A Laboratory Apparatus for Determining the Rate of Extraction of Oil From Oil-Bearing Materials[1,2]

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IN laboratories where experimental work with oil seeds is carried on, frequently a convenient method is needed for evaluating the effects of processing variables upon the rate of solvent extraction of oil from oil-bearing materials. In this laboratory a project dealing with the solvent extraction of rolled whole cottonseed created the immediate need for such a method. A search of the literature uncovered only a small amount of information on the subject of the determination of solvent extraction rates. After testing a few other ideas, an extractor was built which was basically the same as that employed by Boucher, Brier, and Osburn (1) and by King, Katz, and Brier (2) for studies on the solvent extraction of oil from clay plates and from soybean flakes respectively.

Apparatus

A diagrammatic sketch of the extractor constructed for the whole seed project appears in Figure 1. It consisted of an extraction compartment in which the samples to be extracted were immersed and through which heated solvent was circulated. The extraction compartment was about 23 inches square by 5 inches deep inside (58 x 13 cm.) and was fabricated of 16-gauge sheet iron. The compartment was embedded in a wooden box which was filled with cotton linters for insulation against heat loss, and it was covered with a cover of three-quarter-inch thick plywood. The top edge of the extraction compartment was flanged, and a neoprene rubber gasket between this flange and the cover prevented solvent vapors from escaping around the edge. The cover held thermometers which indicated the temperature of the solvent in the compartment. The cover also supported a reflux condenser in a breather hole which was over the discharge pipe in the compartment.

Solvent entered the extraction compartment through a horizontal pipe with holes drilled on the underneath side, which ran nearly the width of the compartment. The solvent flow was distributed evenly across the width of the compartment by level dams at both ends, over which the solvent flowed in passing from inlet to discharge. The discharge dam maintained a solvent depth of about $3\frac{1}{2}$ inches (9 cm.) in the compartment. Solvent overflowing the discharge dam passed into a $1\frac{1}{4}$-inch (3.5 cm. I.D.) pipe and thus returned by gravity to the solvent drum.

The solvent drum was a standard 55-gal. steel drum. Extra fittings were welded on to it for the pump suction pipe and for the solvent line from the heater to the drum. All connections in the top of the drum were screwed so that no vapor could leak out into the atmosphere. Before it could reach the atmosphere, vapor from the drum was forced to pass through the pipe into the extraction compartment and thence through the reflux condenser.

The flow of solvent from the pump to the extraction compartment was regulated according to the orifice meter reading. The pump output not circulated through the extraction compartment was passed through a section of steam jacketed pipe for heating. This flow was returned to the drum through the center of the head and issued from the pipe into the main body of the solvent through a restricted opening. The jet thus produced promoted mixing to eliminate concentration and temperature differences.

The material to be extracted was contained in cylindrical baskets of 20-mesh (0.8 mm. openings) bronze wire screen with soldered joints. The baskets were $2\frac{3}{8}$ inches (6.04 cm.) in diameter and $3\frac{1}{8}$ inches (7.94 cm.) high. They were made with screen bottoms but were open at the top.

Upon withdrawal of the baskets from the extractor, they were centrifuged in an International Equipment Company[3] Size 2 Centrifuge in order to remove the solvent contained in the voids of the material. For centrifuging the baskets were supported on perforated

