TABLE II

Degassing of Phenanthrene in DEHS (5 g.) at 25°C. and 10^{-5} to 10^{-6} mm. Hg in Cold Finger Unit

Expt.	Time (hrs.)	Initial concentration (p.p.m.)	Yield (%)	Residual concentration [a] (p.p.m.)
1	1	144	20	115
2	2	144	39	87
3	3	144	59	59
4	3	58	56	25
5	3	291	50	146
6	3	72	50	38

[a] Calculated by subtraction of the distillation yield from the initially dissolved phenanthrene.

Scope and Limitations of the Method

The aim of the degassing of fats and oils is twofold: isolation of volatile, odoriferous substances in a form which allows further investigation, and preparation of tasteless oil samples for stability studies.

Isolation of volatiles can be achieved with all three degassing units; each of them has its merits. Although the cold finger is evidently by far the most efficient, the spiral capillary is to be preferred when only the highly volatile substances are of interest. The U-tube is used for routine work, generally when larger amounts of distillate are expected and when higher temperatures are necessary. To overcome the relatively long distance between flask and condenser, the connecting bridge B (Figure 1) can be heated electrically to the same temperature as (or slightly higher than) the sample.

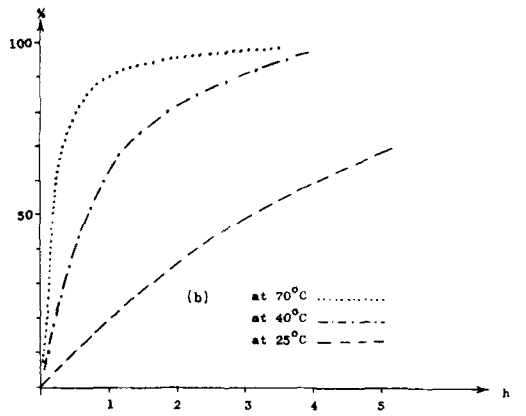

FIG. 6b. Recovery of phenanthrene *vs.* time (cold-finger).

When the total removal of volatile matter is required at the lowest possible temperature (*e.g.*, to prevent decomposition of the sample), the cold finger unit should be used. When, for example, PNO (peroxide content 4.4 mmole per kg.) with a definite "nutty' flavor was degassed for 3 hrs. at 60°C., the residual oil (peroxide content 4.3 mmole per kg.) was found to be completely tasteless. At the temperature used, no appreciable decomposition of peroxides had occurred, demonstrating that the peroxides of PNO are tasteless. This is in agreement with observations of Lea (8).

One of the drawbacks of the degassing method is that only small samples can be treated. By using the manifold a total of 1 kg. oil can be degassed per day. As flavor compounds often occur in extremely low concentrations, the distillate obtained may still be insufficient to permit unambiguous physical and chemical identification.

Water is always present in the samples to be degassed and forms another problem because it may interfere with subsequent analysis, *e.g.*, gas chromatography. Drying before degassing with conventional drying agents (*e.g.*, sodium sulfate) or with a molecular sieve of the Linde type does not always lead to satisfactory results.

The water may also be removed from the distillate by fractional distillation in accordance with the method of Niegisch and Stahl (3). Their degassing methods are similar to that described in this paper. In our method lower pressures are used, thereby reducing the degassing time. Moreover their trapping system is rather complicated and tends to spread the distillate over a much larger surface, which hampers the recovery.

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Filtration-Extraction of Safflower Seed on a Bench Scale

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Data are presented to show that filtration-extraction can be successfully applied on a bench-scale to extract whole or decorticated safflower seed to a residual lipids content in meal of about 1.0%.

Recommended procedure and operating conditions for processing this seed are given. These were found to be adequate within the limitations of the study and are not to be considered optimum. They are similar to those employed for filtration-extraction of most high-oil-content materials except that, for safflower, severe initial rolling is necessary and that efficient processing of decorticated seed requires an additional step of rerolling of the cooked materials prior to extraction.

Based on the close correlation obtained to date between bench- and industrial-scale filtration-extraction results for a wide variety of oil crops, there should be little difficulty encountered in the processing of safflower on a commercial scale.

