THE JOURNAL OF THE American Oil Chemists' Society

Volume 32 DECEMBER, 1955 No. 12

Measurement of Extractability of Raw and Cooked Cottonseed Flakes[1]

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LOW RESIDUAL LIPIDS in the extracted meal, one of the primary requirements of a good solvent extraction process, is obtained primarily as a result of two separate factors, *viz.*, first, high extraction rate or extraction efficiency of the solid matrix in the oil-bearing material and, secondly, high washability characteristics. It is well recognized that any given material may have high extractability, yet if it possesses poor washing characteristics as indicated by large solvent hold-up and poor percolation characteristics, it may extract finally to a high residual lipids content derived from the entrained and incompletely washed-out miscella. High residual lipids may also result with a material having good washability characteristics but with low intrinsic extractability. Separate evaluation of these two factors in respect to meal under extraction becomes essential for deciding whether improvements are needed on the extraction side or on the washing side of the process in order to bring the final lipid content to the desired level. The results reported in this communication are confined mainly to the study of extraction rates and extraction efficiencies of raw and cooked cottonseed flakes.

In conventional extraction systems it becomes difficult to determine separately the extent to which either extraction or washing has proceeded since both processes proceed more or less simultaneously. The rate and degree of extraction for any given flaked material depend on many independent and interdependent variable factors, important among them being condition of the material such as raw or cooked, flake size and thickness, lipids content, moisture content, degree of agitation, concentration of the extracting miscella, relative proportions of the meal and the miscella, temperature of extraction, contact time, static hold-hold-up, percolation rate, type and size of extractor. Extractability of cooked meats as compared to that of raw meats has not been studied extensively, but cooking is generally believed to improve extractability. The cooking-crisping operation is an important step in filtration-extraction (2). Since this process is unique in that actual extraction of the oil takes place in relatively concentrated miscella, it therefore becomes essential to know how and to what extent extractability of raw flakes in various miscella concentrations is affected by the standard cooking and crisping procedures.

Extraction rate studies on oleaginous materials have been widely reported in the literature. The studies have been carried out with various objectives and employ a wide variety of techniques to suit these objectives. Theoretical considerations entering into such studies have been excellently summarized by Coats (1), Fan *et al.* (3), Smith (7), and Karnofsky (5). Need for a rapid, convenient laboratory method for determining extraction rates as a supplement to large scale studies has been emphasized by Wingard and Shand (8), who suggest two simple methods, the percolation method and the batch co-current method. The theoretical studies chiefly aim at understanding the mode of mass-transfer between the solid and the liquid phases and also within the solid phase itself, under conditions which by no means can be considered steady or uniform. Attempts have also been made to formulate extraction or diffusion coefficients which could characterize the extraction operation or could be predicted on the basis of the physical properties of the various components in the extraction system. Such studies have helped to bring out the fact that an ordinary seed flake is highly complex in structure and consists of components having varying extractabilities. Further the extraction operation itself is a composite of operations such as wetting, diffusion, solution, osmosis, dialysis, etc., each proceeding at an unknown and variable rate. Extraction rate therefore should be considered as specific for each type of material, depending on its composition and past history, and generalizations can apply to only a restricted class of materials or systems possessing closely comparable properties.

In the present study no attempt has been made to investigate any theoretical aspects of the problem. The objective was: a) to devise a workable laboratory method to permit measurement of true comparative extraction rates under simple and well defined conditions; and b) to compare the extraction rates of raw and cooked cottonseed flakes at three-flake thicknesses (.005 in., .015 in., and .025 in.) and in three concentrations of miscella (0% oil, 25% oil, and 50% oil). Such a method would serve as a valuable adjunct to the presently used bench-scale technique (4) in connection with the operation of commercial filtration-extraction plants and in the evaluation of various oil-bearing materials for processing by filtration-extraction. In the measurement of intrinsic extraction rates uncomplicated by washing effects, until a method is devised which enables measurement of the oil con-

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tent of the extracting miscella without in any way disturbing the extraction bath, one has necessarily to fall back on elementary gravimetric methods such as those suggested by Wingard and Shand. "Intrinsic extraction rate" as used herein is defined as the rate at which the lipids come out of the porous solid phase into the surrounding liquid miscella without interference by diffusional effects in the liquid phase, and the amount extracted is measured by the enrichment in concentration of the miscella. In the percolation method suggested by Wingard and Shand it is doubtful whether such intrinsic extraction can be obtained. Besides, duplication of results is likely to be vitiated by variation in the packing of the solids and by differences in the drainage of the extracting miscella through the percolating mass. The batch co-current method, on the other hand, is eminently suitable regardless of particle size of the extracting material for isolating intrinsic extraction by agitating the miscella into instantaneous equilibrium concentrations. The batch co-current method has hence been used throughout these investigations, and modifications have been suggested to improve accuracy in sampling and measurements with relatively concentrated miscellas and in simplification of the setup and procedure.

