Lectures of the 1949 Short Course

sponsored jointly by the

AMERICAN OIL CHEMISTS' SOCIETY

and the

UNIVERSITY OF ILLINOIS

at Urbana, August 15-19

Foreword

LAST year the American Oil Chemists' Society, after consideration of several means of encouraging and promoting interest in all phases of vegetable oils and fats, decided to present a general review course in collaboration with the University of Illinois at Urbana. The response was highly gratifying, and the 117 students who attended were enthusiastic about the constructive lectures which were presented by authorities in the industry and the excellent facilities and entertainment provided by the university. The lectures were later published in planographed book form by the university under the editorial supervision of Prof. T. S. Hamilton and R. K. Newton of the university and R. T. Milner, president of the Society.

J. P. Harris

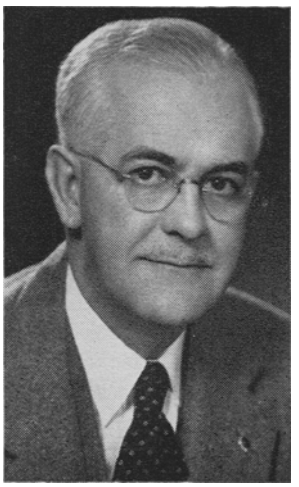
This year 171 students enrolled for the course, and again the excellent program was enthusiastically received. Without remuneration and at their own expense the lecturers made a splendid contribution to the Society and to the industries which it serves. Subject matter included all edible fats and broadened the scope of the information offered by the short courses. Especial credit is due to A. R. Baldwin, editor of the Journal, and the Journal staff for their work in preparing the material for publication.

The Education Committee is proud to present the lectures herewith as a contribution to the field of fats and oils. Reprints of the proceedings will be available.

J. P. HARRIS, chairman.

Address of Welcome

THE dean of University Extension, especially since at this institution he is also the dean of the Summer Session, becomes, ex-officio, an official greeter of many groups who appear on our campus for short courses, institutes, workshops, and conferences. There are many of these, and he is in danger of becoming trite and perfunctory in his performance. After all, there is a limit to the variations that can be played upon but one string. However I must acknowledge that I approach this particular address of welcome with delight for we have seldom been hosts to as appreciative a group, with as ready a willingness to be cooperative and to express gratitude for the pains to which the members of our staff go to provide a successful, useful, and educational program, as the oil chemists. Consequently I can say with genuine sincerity that you are most welcome; we are all glad to see you here again.



R. B. Browne

I cannot forego speaking of this university with some pride. When our forebears came to this continent, not for the sake of empire and exploitation, but to beat a wilderness into submission, to settle and to raise the institutions and to practice the arts of civilization, of all their achievements perhaps the most splendid are the American universities. It was no accident that for the free society of free men which they sought in the new world, they recognized the indispensable element to be education. It is a fascinating story that tells of the development of a universal system of popular education for all the

children of all the people, free, compulsory, and tax-supported, with the responsibility resting with the several states, that is to say, with the people themselves. For the first time in history a whole nation was to be educated, a venture into universal education not found elsewhere at that time. This is one of the grand-scale ideas, and it is, perhaps, the uniquely American idea about America. It had become clear that, as Jefferson said, if a people expected to be both ignorant and free, they expected what never was, and never will be.

I invite your attention to that man, Thomas Jefferson. I have come to hold the opinion that he is our foremost American, and I say this with no wish to belittle the noble, austere Washington or the patient, kindly Lincoln. But it was Jefferson, to whom, more than to any other, we owe our debt for the ideology of Americanism. It was Jefferson who gave us the ringing declaration that man was endowed by his Creator with certain natural rights, which neither he nor anyone else could alienate; that all men are created equal and are entitled to life, liberty, and the pursuit of happiness; that for the sake of making secure these rights governments are instituted among men, deriving their just powers from the consent of the governed. These are magnificent concepts and are worthy of our jealous devotion. How much of the world's misery could be foregone if mankind everywhere could accept them!