SAFFLOWER, a relatively new cash oilseed crop in the United States, is now a well-established and profitable source of oil for the surface-coating industry and of protein for livestock feeds (1). Production of this seed has increased from about 34 million pounds in 1950 to about 228 million pounds in 1959 (2). Trade sources estimate the 1960 crop at 274 million pounds.

Safflower seed oil is a high-grade product for industrial and food uses. The meal is low in protein (18–

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21%) and high in fiber (35%) because of the high hull content. Decortication of the seed, either prior to or after oil removal, is now considered feasible (3) and yields a meal of about 40% protein content.

Safflower seed is processed commercially into oil and meal by mechanical pressing alone or followed by solvent extraction. As far as is known, there are no processes in use today for solvent-extracting this seed directly.

Filtration-extraction is an established commercial process for the continuous extraction of cottonseed, soybeans, sunflower seed, and rice bran (4,5) without prepressing. It has also been applied on a bench- or pilot-plant scale to a wide variety of other oil-bearing seeds, nuts, beans, germs, brans, and press-cakes and has proved efficient with every one tested to date (6). The over-all process is similar for all oleaginous crop materials (6). Only minor process modifications depend on differences in oil content and in inherent physical characteristics. This feature makes it readily adaptable for conversion from one feedstock to another. Previous experimental work has shown that bench-scale data is practically directly translatable to full-scale operations.

This paper therefore presents bench-scale data to show material preparation and extraction conditions found adequate for the processing of safflower seed by the filtration-extraction process. The study was completed in 1957; however publication of the results is believed to be warranted by the increasing importance of safflower as a domestic crop. The results show that this seed, either whole or partially decorticated, can be efficiently processed by filtration-extraction to a residual lipids content of about 1.0 while employing an acceptably low solvent-meats ratio.

Raw Material and Equipment

The seed used in the study was obtained from a commercial processor in California and was representative of the 1956 crop. The cleaned seed analyzed 35.2% oil, 5.7% moisture, and 44.1% hulls.

Decortication was done with a No. 148 Bauer Bros. laboratory attrition type mill, followed by screening. The mill is equipped with 8-in. diameter opposing plates, one stationary and the other rotating at 3,600 r.p.m.

Size-reduction and flaking were done with a French 5-high stand of 12-in.-wide, standard diameter rolls; a set of Allis-Chalmers 1-pair high, 12-in. diameter cracking rolls; and a set of Allis-Chalmers 1-pair high, 12-in. diameter smooth rolls.

Cooking was conducted in a Loomis 15-lb.-capacity, vapor-tight, steam-jacketed, mixer type of vessel equipped for controlled addition and removal of moisture.

All of the above equipment units have been described in greater detail in previous reports (7,8).

Filtration-extraction of the prepared materials was carried out by using a standard 5¼-in. bench-scale filter test unit. A description of this apparatus and detailed instructions for its use are contained in a previous publication (9).

Experimental

The seed was prepared by the standard operational steps for filtration-extraction in the following sequence: decortication (where required), flaking, moist cooking, crisping, and rerolling. The prepared materials were then evaluated for their extraction characteristics.

Based on previous work (6), conditions selected for both preparation and extraction of safflower were approximately those found adequate for the efficient processing of materials of the type characterized by high hull and/or high oil contents, such as flaxseed (10), sesame (7), and peanuts (11).

The experiments were planned to observe the effects on extractability of partial decortication of the seed; moisture level during cooking; moisture level after drying and crisping; and rerolling of the crisped material prior to extraction.

Preparation of Seed for Extraction. The different operating conditions for preparing the seed for extraction are given below and in Table I.

Decortication. For Experiment 4 the seeds were partially decorticated by one pass through the Bauer mill. For the best results, clearance between the plates were carefully adjusted to provide practically complete hulling with minimum shattering of the meats. The large hulls were separated over a standard 10-mesh wire screen. In this manner about 62% of the original hulls were removed. The hull fraction contained no visible meats particles.

Flaking. The 5-high rolls were employed to crack and flake the seeds for Experiments 1, 2, 4; for Experiment 3 the 1-pair-high rolls were used.