Experimental

Extraction Materials. The cottonseed used in the preparation of flakes in this investigation was a prime quality seed obtained from the Planters Oil Mill at Greenwood, Miss. The seed was of normal growth, unsterilized, and was delinted at the mill. Approximately 500 lbs. were moistened before hulling in order to raise the moisture content of the meats from 7.5 to approximately 9.5% so as to insure well-formed flakes. This operation was performed by spraying the excess water on the seed under agitation in a feed mixer, followed by a storage period of 96 hrs. for equilibration. The seed was hulled and separated in small-scale Carver [5] machines to produce 140 lbs. of large meats (whole and half-size) essentially free of hulls (<1%). The reason for using large meats was to ensure that all meats received practically the same distortion (6) (work done on) in flaking and to preclude any possibility of small meats passing through the rolls unflaked. The meats were uniformly mixed in a drum-roller and stored at 33°F. in sealed cans.

Raw Flakes. Five-pound lots were prepared of each of the following thicknesses: .005 in., .015 in., and .025 in. Rolls used were Allis-Chalmers,[5] one-pair high, 12 in. diameter x 12 in., turning at 220 r.p.m. Each lot was prepared separately from the temperature-equilibrated meats 2 hrs. before beginning the series of extraction tests in the three miscella concentrations conducted on that lot. The flakes were screened to remove all traces of hull particles. During the 36-hr. period required to complete the series the flakes were stored at 40°F. in sealed tins. Table I gives the final characteristics of the raw flakes used in the extraction experiments. Although the moisture content was somewhat lower than the 9.5% planned (*ca.* 1.1% loss in flaking and handling), the flakes were of sufficient firmness and structural stability to withstand the agitating action in the extraction baths. Size M, which was separately prepared from somewhat wetter meats, was included to show the effect of higher moisture content.

Cooked Flakes. A 15-lb. lot of each of the three-flake thicknesses was prepared for the three series of tests on the cooked flakes. The meats withdrawn from cold storage were flaked as promptly as possible after temperature-equilibration, and cooking was carried out within 1 hr. after flaking.

The equipment unit used for cooking was a Loomis [5] mixer, size 12 in. x 12 in., equipped with steam-heated sigma mixing blades and having steam-jacketed walls and bottom. Cooking was conducted in accordance with the typical procedure used for filtration-extraction designed to give a material of optimum filterability characteristics through proper moisture adjustment and drying followed by evaporative cooling (crisping). The procedure comprised the following steps: pre-heating of raw flakes charge to 170°F. in 10 min.; water addition to increase moisture content to 20.0% in 4 min.; heating to 212–214°F. in 16 min.; controlled drying at 214°F. to 9–11% moisture content in 15 min. The cooked material was then discharged from the mixer, screened (8-mesh), and spread on a pan to cool evaporatively to room temperature. It was later screened through a 10-mesh screen to remove any remaining hull particles and small agglomerates.

Each lot of cooked and crisped flakes was prepared within 2 hrs. before beginning the series of three extraction tests with that lot. As with the raw flakes, the cooked material was stored at 40°F. during the 36-hr. period required to complete the series. The final cooked material had the physical characteristics and analysis as shown in Table I.

Oil. Deodorized, winterized salad oil (Wesson [5]) purchased in sealed tins was used for preparation of the miscellas in the extraction tests. The oil had practically no moisture content and only negligible (<0.015%) free fatty acid content.

Hexane. Hexane used for extraction was commercial hexane (Skellysolve B[5]), which on evaporation left a residue of less than 0.0005%.

[5] In using the names of manufacturers of equipment or products, it is understood that their equipment or products are not endorsed or recommended over that of other manufacturers.

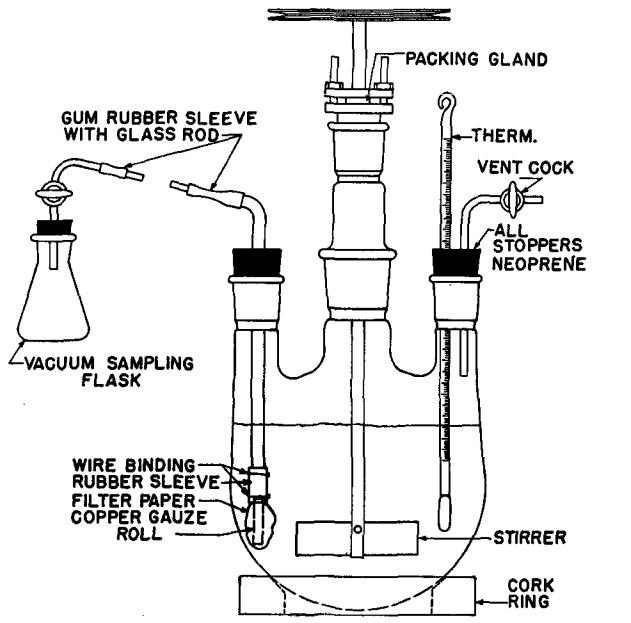

FIG. 1. Laboratory extraction bath assembly for determination of extraction rates.