One of the great shortcomings in my own early schooling was that of getting to know Jefferson so little. I was introduced by my teachers to Washington although I must confess he remained to me something of a marble statue on a pedestal. I came to feel almost an actual aquaintance with Lincoln as a warm, human being of high nobility and greatness. But Jefferson was never much more than a collection of uninspiring facts in the history book. It was much later that I learned how deeply I was in his debt, and how versatile a genius he was. That he was the father of American architecture, and of scientific agriculture in America, a respectable musician, and philosopher, is illustrative of this last. But he was also, in a real sense, the father of the American school system.

You are today on the campus of one of America's very good universities. It is one of our state universities, which are capstones of our state systems of public schools. It has become a very large and complex enterprise with a distinguished faculty and a student body that comes from all over the world. I wish to express the hope that you men may have a feeling of becoming part of the Illini family and may gain, in some measure, a sense of attachment to the University of Illinois; not the same loyalty you keep for the college or university of your own years of study, but nonetheless a certain interest in this institution. I can vouch for your doing this without apology and with pride for it is no mean university.

The program that has been planned cooperatively with your committee appears to be a good one. I would be most remiss if I did not acknowledge my gratitude to Prof. Tom S. Hamilton of the College of Agriculture, who carries the major responsibility for our part in the success of this course. Then too I should like to thank my own reliable lieutenant, Robert K. Newton, who is tireless in his attention to the thousand details of scheduling and operating this short course. I hope you find your stay here as comfortable as our genuine prairie summer will permit and that you will go away with feelings of satisfaction at having attended. For our part we enjoy your visit with us and trust that you will want to come again.

R. B. BROWNE.

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Some Economic Aspects of the Edible Fats Industries

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THE present discussion is concerned with three related topics in the edible fats industries: recent production trends, competitive relationships between animal and vegetable fats, and some general economic and technological interrelationships.

Part 1. Recent Production Trends

A. B. Paul

The edible fats economy of the United States is in high gear. In 1948 production of food fats was 7.4 billion pounds, the largest since the record levels of 1943 and 1944 when 8.1 and 7.8 billion pounds, respectively, were produced. The 1948 production was 14% higher than the 1937-41 average. (This compares with a human population increase of only 9%).

The upswing in food fat production continues. The first third of 1949 showed a 20% increase over the first third of 1948. The calendar year output for 1949 would set a record if it is maintained at more than 10% over 1948. Prospects for this depend largely upon the current production of hogs, cottonseed, and soybeans. These crops will furnish the major supplies of food fats in the last quarter of 1949. With the 15% increase in the spring pig crop and the 14% increase in the cotton acreage, a new record may be set.

The 1948 increase in food fats over 1947 resulted from increased supplies of vegetable oils (largely cottonseed and soybean) that more than offset decreased supplies of animal fats (largely lard and butter). Table I. The reverse situation appears to be developing in 1949; production of the animal fats probably will increase relatively more. This situation would intensify the already weakened competitive positions of animal fats. This problem will be examined now in greater detail.

Part 2. Competitive Relationships Between Animal and Vegetable Fats

An important development in the food fats industry is the weakened market position of animal fats in relation to vegetable fats. Lard sells for less relative to shortenings under a given supply situation than it formerly did. The same thing applies to butter in comparison with margarine. In both cases users' preferences have changed in favor of vegetable fats. This presents a serious problem for the farm producers and processors of lard and butter. Let us examine some of the evidence of the changes.

A. *Lard vs. Shortenings.* Commercial bakers as a group prefer shortenings. Census data show this fact in the 1923-1939 period, Table II. Use of shortenings by bakeries increased substantially in the 17-year period, but the use of lard did not. The change in favor of shortenings did not occur in response to relatively cheaper shortening prices; something other than prices caused the change. The price of lard and shortenings used by bakers were about the same in 1923, 1929, 1931, and 1937 but the quantities of shortenings relative to lard they used consistently increased. The quantity ratios were 0.4, 1.0, 1.1, and 2.5, respectively. Similarly, the 1927 and 1935 price ratios were equivalent, but the quantity ratio increased from 1.3 to 2.4. Thus with given price relationships, bakers increased their use of shortenings.

