship of the changes to the color stability of the oils.

Data showed that the color of most of the filtration-extraction cottonseed oils were relatively stable under severe storage conditions. Color stability was slightly better than that obtained with oils produced by hydraulic pressing and direct solvent extraction of uncooked flaked meats. Some of the hydraulic pressed oils which were initially slightly better in color had a higher rate of reversion and resulted in final oil colors, after storage, that were similar to the colors of the comparable filtration-extraction processed oils. No quantitative relationship could be established between the amount of gossypol-like materials which disappeared during storage and the increase in red color of the refined and bleached oils. Gossypol loss and red color increase appear to be related, but apparently other factors such as degree of gossypol breakdown, age and nature of the seed, and the presence of other minor components affect the relationship.

Commercial Application of the Filtration-Extraction Process. Many of the above process modifications, as well as the earlier pilot-plant data, have been applied to the first commercial filtration-extraction plant, recently designed and placed into operation for the Mississippi Cottonseed Products Company, Greenwood, Miss., by the Lukenweld Division of the Lukens Steel Company.

Meats preparation conditions for filtration-extraction at Greenwood were obtained with minor modifications of the existing equipment. It was necessary only to install pipe lines, including rotameters, to permit the addition of water and steam to the second ring of the cooker and water to the flakes in the conveyer between the rolls and the flake surge bin. The flakes were fed to the cooker from the surge bin at a constant rate; the excess was discharged into a "run around" conveyer and back to the surge bin.

As in the pilot-plant runs, the dry seed being processed at Greenwood was better prepared for filtration-extraction by the addition of part of the water to the flakes. Good operation was obtained with flake moisture increased up to 11 to 12%. Above 12% moisture tended to hamper operations in that the opening to the first ring of the cooker would periodically plug. Addition of all of the required moisture into the cooker resulted in lower mass velocities verifying the pilot-plant findings.

Crisping was attained by discharging the cooked material to an open-top 10-ft. conveyer and then to an aspirated bucket elevator and aspirated belt conveyer. Two belt conveyers were installed to convey the cooked material 450 ft. from the preparation building to the solvent extraction building. The use of a shaker screen installed at the end of the first belt and start of the second belt was not deemed necessary when operation got under way.

The conditions used in the extraction and product recovery end of the process were comparable to those used in the pilot-plant work. The following examples are given: extraction and filtration temperatures are 115 to 125°F.; filter medium is a 60 x 60 mesh plain weave stainless steel screen; first miscella filtrate is recycled; a cake thickness of 2 in. is used; the solvent to cooked meats ratio is about 1.1 to 1; mass velocities of 2,500 to 3,000 were attained; vacuum requirements were 7 to 11 in. of mercury. The oil and solvent from the miscella, and meal and solvent from the marc were recovered in conventional equipment.

Summary

Improvements and refinements in the process for filtration-extraction of cottonseed resulting from further pilot-plant development studies are described as well as their adaptation to the first commercial plant. These improvements which depict the present status of the process for cottonseed include principally certain modifications in the method of conditioning of the meats or flakes prior to cooking and in the pro-

[4] The mention of trade products does not imply that they are endorsed by the Department of Agriculture over similar products not mentioned.

cedure for crisping; selection of best conveyor type for conveying cooked material over relatively long distances without objectionable comminution; selection of filter medium combining the desired properties of durability, non-fouling, and low fines retention; determination of optimum filter-cake thickness; and development of a method for clarification of the product miscella by continuous recycling through the formed cake on the filter. Also discussed is the quality and color stability of the oil produced from comparable lots of cottonseed by the filtration-extraction process, as compared with that by hydraulic pressing, and by solvent extraction of uncooked flakes.

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Solvent Extraction of Fish Offal[1]

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SOLVENT EXTRACTION, which has been applied extensively to certain oilseeds, such as soybeans, has had a relatively limited application to fish and fish products. Most of these applications have been to fish livers or whole fish (1, 7, 8). The large amounts of fish offal and surplus fish which are wasted or inefficiently processed have aroused an interest in the industry in the application of continuous countercurrent solvent extraction to these materials.