TABLE I
Characteristics of Raw and Cooked Flakes

Flake Thickness, Inch	Screen Size Mesh		Moisture,[a] %		Residual[b] Lipids (M.F.B.), %[c]	
	R	C	R	C	R	C
0.005	10–30	10–20	8.18	9.54	37.06	35.68
0.015	3–5	10–20	8.54	8.24	....	....
0.015M[d]	3–5	....	9.85	....	....	....
0.025	3–5	10–20	8.24	9.57	....	....

[a] Official A.O.C.S. Method Ba 2-38.
[b] Official A.O.C.S. Method No. Ba 3-38, but using commercial hexane.
[c] Moisture-free basis.
[d] Prepared from meats of higher moisture content.

Extraction and Sampling Apparata. The extraction bath consisted of a 3-necked 3,000-ml. round-bottom flask mounted on a cork ring (Fig. 1). The central wide neck carried a vapor-tight stirrer and also served as inlet for addition of flakes. The stirrer was mounted in a ground glass joint with packing gland and carried a flat 1 in. x 2½ in. stainless steel blade situated about 1½ in. from the bottom of the flask. The stirrer was actuated by compressed air motor. The other two necks carried stoppers with a thermometer and vent stop-cock in one and the sampling filter-tube in the other.

Extensive exploratory work suggested many modifications to the original set-up and procedures as employed by Wingard and Shand, which could ensure easier manipulation, more speed in assemblage, and accuracy in measurements. Repeated checks showed that extractions carried out with agitation over a period of an hour at 200–250 r.p.m. with 1,300 g. of hexane in the bath at temperatures of 80–82°F. in an air-conditioned room entailed practically no loss of hexane (<0.1 g.) hence the water-cooled condenser used by Wingard and Shand was dispensed with. A condenser however may be necessary for extractions at higher temperatures. Sampling with fritted capillary filters was found too slow to draw a sufficient quantity of sample in a reasonable amount of time on account of rapid blinding. In its place a filtering device was used which consisted of a No. 40 Whatman[5] 12.5 cm. filter paper carefully folded over a roll of copper gauze which together could be tightly slipped into a short neoprene rubber sleeve that in turn could be slipped over the submerged end of the 8-mm. glass filter-tube. The discharge end of the filter-tube was drawn out to accommodate the small diameter rubber sleeve. Joints between the filter, rubber, and glass were made tight with steel wire bindings. Such a filtering device enabled withdrawal of about 40-cc. miscella samples completely free of fines and within 10–15 seconds under moderate vacuum. Sampling flask was a 60-cc. conical flask with ground neck, carrying a single-hole rubber stopper fitted with a bent inlet tube with stop-cock, over the end of which was slipped a piece of tightly fitted rubber tubing with a glass-rod piece. This arrangement made unnecessary the 3-way stop-cock used for breaking vacuum. Glass joints were lubricated with hexane-insoluble starch-glycerine paste.

Extraction and Sampling Procedures. Proportions of hexane, oil, and flakes added into the extraction bath for the various tests were selected so to give specific representative conditions. The amounts used were so chosen as to provide a solvent-to-flakes ratio of 10:1 throughout, also the same approximate volume of liquids in the flask for all concentrations of the extracting miscella. Weights of hexane, oil, and flakes for the tests with 0% miscella concentration were 1,300, 0, and 130 g., respectively; with the 25% concentration, 1,050, 350, and 105 g.; and with the 50% concentration, 770, 770, and 77 g. The solvent ratio was sufficiently high to ensure resultant miscella concentrations at the end of the extraction only slightly higher than the respective starting levels. (Resultant concentrations were *ca.* 3.2, 26.8, and 50.8% oil, respectively.) In each case hexane was weighed correct to 0.1 g. Oil was weighed correct to 0.001 g. and transferred with hexane into the extraction bath. Flakes were weighed separately in a beaker, together with a funel and rod, correct to 0.001 g., and the actual weight was determined by difference after transfer into the extraction bath.

In charging, the extraction flask was first stoppered and weighed on an accurate torsion balance to 0.1 g. The oil (no oil in the case of 0% miscella) was transferred, using the bulk of the calculated amount of hexane, and the remainder was added, correct to 0.1 g. The oil and hexane were thoroughly mixed by gently handshaking the stoppered flask to insure requisite strength of the extracting miscella from the start. The flask containing the miscella was then mounted on a cork ring under the agitator assembly. Flakes were quickly added through the central neck by means of the funnel and rod, and the neck was quickly closed with the vapor-tight stirrer, and agitation started at 200–250 r.p.m. Stop-watch was started when the meal was half added. The interval between the starting of the stop-watch and starting of agitation was less than 2 min. The speed of the stirrer in each case was regulated so as to tumble the meal in suspension without positive comminution and was fast enough to effect almost instantaneous equalization of concentration in the liquid phase.