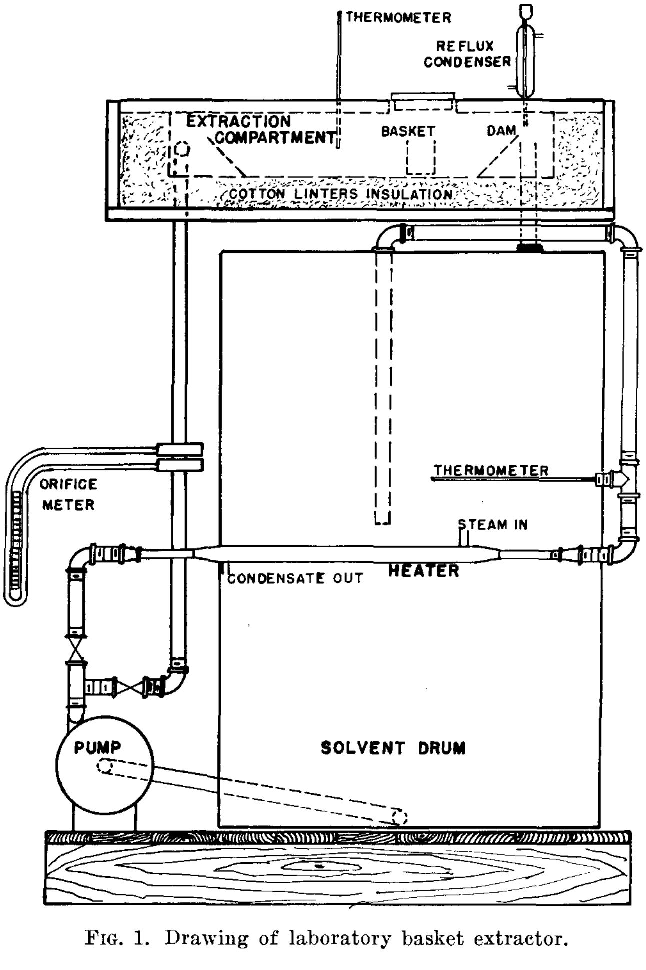

FIG. 1. Drawing of laboratory basket extractor.

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[1] A report of work done under a contract between the Cotton Research Committee of Texas and the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract is being supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

[2] Presented at the Spring Meeting, American Oil Chemists' Society, New Orleans, La., May 1-3, 1951.

metal plates about ¾ inch off the bottom of International Equipment Company[3] No. 373 centrifuge cups. The solvent collecting in the false bottom during centrifuging was absorbed by a piece of cotton, which was placed there in order to prevent the possibility of the solvent rewetting the solids in the basket as the centrifuge was stopped.

Although it is generally known that the material extracted from oil-bearing materials by the solvent is not all oil but a mixture of lipids and other soluble materials whose composition depends on the solvent, the temperature of the extraction, the history of the sample, and other variables, it is nevertheless simpler to refer to the material extracted under the conditions specified as oil. The term oil will be used in this sense in the discussions to follow.

The residual oil in the extracted solids was determined in either of two ways. For homogeneous materials, such as cottonseed meats, which could be ground easily and reduced to small representative samples, the official methods of the American Oil Chemists' Society for oil seed meals were followed (Ba 3-38), with the exception that usually commercial hexane was substituted for petroleum ether. For materials like rolled whole cottonseed, which could not be reduced easily to small representative samples, the residual oil contents of the extracted samples were determined by 22-hour Soxhlet extraction of the entire samples in 500-ml. capacity extractors (Corning No. 3720, Extra Large[4]). The wire baskets were placed in the Soxhlet extractors on top of plugs of cotton, which retained within the extractor any solids escaping from the basket. Hexane was used as the solvent, and the boiling flasks were heated on steam baths in order that extraction might continue overnight without danger of fire should the flasks boil dry.

To test the basket extractor after it was constructed, a number of runs were made on flaked cottonseed meats. Replicate samples of meats contained in the baskets were arranged in the extractor in different ways and were extracted for the same periods of time under uniform conditions of solvent temperature and flow rate. After extraction, centrifuging, and atmospheric desolventizing, the samples were ground and analyzed for residual oil.

The different basket arrangements all gave about the same results in amount of oil extracted and in degree of variation among replicate samples. Basket arrangement apparently had no effect upon the results; therefore the simplest arrangement was selected for standard operation. This was uniform placement in a row of seven across the compartment at right angles to the flow of solvent. The results for the samples on the ends of the row were less precise, and these positions were not used for test samples.

With several of the different basket arrangements, runs were made at average linear velocities of solvent through the compartment ranging from 0.6 to 1.25 feet per minute. Solvent velocity had no effect upon the amount of residual oil remaining in the flasks. Consequently a solvent velocity of 0.6 fpm. was selected for standard operation because this allowed the maximum amount of solvent to be introduced into the solvent drum through the jet to promote mixing. The lack of any effect upon extraction by the solvent velocity agrees with conclusions reached by Boucher *et al.* (1) that the liquid film resistance is negligible compared to the resistance to diffusion within the solid.