The reverse situation is also true. With constant consumption ratios bakers paid increasingly more for shortenings relative to lard. For example, the 1927 and 1939 consumption ratios were nearly alike, but

TABLE I

Food Fats Produced from Domestic Materials (Million Pounds)

Product	Average 1937-1941	Calendar Year						Jan.-April	
		1943	1944	1945	1946	1947	1948	1948	1949
Creamery butter	1780	1674	1489	1364	1171	1322	1214	347	419
Farm butter	431	341	329	337	334	316	316		
Total butter	2211	2015	1818	1701	1505	1638	1530		
Fed. insp. lard	1224	2080	2367	1311	1344	1722	1680	566	666
Other lard	719	785	687	755	794	705	650		
Total lard	1942	2865	3054	2066	2138	2427	2330		
Ed. tallow, stearine, etc.	213	259	198	202	124	184	138	44	62
Total animal fats	4366	5139	5070	3969	3767	4249	3998	(957)	(1147)
Corn oil	155	239	211	205	198	247	203	63	74
Cottonseed oil	1472	1313	1132	1273	966	1117	1462	467	613
Olive oil, edible	6	10	6	4	2	3	3	2	5
Peanut oil	87	153	108	95	101	132	138	54	32
Soybean oil	419	1234	1246	1392	1454	1542	1603	566	638
Total vegetable oils	2139	2949	2703	2969	2721	3041	3409	1152	1372
Total food fats	6505	8088	7773	6938	6488	7290	7407	(2109)	(2519)

United States Department of Agriculture, *Fats and Oils Situation.*

TABLE II

Quantities of Shortenings and Lard Used by Bakeries and Average Prices Paid, 1923-1939

Year	Million Pounds[1]		Cents Per Pound		Shortening-Lard Ratio	
	Shortening	Lard	Shortening	Lard	Quantity	Price
1923	118	271	13.0	13.6	.4	1.0
1925	.....	.....	.....	.....	....	....
1927	259	201	13.0	14.6	1.3	.9
1929	285	279	12.5	12.2	1.0	1.0
1931	282	257	9.2	8.8	1.1	1.0
1933	.....	.....	.....	.....	....	....
1935	394	162	12.1	13.5	2.4	.9
1937	465	185	11.9	12.0	2.5	1.0
1939	420	290	9.9	7.9	1.4	1.2

Based on Census of Manufactures data. [1] Adjusted for sample variation.

the price ratio increased from 0.9 to 1.2. The data are insufficient to work out either the mathematical increase in this demand for shortenings or (what undoubtedly is the case) the decreased rate of substitution within the period.

It appears that increased preference for shortenings by bakers has two aspects. The first is the greater increase in production of bakery products that normally require shortenings over those that normally require lard—e.g. cakes relative to breads. The second is the displacement, wholly or in part, of lard by shortenings in bakery formulas.

A second set of evidence of the deteriorated market position of lard is shown in an analysis of the over-all U. S. market for lard and shortenings. When annual shortening-lard consumption ratios are plotted against corresponding price ratios, two distinct substitution curves are suggested (Figure 1). One curve fits the 1935-41 observations, the other fits the 1921-26 observations. The intervening observations suggest a consistent transition from one average position to the next. (The substitution curve traces out the amount of change in consumption ratios associated with a unit change in price ratios—shown by the slope of the curve.) Two important facts are evident in Figure 1. First, the price position of shortenings relative to lard has progressively improved during the period. That is, for most consumption ratios the price of shortenings relative to lard has moved to a higher level. Second, the substitution between the two fats has decreased. Fat users do not switch readily from one product to the other in response to a price inducement. This fact is indicated by the increased slope of the 1935-41 curve: a given change in price ratios is associated with a smaller change in consumption ratios in the 1935-41 period than in the 1921-26 period.

We can now see an important consequence of this change in preference patterns. When the supplies of one of the competing fats increase by a given amount, its price will decline more, relative to the other fat, than it would have declined in former years. From this standpoint the lard industry suffers more than the shortening industry because the former has little control over its production. Lard is a by-product of pork production, and large supplies cannot be avoided when prices are low. The production of shortenings however is adjusted to the supplies of lard. This is the reason for the low levels to which lard prices have dropped in some recent years. It is a serious problem for the lard industry.

In a sense this is a remarkable development. The shortening industry developed in a market environment in which lard called the turns in supplies. But with these output fluctuations it established itself as a more vigorous competitor, price-wise, than lard. It is a great tribute to the effectiveness of fat technologists and others who have been responsible. At the same time it ought to provide the stimulus needed to improve the market position of lard. In this fat technologists can play one of the key roles.