Samples of miscellas were drawn at the desired time intervals in the following manner. After the bath became stabilized, which took nearly 5 min. from start, the sampling filter-tube carrying a stopper was inserted through one of the necks. About 20 seconds before drawing a sample the filter-tube was thoroughly wetted by aspirating the miscella up and down the tube by means of a rubber bulb (previously filled with hexane vapor) attached to the end of the filter-tube. This obviated any loss of hexane vapor and purged the filter tip and the tube of any previous miscella concentration. Before conducting a typical test, the five sampling flask assemblies were each weighed correct to 0.1 mg. In taking a sample, the assembly was evacuated to a previously adjusted vacuum and then connected to the end of the filter-tube. On opening the stop-cock on the sampling flask and the vent stop-cock on the extraction flask, requisite amount of miscella sample could be drawn under equilibrated conditions which allowed the hexane vapors to condense. The rubber sleeve was then carefully detached from the filter-tube, and the rod was immediately inserted in the end. The open end of the filter-tube was also similarly sealed. The sampling assembly was then weighed to give by difference the weight of the miscella drawn. The above procedure ensured in the sampling flask almost the same equilibrium conditions between the hexane vapor, air, and miscella as present in the extraction bath so that any vapor space corrections were unnecessary. Test runs and blank tests (described below) showed that such equilibrated conditions were necessary to ensure

TABLE II

Typical Extraction Test Data

Material-Cooked Cottonseed Flakes		Miscella Concentration, %	25.00
Material flake thickness, in.	.015	Wt. oil, g.	350.000
Material moisture, %	8.24	Wt. hexane, g.	1050.0
Material wt., g	104.970	Temp. extraction, °F.	82–84
Material total extractables (M.F.B.), %	35.68	Stirrer Speed, r.p.m.	230

Time, min.	Oil in sample, g.	Hexane in sample, g.	Hexane in bath, g.	Oil in bath, g.	Oil extracted per 100 g. flakes, g.	Residual lipids, % (M.F.B.)	Residual lipids, % (M.O.F.B.)	Extraction efficiency, %
0	0	0	1050.0	350.00	0	35.69	55.49	0
7.5	7.4695	20.5180	1050.0	382.76	31.21	1.68	2.60	95.3
15	6.8393	18.7553	1029.5	375.41	31.32	1.55	2.41	95.6
25	4.3003	11.7821	1010.7	368.90	31.64	1.21	1.88	96.6
40	7.6104	20.8371	998.9	364.83	31.86	0.97	1.50	97.3
60	7.1474	19.5532	978.1	357.53	32.16	0.64	1.00	98.2

duplicate and accurate results, particularly with miscellas of high concentration. Samples were withdrawn at intervals of 7.5, 15, 25, 40, and 60 min.

After ascertaining the weight of each miscella sample, the stop-cock attachment on the sampling flask was carefully washed down with hexane into the flask and the major part of the hexane was evaporated on the steam bath, using a mild jet of air to minimize ebullition and possible resultant carry over. A few small porcelain pieces previously added to the flask ensured smooth evaporation without bumping. Since, in the final results, weights of hexane and oil in the extraction bath at the time of sampling were to be calculated on the basis of the small quantities drawn in the sample, it was necessary that the sampled miscellas be completely desolventized to give oil weights correct to 0.5 milligram. Last traces of hexane from the 12-g. samples of oil could be removed only under drastic vacuum (1–2 mm.) for 2–4 hrs. with a jet of nitrogen impinging on the surface of the oil. The nitrogen desolventization assembly designed to handle five samples at a time is shown in Figure 2. A small

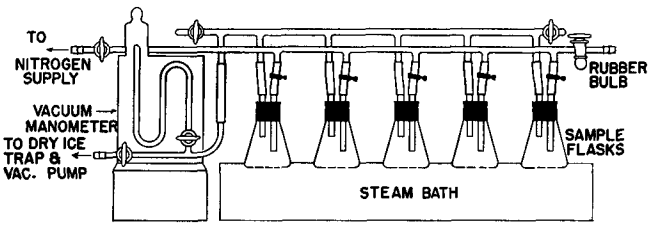

FIG. 2. Laboratory assembly for vacuum desolventization of samples with nitrogen.

rubber bulb attached to the nitrogen line facilitated breaking of the vacuum with nitrogen without developing excessive pressure in the system.

The sample flasks after desolventization were cooled in vacuum desiccators and weighed under stoppers against an empty tare of the same size and shape. This prevented errors in weights due to temperature fluctuations, moisture depositions, and possible absorption of hexane from the laboratory atmosphere. Also it was found necessary to desolventize completely in vacuum any rubber attachments used in the weighing assembly before reuse. A typical example of data obtained in an extraction test together with a sample calculation of residual lipids and extraction efficiency based on the usual material balance procedure is shown in Table II.

Blank Tests. It has been rightly emphasized by Wingard and Shand that "the method, depending as it does on measurement of small differences in relatively larger quantities, demands extreme care in experimental manipulation, precision of weighing, and mathematical treatment of the results." It was observed that care was all the more necessary in handling miscella concentrations as high as 50%. It can be calculated that with sample weights used herein of approximately 1, 7, and 12 g. of oil, respectively, for the miscella concentrations of 0%, 25%, and 50% oil, the magnitude of the error in the final percentage of residual oil (m.f.b.) content that is attributable directly to a 1-mg. discrepancy in the weight of a desolventized oil sample, is equivalent to .03%, .05%, and .09% for the 0%, 25%, and 50% miscellas. Similarly the magnitude of the error due to a 1-mg. discrepancy in the hexane weight of a miscella sample is equivalent to .001%, .02%, and .08%, respectively, for the three miscella concentrations.