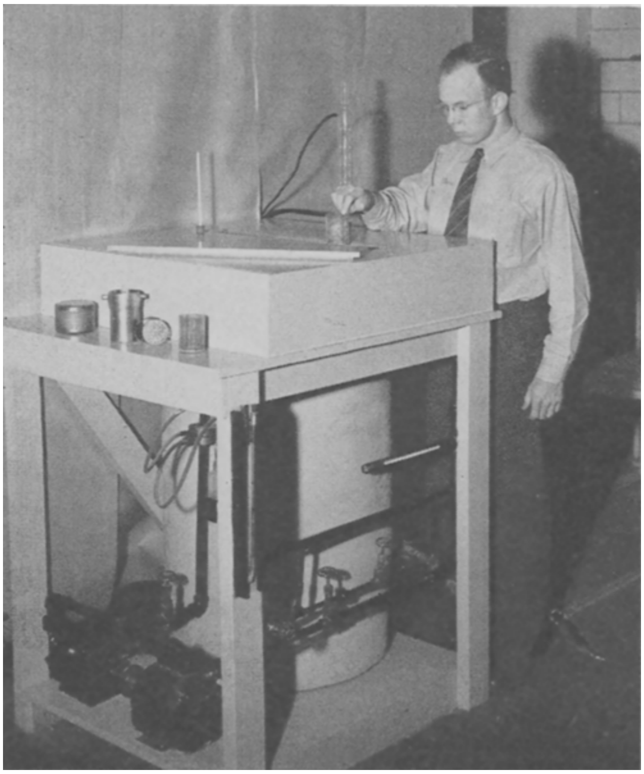

FIG. 2. Photograph of extractor.

Method

Most of the experiments using the basket extractor were run on whole, undelinted cottonseed which were comminuted by rolling in laboratory size flaking rolls. Commercial hexane was the solvent used. However, because more persons are familiar with the appearance and properties of flaked cottonseed meats, the method will be described for testing the latter material instead.

Meats entirely free of hulls were usually employed. If moisture adjustment of the meats was desired, this was made about one hour before the meats were to be used. Then 14 55-g. samples of meats were weighed out to plus or minus 0.5 g. The samples were rolled, and after rolling they were placed in tared, covered metal cans to minimize moisture loss and were weighed to 0.01 g. Two samples were employed for moisture determination by oven drying, and two samples were used in flake thickness measurements employing standard micrometer calipers. As needed, the rolled meats were poured from the cans into the baskets which were placed on a sheet of clean paper to catch fine particles sifting through the screen. Fifty-five grams of rolled meats filled a basket slightly less than level full without packing. As soon as possible after filling, a basket was placed in the extraction compartment through the small opening in the plywood cover. The baskets were arranged side by side across the width of the compartment with about ⅞ inch between adjacent baskets. In order to minimize disturbances in the solvent flow, except when changing baskets, all positions were kept filled at all times, with baskets being extracted or with

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[3] Mention of names of firms or trade products does not imply that they are endorsed or recommended over other firms or similar products not mentioned.

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"blanks" filled with rolled meats not being tested. Because the two end positions next to the walls were filled only with blanks, five positions were left available for use.

The 10 different samples were extracted for periods of 3, 6, 12, 18, 24, 30, 44, 60, 90, and 120 minutes. Each basket was removed from the extractor about 20 seconds before the end of its extraction period, allowed to drain for 10 seconds, and placed in the centrifuge cup. Another 10 seconds was estimated to elapse before the centrifuge was turning fast enough for most of the solvent to have been forced into the false bottom. The basket was centrifuged at 800 rpm. for about 90 seconds. Higher speeds packed the meats into the basket, and 800 rpm. was judged to remove all of the solvent which could be removed by this means. The samples were allowed to desolventize by exposure to the atmosphere of the room overnight. They were then ground and analyzed for residual oil.

With the large volume of solvent contained in the extractor drum, the change in concentration of oil in the solvent during a run was small. After several runs the solvent was replaced with fresh solvent so that the oil concentration was always maintained below about 0.75%. The solvent in the extractor was sampled before and after each run and analyzed for oil content. Each type of material tested was found to retain a fairly constant quantity of solvent on the surface of the solids after centrifuging. Using the average concentration of oil in the solvent before and after the run, the residual oil percentages in the extracted samples were corrected for the oil in the solvent retained by the extracted solids after centrifuging.

The original oil content of the meats was determined by Butt extraction of a ground sample with hexane. The residual oil was usually expressed in percentage, based upon the calculated weight of oil- and moisture-free solids. This was equivalent to the weight of residual oil per unit weight of oil- and moisture-free solids, multiplied by 100. Percentage residual oil plotted against time for the 10 samples comprising a run produced an extraction curve. Plotted on log-log paper, these extraction curves approached straight lines as shown in Figure 3. By the use of extraction curves, comparison of the extractability of the oil from materials prepared or extracted under different conditions was convenient.