Cooking and Crisping. Cooking was conducted in a manner which simulated the operation of a conventional stack-type cooker, *i.e.*, the cooking cycle was carried out in the following successive stages: material preheating, moisture addition, mild cooking, and partial moisture removal by drying. In the first stage the material was heated to 170°F. in a period of about 18 min. The required amount of water was spray-injected over a period of about 6 min. while the temperature was simultaneously elevated to about 212°F. In the next stage these temperatures and moisture levels were maintained under reflux conditions for about 10–25 min. The final stage was partial drying. Total cooking cycle was about 45 min. The hot, moist material was discharged from the cooker and passed through an 8-mesh screen. It was then spread on open trays for about 20 min. while

TABLE I
Preparation of Safflower Seed for Extraction

Experiment No.	1	2	3	4
Raw material.				
Decorticated (yes/no)	No	No	No	Yes
Hulls removed, % of total	0	0	0	62
Lipides, % [a]	35.6	35.6	.....	48.9
Moisture, % [b]	4.7	4.7	6.1	4.0
Flaking:				
Rolls, type	5-high	5-high	1-pr.-high	5-high
Clearance, corrug., in.	.025	.025	.040	.025
Clearance, smooth, in.	.016	.016	.007	.016
Clearance, smooth, in.	.008	.008	.....	.008
Clearance, smooth, in.	.002	.002	.....	.002
Cooking (yes/no)	No	Yes	Yes	Yes
Moisture, maximum, %	.....	20.8	11.7	35.8
Temp., maximum, °F.	.....	212	210	208
Time, min	.....	44	47	45
Moisture, % after cooking	.....	17.7	10.6	29.7 [b]
Moisture, % after crisping	.....	13.0	8.3	17.8
Rerolling (yes/no): [c]	No	Yes	Yes	Yes
Type rolls	.....	5-high	1-pr.-high	1-pr. high
Clearance, smooth, in.	.....	.008, .002	.003	.003
Moisture, %	.....	12.9	8.9	16.7

[a] Flaked seed analyzed by Official and Tentative Methods of American Oil Chemists' Society.
[b] Cooked material further dried to 20.0% moisture content, before crisping.
[c] Only half of material was rerolled.

the moisture content was further reduced by flashing and the material became crisp and granular.

For Experiments 2, 3, and 4 the maximum moisture content during cooking was varied between 11.7 and 35.8%. Moisture content after cooking varied between 10.6 and 20.0%.

Rerolling. Because previous work with high oil content seed had indicated that better extraction efficiency could be obtained with improved comminution, a portion of each cook batch was passed through either the 5-high or the 1-pair-high rolls to evaluate the effect of further reducing the average-particle size.

Extraction. The standard filter test apparatus employed for extraction was specifically designed to simulate closely the operating steps and conditions for slurrying, vacuum filtration, countercurrent washing, etc., to which a prepared material would be subjected on a pilot- or commercial-scale continuous rotary horizontal vacuum filter. Criteria used were the same as for other oil-bearing materials, *i.e.*, extractability, as measured by percentage of residual lipids in extracted meal; and mass velocity (rate of filtration of liquids through the filter bed, expressed as pounds per hour per square foot of filter screen area).

Conditions employed for extracting the various preparations are listed in Table II.

The solvent-extracted meals were air-desolventized, and each was analyzed for moisture and residual lipids content.

TABLE II

Bench-Scale Filtration-Extraction of Prepared Safflower Seed [a]

	Raw flakes	Cooked Flakes					
Experiment No.	1	2 A	2 B	3 A	3 B	4 A	4 B
Decorticated (yes/no)	No	No	No	No	No	Yes	Yes
Rerolled (yes/no)	No	No	Yes	No	Yes	No	Yes
Operating conditions:							
Hexane-meats ratio, lb./lb.	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Slurrying time, min.	40	40	40	40	40	40	40
Slurrying time, °F.	125	145	140	130	125	130	130
Cake thickness, in.	....	1 7/8	2	2	2	1 5/8	1 1/2
Vacuum, in. Hg	4–7	4	2–4	2–4	2–4	4	4
Washes, temp., °F.	125	135	135	130	125	130	130
Extraction results:						....	....
Marc, % hexane	43	35	34	....	28		
Mass velocity, lbs./hr./sq. ft.	90	3400	3200	....	3300	2900	2900
Extr. meal, desolventized:							
Lipides, %[b]	0.33	1.17	0.68	2.10	1.50	2.52	1.30
Mosture, %[b]	7.8	9.5	9.0	9.3	9.2	19.0	16.6

[a] Three washes using oil-free hexane; filter-screen size, 60 x 60 mesh.
[b] Analysis by Official and Tentative Methods of American Oil Chemists' Society.