In order to ascertain whether vapor space corrections were necessary and whether the procedure adopted gave sufficiently accurate and duplicate results, blank tests were carried out with procedure identical to that in the actual extraction rate tests, but without adding flakes, and then back calculating from the samples the total amount of hexane initially added to the bath. Sample blank test results obtained with 50% miscella are given in Table III. Similarly,

TABLE III

Typical Results of Blank Tests

Wt. of hexane	770.0 g.	Temp., °F.	82–85
Wt of oil	770.000 g.	Stirrer speed, r.p.m.	230

Time, minutes	Sample: Wt. of Oil, g.	Sample: Wt. of Hexane, g.	Calc. Wt. of Hexane in Bath, g.
7.5	8.9608	8.9634	770.22
15	9.2499	9.2573	770.62
25	10.2350	10.2360	770.05
40	9.6506	9.6472	769.73
60	10.7964	10.7887	769.45

blank tests, made with each of the other two miscella concentrations used, showed definitely that procedures adopted were such as to represent correctly conditions in the extraction bath and that the loss of hexane during extraction was too insignificant to be taken into account in the calculations.

Total Extractables. In order to express all extraction rate results in terms of comparative residual lipids it was necessary to adopt a common basis for evaluating total extractables. Total extractables were determined on the finest size (0.005 in.) of the raw and cooked flakes by two methods. In one, the A.O.-C.S. official method Ba 3-38, but using hexane, was employed. In the other method sealed extraction bath flasks identical with those set up for measuring ex-

traction rates at the three miscella concentrations were set up and allowed to stand at room temperature (82–84°F.) for an extended period under daily handshaking. After 10 days' extraction time the total extractables were determined by employing the identical sampling procedure used in the extraction rate tests. The results (Table IV) showed that a slightly

TABLE IV
Total Extractable in Raw and Cooked Flakes

Miscella Concentration, %	Raw Flakes (0.005 in.)		Cooked Flakes (0.005 in.)	
	Extractables by A.O.C.S. (M.F.B.), %	Extractables by 10 days' Soaking (M.F.B.), %	Extractables by A.O.C.S. (M.F.B.), %	Extractables by 10 days' Soaking (M.F.B.) %
0	37.06	36.92	35.69	35.37
25	37.06	36.91	35.69	35.20
50	37.06	36.95	35.69	35.56

higher percentage of lipids was extracted by the A.O.C.S. official method than by 10 days' soaking and that the change in miscella concentration made practically no difference in the amount extracted. Also noted in Table IV is that hexane extracted a considerably higher percentage of lipid material from the raw than from the cooked flakes. Contrasts in the color shades of the miscella were particularly noticeable. While those from the raw flakes were tinged deep red, the ones from cooked flakes were light yellowish brown, indicating the fixation in the meal of gossypol and other color bodies during cooking of cottonseed flakes.

Results and Discussion

The rates of extraction with hexane of raw and cooked cottonseed flakes of different thicknesses, prepared as stated, and extracted with different concentrations of miscella under the specified conditions of time, temperatures, agitation, solvent ratio, and flake moisture content are shown by the graphs in Figures 3, 4, and 5. The percentage of residual lipids is expressed herein on a "moisture- and oil-free basis" (m.o.f.b.) since this basis is most suitable where small changes over a narrow range of lipid content are to be represented graphically.

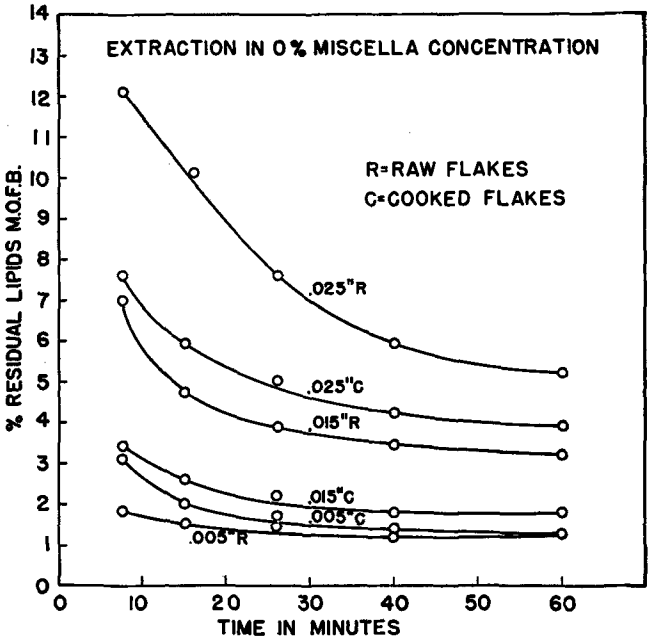

FIG. 3. Extraction rates of raw and cooked flakes of various thicknesses in hexane miscella of 0% oil concentration.