Typical Experimental Results

The data in Table I are examples of the precision which can be obtained by the method. Runs No. 49 and 50 were made one immediately following the other on hull-free flaked cottonseed meats. Run No. 51 was made on some of the same flakes which had been stored in a closed container for 9 days. (The free fatty acid increased from 0.5 to 0.8% during this period.) Additional data on these flaked meats and data on three other materials which were tested in the basket extractor appear in Table II.

TABLE I

Solvent Extraction of Rolled Cottonseed Meats in Laboratory Basket Extractor

Extraction time, minutes	Per cent residual oil, oil and moisture free solids basis		
	Run No. 49	Run No. 50	Run No. 51
3	4.70	4.91	5.02
6	3.26	3.55	3.64
12	2.55	2.60	2.58
18	2.34	2.37	2.30
24	2.29	2.29	2.28
30	2.12	2.11	2.07
44	2.12	2.00	2.05
60	1.91	1.88	1.84
90	1.78	1.95	1.75
120	1.84	1.71	1.52

TABLE II

Materials Extracted in Laboratory Basket Extractor

Material	Moisture	Flake thickness	Initial Oil Content
	Per cent	*Inches*	*Per cent*
Rolled cottonseed meats	8.9	0.011	36.5
Rolled whole cottonseed	11.2	0.011	18.0
Prepress cake	8.0	....	12.9
Reflaked prepress cake	12.0	0.012	12.9

The data on rolled whole cottonseed are the averages for six closely agreeing runs. The only treatment of the seed before extraction was moistening. This took place about 48 hours before rolling in laboratory flaking rolls. The prepressed cake was made by rolling the meats, cooking them in a 4-high atmospheric stack cooker, and prepressing them in an Anderson No. 1 Expeller. Portions of this expeller cake, crumbled into pieces about ¼ inch in diameter, were used as the prepress cake sample for the extraction test. The reflaked sample was prepared by passing the prepress cake through an attrition mill, which broke it into approximately ⅛ inch diameter pieces. The cake was then moistened to about 12% moisture by spraying with water and was rolled in laboratory flaking rolls. Other data on the prepress experiments are contained in a publication of the Texas Engineering Experiment Station (3).

The averages of the data for the three runs in Table I are plotted in Figure 3 along with the extraction curves for the other materials described in Table II. For all four of these materials the extraction solvent was commercial hexane, and the extraction temperature was 120°F.(49°C.). These data are presented merely to show the kind of information which the

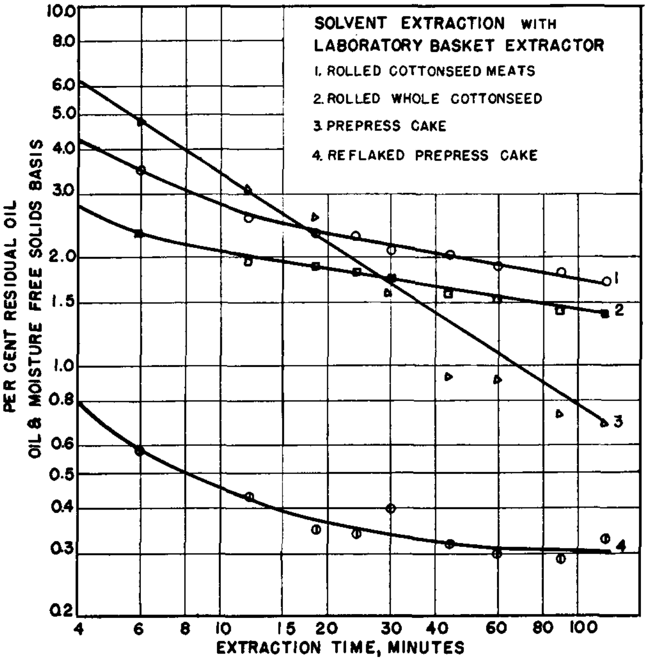

FIG. 3. Plot of data obtained with laboratory basket extractor.

method will supply and not to compare the rate of extraction of oil from the four different materials. These extraction rates can be compared only in a general way because the residual oil in the different materials was not determined by the same procedure. In addition, while the residual oil percentages for both meats and seed are expressed on a pure meats basis, the percentages for the prepressed materials are based on solids containing hull particles.