Results and Discussion

The results show that safflower seed, either whole or decorticated, can be processed by the standard filtration extraction-procedure to yield materials which can be extracted at high filtration rates to about 1.0% residual lipids content.

Experiment 1 demonstrates that flaked safflower seed cannot be successfully processed in the raw state and that it must be moist-cooked to agglomerate "fines." This is necessary to insure an adequately rapid rate of filtration of liquids through the cake bed.

In Experiments 2, 3, and 4, with the cooked flakes, filtration rates obtained throughout are in acceptably high range (9) for commercial-scale application at the solvent-meats ratio employed. Residual lipids content of the extracted meals from the rerolled cooked materials is in the desirably low range of 0.67 to 1.50%. Solvent content of the solvent-damp extracted meal (marc) averaged 33% by weight. This is considered relatively low in comparison with that obtainable with other commercial processes and is attributed to the effectiveness of vacuum drainage. Solvent-meats ratio of 1.3 to 1.0 is considered comparatively low in comparison with other extraction processes for a material of this high oil content.

Investigation of cooking conditions for safflower seed indicated that moisture content, temperature, and cooking cycle are not critical factors and can be varied within reasonable limits.

Experiment 2 gave the best over-all results with undecorticated seed and shows that acceptable extraction was achieved by severe initial rolling of the seed, as was found necessary for the processing of flaxseed (10) and sesame (7). The data further show that rerolling was not required to insure residual lipids reduction to around 1.0%. The importance of severe rolling is demonstrated by the higher residual lipids values obtained in Experiment 3, in which relatively mild rolling was employed. In Experiment 2 the high filtration rates obtained with the rerolled preparations allow considerable margin for further reduction of the residual lipids content through the use of more severe initial comminution. Since rerolling insures further reduction in residual lipids, a plant operator could elect to employ this additional step to achieve better extraction or equal extraction at a lower solvent-meats ratio or with a shorter slurrying period or with less severe initial comminution.

Experiment 4 shows that partially decorticated safflower (62% of hulls removed) can be processed as efficiently as whole or undecorticated seed except that rerolling was required to achieve extraction down to around 1.0%. Residual lipids content was 2.5% without rerolling but, with rerolling, was reduced to 1.3%, which is equivalent to about 0.8% on an undecorticated meal basis. Solvent-meats ratio of 1.3 to 1.0 is extremely low, considering the high oil content of the seed after decortication. Moreover the high filtration rate or mass velocity (2,900) obtained indicates that residual lipids in meal could be further reduced by employing more severe flaking up to the point where the filtration rate would be lowered to a value of around 2,000, which is still sufficiently high for commercial application.

The processing of decorticated safflower would present a number of important economic advantages over processing of the undecorticated seed. A sizable reduction in the amount of hulls to be handled would permit use of smaller equipment units throughout for any given plant capacity and attainment of higher protein content (up to 40%) in the meal product without requiring meal screening equipment. Against these advantages would be balanced the equipment required for decortication and disposal of the separated hulls.

On the basis of results obtained in this investigation the following conditions are recommended as adequate (not necessarily optimum) for the filtration-extraction of safflower seed.

a) *Undecorticated Seed.* Conditions for preparation are: flaking through 5-high rolls to a thickness of 0.004–.006 in.; preheating to 170°F.; addition of water and/or steam to a moisture level of 12–18% in 5–10 min.; cooking at 212–215°F. for 10–20 min.; drying at 215–225°F. to a moisture content of

10–12%; crisping by evaporative cooling to a temperature of about 130°F.; and a moisture content of about 8–10%. Conditions suitable for extraction are: slurring for 40 min., hexane-meats ratio of 1.2–1.4 to 1, three washes, cake thickness of 2 in., vacuum of 3–6 in. of mercury, and temperature of slurrying and washes of about 140°F.

b) *Decorticated Seed.* Conditions recommended would be the same as for undecorticated seed except that, prior to extraction, the crisped material would be rerolled in 1-pair-high flaking rolls set at a clearance of about 0.002–.003 in.