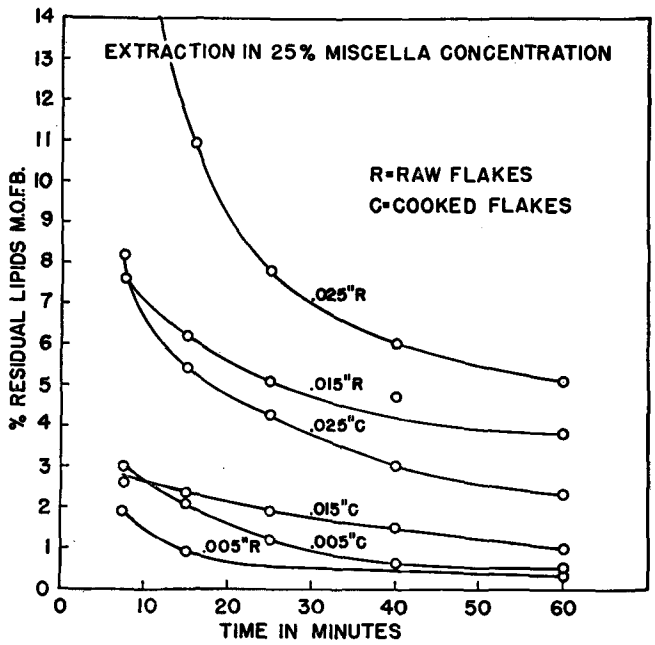

FIG. 4. Extraction rates of raw and cooked flakes of various thicknesses in hexane miscella of 25% oil concentration.

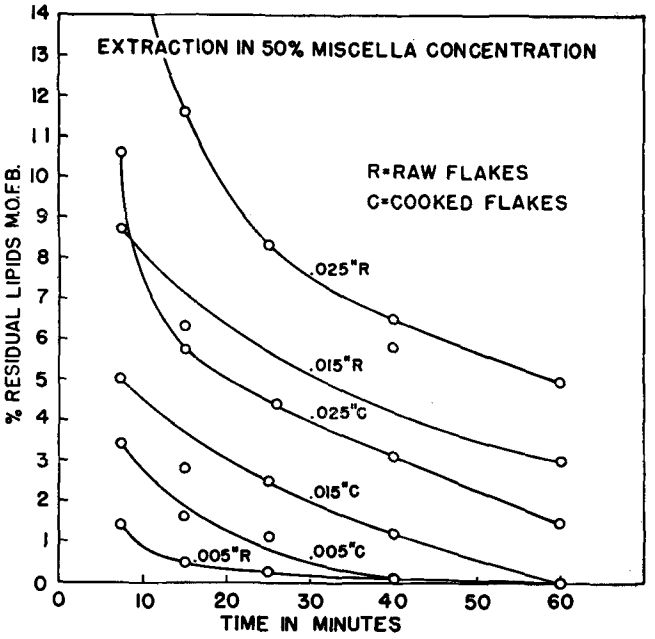

FIG. 5. Extraction rates of raw and cooked cottonseed flakes of various thicknesses in hexane miscella of 50% oil concentration.

The curves bring out the differences reached in the residual lipid levels after the various time intervals in each case and show that cooking and crisping improved the extractability in all flake thicknesses except the very thin flakes. It is apparent from the shapes of the curves that, with the exception of the very thin flakes, cooking increases the "free oil" content of raw flakes and also makes the cell-walls more wettable and penetrable by the miscella, thus facili-

tating extraction of the "diffusible oil." The tendency of the curves to run nearly parallel after 30-min. intervals shows that in the final stages the rate of change of residual lipids is nearly the same in all cases, independent of the flake thickness or the miscella concentration, and, as suggested by Coats (1), the residual lipids reached is mainly a matter of soaking time.

To bring all the results in proper perspective for the purposes of comparison they have been represented in the block diagram or bar graph in Figure 6,

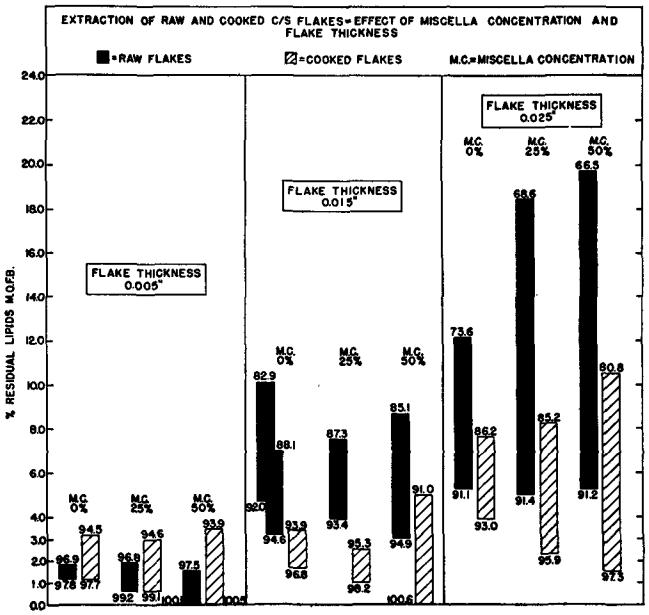

FIG. 6. Bar graph showing residual lipids levels and extraction efficiencies of cottonseed flakes relative to flake thickness and miscella concentration during extraction for the period 7.5–60 min.