B. *Butter vs. Margarine.* Margarine improved its market position relative to butter in recent post-war years. The consumption of margarine relative to butter increased substantially in the past two and one-half years compared with pre-war while the margarine-butter price ratios tended to remain unchanged. Relatively short supplies of butter do not sell at any greater premium than did larger supplies of butter in pre-war years. This development suggests that if per capita butter supplies increase in the future, the price premium for butter will decline. The incomes of butter producers and the price and income structure for all dairy products would be affected. It is fortunate for the dairy industry that more profitable markets for butterfat developed in recent years for other dairy products requiring butterfat. This was the major cause of the short supplies of butter.

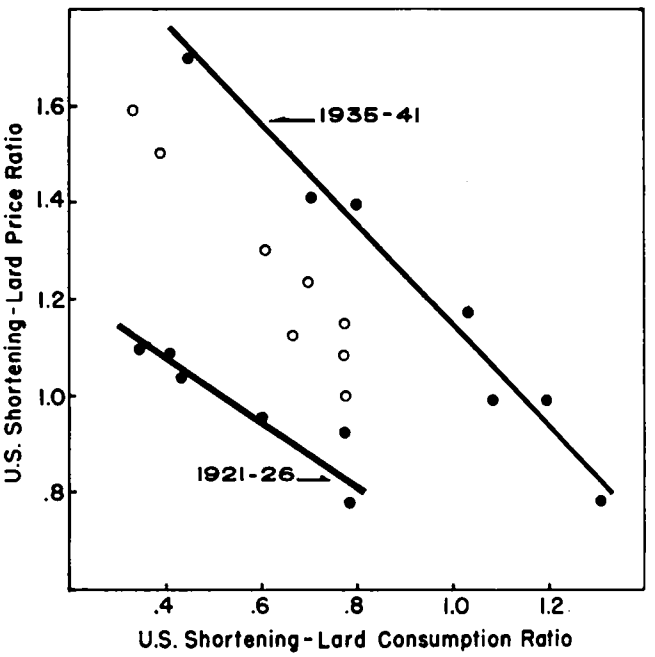


FIG. 1. Relationship between shortening and lard consumption and price ratios, 1921-41.

It is important to note that decreased supplies of butter do not necessarily mean proportionate decreased supplies of butterfat. Butterfat consumption held up better than butter consumption in recent years. Since margarine tends to compete with all forms of butterfat in the human diet, this explains in part the incomplete substitution of increased margarine consumption for decreased butter consumption.

Technologists played an important role in making margarine more acceptable. Not the least of their accomplishments is the built-in device for coloring the product. It is one of the effective ways of lessen-

ing the impact of discriminatory legislation on margarine consumption. It seems to this observer that if improvement in the competitive position of butter is to come it will be through product improvement and merchandising rather than through regulating the sale of the competing product through legislation. These are the competitive weapons the margarine and shortening industries have used successfully.

Part 3. Some General and Technological Interrelationships

The changed market positions of animal and vegetable fats presents only one of numerous interrelationships between economics and technology in the food fats industry. The general nature of such interrelationships are illustrated below. Two types are considered, a) those arising out of economic situations, and b) those arising out of technological situations. While the discussion applies to areas in which economics and technology are clearly related, the conclusion should not be drawn that most economic problems can be solved through technological means.

A. *Economic Situations.* Some economic problems call for technological solutions.[1] The economic problem is revealed when 1. there is a marked change in the economic situation or 2. when we become dissatisfied with a situation that has existed for some time. The rapid deterioration of the price position of lard in the 1930's is an example of a changed economic situation. The relatively low processing yields of cottonseed oil is an unsatisfactory situation that has existed for many years. Perhaps another is the undervaluation of soybean oil in relation to other edible oils. Technological effort has been and is being applied in these problem areas. The hope is to increase the returns per unit by improving yield or quality.

Returns from processing are also affected by short-term market price fluctuations. Industries that carry heavy inventories are vulnerable to price declines, particularly if they have no satisfactory method for shifting this risk. The solution may lie largely outside of the technologists' sphere, but not entirely. An important result of technological improvement in a product is that with proper selling effort some degree of consumer allegiance can be secured for it. This would enable the firm to get out from under high cost inventories with a smaller decline in selling price than otherwise. Of course some industries are better situated to benefit from this than others.