Although the use of the extractor on rolled whole cottonseed has been mentioned only briefly for the reasons stated earlier, the extractor was a valuable tool in exploring the effects of heating before rolling, moisture, and flake thickness upon the extractability of the oil from this material. Use of the basket extractor greatly reduced the number of runs which had to be made with the pilot plant extractor.

Commercial hexane was the only solvent used in any experiments; however other appropriate solvents could be used.

Summary

The equipment and the method have been described for measuring the rate of extraction of oil from oil-bearing materials by solvent. The method consists essentially of immersing wire baskets containing the oil-bearing material in a circulating stream of solvent for varying periods of time. After extraction, the baskets are centrifuged to remove excess solvent, and the residual oil in the solids is determined. The method is patterned after one devised by Boucher *et al.* (1) but has been modified and extended to other oil-bearing materials.

REFERENCES

1. Boucher, D. F., Brier, J. C., and Osburn, J. C., Trans. Am. Inst. Chem. Eng., *38*, 967-993 (1942).
2. King, C. O., Katz, D. L., and Brier, J. C., Trans. Am. Inst. Chem. Eng., *40*, 533-556 (1944).
3. Rea, H. E. Jr., and Wamble, A. C., Research Report No. 11, Texas Engineering Experiment Station, College Station, Tex.
4. Wingard, M. R., and Shand, W. C., J. Am. Oil Chem. Soc., *26*, 422-426 (1949).

[Received September 12, 1951]

The Glycerolysis of Fat in Tertiary Aromatic Nitrogeneous Bases to Increase Monoglyceride Yield

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THE interesterification of fats with glycerol at elevated temperature yields a mixture of mono-, di-, and triglycerides and unreacted glycerol. In commercial practice the yield of the desirable, surface-active monoesters (1) is always less than 50% because of the limited mutual solubility of the reactants (2).

In the past a number of solvents have been proposed to increase this solubility (3), and claims for increased yields have been cited in a number of patents (4, 5). In general, these have not proved satisfactory. For example, phenol (3, 4) acts not only as a solvent but enters into the reaction to an undetermined extent. Others have proposed dioxane (5), but in our laboratory we have not been able to duplicate the reported yields.

Consequently a survey of various solvent types was undertaken, and it was found that pyridine, in the presence of catalytic amounts of sodium methoxide, will slowly dissolve fat and glycerol simultaneously even at room temperature. If the mixture is warmed to steam bath temperature, solution takes place in a few minutes.

Yields of monoglycerides above 70%, as measured by the periodic acid titration of Pohle and Mehlenbacher (6), are obtained in these homogeneous mixtures. The maximum yield obtained in this series of experiments, run under a variety of conditions, was 79%. Although this does not compare very favorably with the 90-95% available through molecular distillation (7), this method has certain advantages of simplicity.

Specifically the method involves mixing fats with at least 0.5 part of glycerol by weight, 4 parts by weight of solvent, and at least 0.003 part of catalyst. In the temperature range of 80-100°C. homogeneity and a maximum percentage of monoesters are attained in about 5 minutes, and the product can be isolated immediately thereafter by neutralizing the catalyst with mineral acid, distilling the solvent at reduced pressure, and settling the excess glycerol. Without a solvent the reaction requires several hours at much higher temperature for completion, and then only 40-50% of monoesters results.

The proportions used in the solvent process are critical. If the glycerol-fat weight ratio is cut below 0.5, yields over 60% are not obtained. The solvent-fat ratio must be at least 4:1, or else an extended heating period is necessary. Below 2:1 it is difficult to obtain homogeneity, and the yields are low even after several hours of refluxing.

Solvents other than pyridine which have been tested and found to be satisfactory include γ-picoline, β-picoline, 2,6-lutidine, quinoline, and isoquinoline. With α-picoline, for some obscure reason, the yields are low.

The products can be given a short deodorization at 200°C. without deterioration. In fact, the percentage of monoesters usually increases slightly due to the removal of free glycerol.

Experimental

Table I summarizes data on a series of monoglyceride preparations using various fats in several different heterocyclic nitrogeneous aromatic solvents. The experiments are reported in more detail in the following section.

High gravity glycerol was used in all the preparations. The pyridine was denaturing grade while the α-, β-, and γ-picolines, 2,6-lutidine, and isoquinoline were practical grade reagents obtained from Eastman Kodak Company. The quinoline, also a practical grade material, was distilled under reduced pressure prior to its use.

1. One part of oleo oil and one part of glycerol were mixed with 2 parts of pyridine, to which was added