which clearly brings out, within what limits and at what levels of residual lipids, extraction proceeded in each case. Tops of the bars or columns represent the residual lipid level at 7.5 min. extraction time, and the bottoms show the levels reached after 60 min. extraction. Variations during this period in the cumulative extraction efficiencies defined as

$$\frac{\text{amount extracted}}{\text{amount extractable}} \times 100$$

are shown alongside each bar. As an example, the third column under 0.015-in. flakes indicates that raw flakes of that size, when extracted with miscella of 25% initial concentration, change in residual lipids content from 7.48% at 7.5 min. to 3.90% at 60 min., with an increase in percentage extraction efficiency from 87.3 to 93.4.

Examination of the data in Figures 3 through 6 indicate that in the 0.005-in. size the raw flakes extracted somewhat faster and with equal or slightly greater (within experimental error) average extraction efficiencies than the cooked flakes, whereas for the .015 in. and the .025 in. thickness the cooked flakes extracted much faster and at much greater extraction efficiency than the raw flakes. The improved extraction efficiency due to cooking is probably attributable to the smaller average particle size of the cooked material, to rupture of more oil cells due to cooking, and to the fact that cooking appears to bind the bulk of the free gossypol and phosphatide components of the flakes so as to render them practically unextractable by the solvent under the conditions of the tests. However these factors appear to be of minimum importance when the flakes are rolled as thin as .005 in. The curves also show the decrease in extractability of raw and of cooked flakes in each of the miscella concentrations with increase in flake thickness, as would be expected. It is important to note here that while raw flakes of the order of thickness of .005 in. may be considered ideal for extraction purposes from the standpoint of extraction rate and efficiency, it is common knowledge among solvent processors that the use of such flakes is impracticable since not only are they expensive to produce (lowered capacity and higher power requirements for rolling) but they disintegrate excessively into "fines," which clog the beds of continuous percolation-type extractors and are carried out of the extraction vessel with the miscella in the case of immersion-type extractors.

The results show that the general effect of increase in miscella concentration is to slow down the initial rates of extraction. The results also demonstrate that in the extraction of cooked flakes the effect of increase in miscella concentration is to improve the degree of extraction regardless of flake thickness; whereas, for the raw flakes, the effect is to improve the degree of extraction of only the very thin size. This indicates that a mixture of solvent and oil up to 50% concentration by weight does a more efficient job of extracting cooked cottonseed flakes than the solvent alone.

It is observed that almost complete intrinsic extraction is obtained in the extraction with 50% miscella of the 0.005-in. raw and cooked flakes, and of 0.015-in. cooked flakes. Since raw flakes contain a small amount of difficultly extractable non-oil lipid materials (Table V), it is apparent from the results

TABLE V

Analysis of Extracted Lipids (Total Extractables) from Raw and Cooked Cottonseed Flakes After 10 Days' Soaking Extraction

	Raw Flakes	Cooked Flakes
Moisture and volatiles, %[a]	0.10	0.10
Phosphatides (25 times P), %[b]	2.30	0.20
Gossypol, %[c]	0.39	0.01
Neutral Oil, %[d]	94.75	98.47

[a] Analyses by A.O.C.S. Official Method.
[b] Ashing with alcoholic magnesium nitrate solution followed by determination of phosphorus by method of Pons and Guthrie, Ind. Eng. Chem., Anal. Ed., *18*, 184–6 (1946).
[c] Method of Pons *et al.*, Am. Oil Chemists' Soc., *28*, 8–12 (1951).
[d] Method of Linteris *et al.*, Am. Oil Chemists' Soc., *27*, 260–4 (1950).

that these components were more readily and thoroughly extractable from the very thin flakes when the solvent (hexane) contained oil in amounts up to 50% by weight. However as the flake thickness increases, these less soluble components are not only among the last to be extracted but probably have some effect of hindering the extraction of the oil. It is noted that almost complete intrinsic extraction is obtained in the extraction with 50% miscella of the 0.005-in. raw and cooked flakes and of the .015-in. cooked flakes. The improvement in extraction efficiency with increase in oil concentration of the extracting miscella appears to be in disagreement with the data of other investi-

gators (1, 6). This is believed explainable largely by the higher rate of agitation used in this investigation.

Effect of higher moisture content in the single test made on .015-in. raw flakes in 0% miscella was to slow down the extraction rate and extraction efficiency and to raise the residual lipid level to which extraction proceeded, as would be expected. (See the first two columns under 0.015-in. raw flakes in Figure 6.)