This investigation is concerned primarily with the solvent extraction with trichloroethylene of fish meal produced by the wet cooking of fish wastes. The material used in this study contained from 13 to 19% oil and 20 to 45% moisture and was prepared for extraction in the laboratory static-bed rate extractions by passing it through a Universal No. 2 household food chopper with a coarse cutter. The material used in the pilot plant model of the Iowa State College extractor was prepared for extraction by passing the fish meal through a John Deere No. 10-A hammer mill operating at 3,150 r.p.m. with a screen having ½-in. square openings.

Laboratory Studies

The laboratory data were obtained by means of normal static-bed rate extractions. The apparatus (4) for this investigation consisted of a 1-in. jacketed glass tube with the necessary auxiliaries to permit the bed of fish meal and the incoming solvent to be maintained at a constant temperature. The overflow miscella rate was 10 ml. per minute.

The screen analysis of the fish meal after passage through the food chopper is given in Table I. The variables investigated in the laboratory were temperature, particle size, moisture, and wetting agents. The results of these experiments for the first three variables are given in Figures 1, 2, and 3.

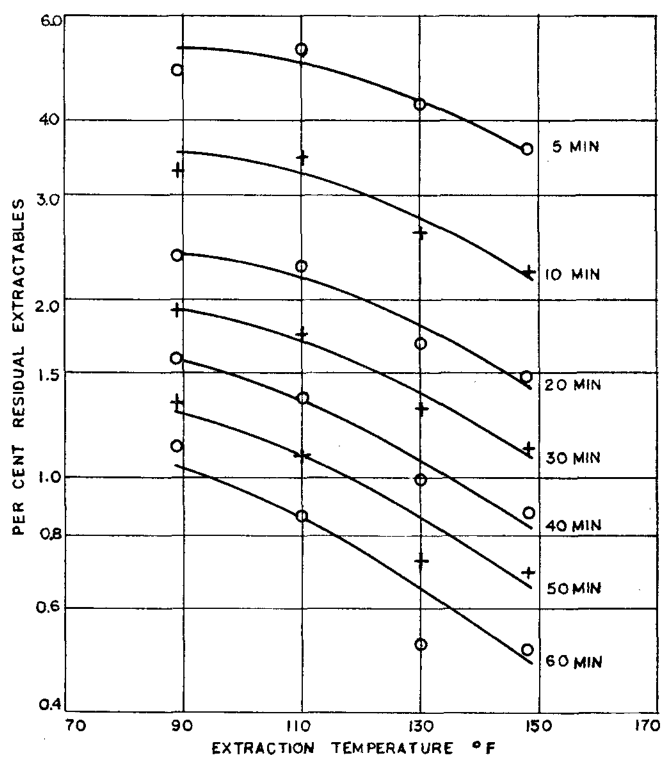

FIG. 1. Variation of residual extractables with temperature in laboratory studies.
Moisture content of feed: 25.4%
Residual extractables on moisture-free basis.

The fish meal used in the study of the effect of temperature on the extraction had a moisture content of 25.4%, and it will be shown later that moisture content influences the results appreciably. The effect of temperature on the residual extractables[2] is not great because the extracting solution is almost pure

[1] Presented at fall meeting, American Oil Chemists' Society, Minneapolis, Minn., Oct. 11-13, 1954.

[2] Residual extractables are determined by means of a Soxhlet extraction using trichloroethylene as a solvent. The ratio of hexane extractables to trichloroethylene extractables has been found to be 0.86.

TABLE I
Screen Analysis of Fish Meal Used in Laboratory and Pilot Plant Studies

U. S. Screen Size	Screen opening	Percentage passing screen	
	Inches	Laboratory	Pilot plant
....	0.371	98.3	94.5
3	0.263	90.7	87.2
4	0.185	72.4	81.8
6	0.131	58.4	77.4
8	0.093	42.1	70.5
12	0.065	27.7	60.8