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Effects of Oxidized Soybean Oil on the Vitamin A Nutrition of the Rat[1, 2, 3]

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Three lots of cold-pressed soybean oil were treated with bubbling oxygen for 70, 80, and 180 hrs. at 70°C. and fed to rats at a level of 18% in diets which were nutritionally adequate but devoid of vitamin A. Untreated soybean oil was fed in similar control diets. Subgroups of 15 weanling rats each were given graded injections of vitamin A acetate intramuscularly each week.

Diarrhea developed in the rats fed the diets containing oxidized oil. This condition soon subsided in the groups receiving vitamin A injections but not in the vitamin A-free group. Diarrhea was not noted in the rats receiving the untreated soybean oil, without respect to the amount of vitamin A they received.

The rats on the vitamin A-free diets developed deficiency more rapidly when the diet contained oxidized rather than the untreated oil. The food efficiencies of the groups fed the oxidized oils were lower than the controls. The intestines of the groups receiving the oxidized oils were distended with fluid and were hemorrhagic. Enlarged kidneys were noted in the vitamin A-deficient control as well as in test rats.

The retroperitoneal lipids of the groups on the oxidized oil were less unsaturated, had lower refractive indices, higher peroxide values, and higher carbonyl values than comparable groups fed the control oil.

Vitamin A deficiency decreased the unsaturation of the kidney and liver lipids but increased that of the retroperitoneal lipids. Injections of increasing amounts of vitamin A produced increases in the unsaturation of the body lipids.

The kidney lipids of the groups on the oxidized oil diets were less unsaturated and contained more peroxidic compounds than the controls. Vitamin A deficiency increased the peroxidic compounds in the kidney and liver lipids, even in rats fed the control oil. The liver lipids of the groups fed oxidized oil were less unsaturated, lower in vitamin A content, and higher in peroxide compounds than the controls.

The vitamin A content of the whole blood varied in relation to the amounts injected. The content of tocopherol in the tissues were not affected significantly by the oxidized oil in the diet.

The evidence indicates that severely oxidized oil may destroy vitamin A in the tissue of the rat, thereby hastening the development of deficiency on vitamin A-free diets, reducing the storage of injected vitamin A, and increasing the vitamin A requirement.

These effects are with abused oil and should not be interpreted to mean that the mildly oxidized oils and fats, such as those in the diets of human beings in this country are toxic.

A NUMBER of feeding studies have been conducted with oxidized or heated oils and fats in recent years. Depending on the type of lipid, the extent of treatment, and the level of feeding in the diet of experimental animals, investigators have observed diverse effects, ranging from no observed reaction (1), to slight decrease in body weight (2), to death of the experimental animals (3). The effects of these treated lipids may result from destruction of dietary nutrients, interference with diet absorption, interference with nutrient metabolism, and/or direct toxic reaction with the tissues.

In an unpublished study conducted in these laboratories in 1952 soybean oil was treated at 350°F. for 8 hrs. and fed at a 15% level in a nutritionally-complete diet to rats. The animals grew poorly, developed severe diarrhea, and died within three weeks. This experiment was repeated, but this time the heated oil was freshly incorporated into the diet each day, and the diet not consumed within 24 hrs. was discarded. These rats grew fairly well, they developed a mild diarrhea which cured spontaneously within several days, and most survived the 35-day experiment. Assay of the nutrients present in the diet after it had been stored at room temperature for 14 days revealed that major proportions of the fat-soluble vitamins (vitamins A, D, K, and E), and significant amounts of the water-soluble vitamins had been destroyed. A control diet containing the untreated oil which had been stored under the same conditions showed very small losses in these vitamins. It was apparent that

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