Chemical analysis of the "total extractables" (Table V) shows that hexane extracted considerably more non-oil lipid material (phosphatides, gossypol, etc.) from the raw than from the cooked flakes, which doubtless accounts for the higher percentage of total extractables content in the raw flakes. Since these materials are known to affect adversely the oil loss and the color upon alkali refining, the total extractables or crude oil from the raw flakes, although in higher yield, would be considered of lower quality than that from the cooked flakes.

In speculating as to effect of miscella concentration on the degree of extractability, while the scope of this work is not sufficiently extensive to warrant any hard and fast conclusions, the fact that with the cooked flakes lower levels of residual lipids with increasing miscella concentration are consistently reached indicates that in addition to the solubility and diffusional factors, probable wetting ability, and the penetrating power of the extracting miscella to establish an equal concentration of extractables within the solids matrix must figure in any theoretical consideration.

The 60-min. co-current method carried out according to the procedure described above is suggested as a control laboratory method in filtration-extraction practice readily to test the comparative intrinsic extractabilities of two materials. The batch co-current method, aside from its specific applicability for determining the intrinsic extractability of variously prepared oil-bearing materials, is a valuable adjunct to the bench-scale method and apparatus (4) presently used as an evaluation unit in connection with the filtration-extraction process. The bench-scale method integrates the percentage of residual lipids (after counter current washing) with factors such as contact time, temperature, solvent ratio, cake thickness, mass velocity, solvent hold-up of cake, filter media, and quality of oil and meal products.

Summary

A batch co-current laboratory method for measuring comparative extraction rates and extraction efficiencies of oleaginous materials in solvent is described. The method, a modification of that by Winward and Shand, was carefully tested with raw and cooked cottonseed flakes of various thicknesses and in various hexane miscella concentrations. It enables measurement of intrinsic extraction rates and extractabilities of materials, unaffected by diffusional effects in the liquid medium, and yields accurate and concordant results even with extracting miscellas of considerably high concentration. It is equally applicable for evaluating and predicting the effect upon extractability of different material preparation operations, particle sizes, moisture contents, temperature, solvents, etc.

The method was used in this investigation to compare the rate and degree of extraction under the specified testing conditions of raw and cooked cottonseed flakes of .005-in., .015-in., and .025-in. thicknesses in miscella concentration of 0%, 25%, and 50% oil. The results may be summed up as follows:

a) the extractability of both raw and cooked flakes in each of the miscella concentrations decreases as the flake thickness increases.

b) the cooked material prepared from the medium and thick flakes extracted at a more rapid rate and to a greater degree in all miscella concentrations than the raw flakes of comparative thicknesses, but the rate and degree of extraction were about equal for the very thin flakes.

c) the effect of increasing miscella concentration for both the raw and the cooked flakes of medium and thick sizes was to slow down the initial extraction rate; but for the very thin flakes the effect was negligible.

d) the effect of increasing miscella concentration in extracting the cooked material, regardless of flake thickness, was to increase the degree of extraction. For the raw flakes the effect was to increase the degree of extraction only of the very thin flakes.

Acknowledgment

The authors are indebted to the Planters' Oil Mill, Greenwood, Miss., for furnishing the cottonseed used in this investigation; to Nestor B. Knoepfler for preparation of the cooked flakes; and to George I. Pittman for preparation of the drawings. The authors are also grateful to Evald L. Skau for his helpful suggestions and advice.

REFERENCES

1. Coats, H. B., and Karnofsky, G., J. Am. Oil Chemists' Soc., *27*, 51–3 (1950).
2. D'Aquin, E. L., Vix, H. L. E., Spadaro, J. J., Graci, A. V. Jr., Eaves, P. H., Reuther, C. G., Molaison, L. J., McCourtney, E. J., Crovetto, A. J., Gastrock, E. A., and Knoepfler, N. B., Ind. Eng. Chem., *45*, 247–54 (1953).
3. Fan, H. P., Morris, J. C., and Wakeham, H., Ind. Eng. Chem., *40*, 194–9 (1948).
4. Graci, A. V. Jr., Spadaro, J. J., Paredes, M. L., D'Aquin, E. L., and Vix, H. L. E., J. Am Oil Chemists' Soc, *32*, 129–131 (1955).
5. Karnofsky, G., J. Am. Oil Chemists' Soc., *26*, 564–9 (1949).
6. King, C. O., Katz, D. L., and Brier, J. C., Trans. Am. Inst. Chem. Engrs., *40*, 533–56 (1944).
7. Smith, A. S., J. Am. Oil Chemists' Soc., *29*, 421–5 (1952).
8. Wingard, M. R., and Shand, W. C., J. Am. Oil Chemists' Soc, *26*, 422–6 (1949).

[Received May 13, 1955]

CORRECTION

L. H. Dunlap, Armstrong Cork Company, Lancaster, Pa., reports that an error was made in the paper entitled "Urea Adducts of Mono- and Diesters of Fatty Acids," published in the April 1955 issue of the Journal, page 227. In paragraph two of the section on Urea Extraction of Technical Glycerol Monolaurate the statement should be that "glycerol monolaurate has a saponification number of 205" (not 246).