Another set of economic problems is concerned with the lowering of costs. There are many problems here but only one will be discussed—the under-utilization of plant and equipment—a serious economic problem for the firm as well as for society at large. One has only to note the large fluctuations in output (short-term, seasonal, annual, cyclical, and secular) of different industries to be aware of its magnitude. In 1921 and 1923 the census collected data on excess capacity in manufacturing. The typical food industry used only about 60% of its capacity in these years; the range was 30% to 83%. Cottonseed mills reported 52% utilization of plants in 1921, and 48% in 1923; margarine plants reported 42% and 69% utilization. The situation in most years would show substantial underutilization in many food industries.

[1] This does not say that technological changes usually take place in areas of greatest economic need. This is an interesting, but separate problem.

Under-utilization results from 1. fluctuations in materials supply, as illustrated by the oilseed crushing and lard producing industries; 2. fluctuations in demand, as illustrated by the shortening and margarine industries; 3. structural readjustments, as illustrated by geographical shifts in areas of supply or modes of transportation (cottonseed, flaxseed, and the lard producing industries are good examples); 4. obsolescence of existing equipment by new methods.

Under-utilization of plant and equipment appears to be unavoidable in a free enterprise economy with advancing techniques, changing supplies, and changing markets. The role of the technologist in fuller utilization of equipment probably is restricted to his efforts to adapt existing equipment to new uses and to help in the design of equipment and processes that have greater flexibility.

B. *Technological Situations.* Technological situations often call for an economic appraisal of their consequences or of their feasibilities. What are the economic consequences of the trend to solvent processing of soybeans? To consumers it meant 110 million pounds additional soybean oil was made available from the 1947-48 crush than otherwise would have been possible (the 61.0 million bushels that were processed in solvent plants yielded 1.8 pounds per bushel more oil than yields obtained from screw presses). To farmers it meant a greater return for the soybean crop. The greater net value of product per bushel appears to have been translated, in part, to farmers through a greater mill demand for beans. Evidence of this is that screw plants tend to greater idleness than solvent plants.

To the soybean milling industry it means readjustments in output among mills. Mill capacity has risen sharply in post-war U. S. A. and the industry will probably experience, more or less acutely, excess capacity from time to time. In what manner will a relatively short supply of beans be distributed among the mills? The answer depends largely upon the interaction of several economic variables.

1. The availability of beans in the supply area normally serving a mill will, in part, determine the volume of its operations. Production of soybeans may not decrease uniformly in all producing areas.

2. The operating costs per bushel may behave differently for different mills with changes in volume. For any given season the quantity of labor that can be treated as an operating cost, and the quantity that can be treated as an overhead cost may vary from mill to mill. Labor that is hired for the season—or labor that is hired primarily for another company enterprise such as a grain elevator or feed mill—is in effect an overhead cost; labor that is hired and discharged in accordance with mill needs is an operating cost. The strongest competitors for beans will be those with a minimum amount of variable labor costs. Of course, this does not mean they will be the most profitable, or least unprofitable in the season. Profits depend upon the excess of revenue above total costs.

3. The optimum rate of extraction may vary with the season for certain mills. Some mills may have more leeway in adjusting the rate than others.

4. Other considerations involve the character of the firms. In an integrated firm the relationship between the output of soybean mills and the next stages of processing may be a deciding factor. The financial position of the firm may be a factor.

What are the economic consequences of a new product? For example, what effect will the new bland lard products have upon lard prices and sales, and what effect upon the market for shortenings? What effect will the widely discussed "bread softeners" have upon the demand for lard and shortenings? Time and space do not permit speculation here about the economic consequences of these technological changes, but it is desirable to undertake a systematic appraisal of these problems in view of their great importance. Incidentally, I believe the possible displacement of shortenings or lard in bread by the use of softeners has been exaggerated by many people. In 1939, the commercial baking industries reported the use of 767 million pounds of fats; probably not over 150 million pounds of this was used in bread, the remainder in cakes, biscuits, pies, etc. If there is to be a profound effect on the market for fats, the possible changes in the latter formulas are the more important.

The second general problem is to examine the economic feasibility of a proposed technological change. Should a firm install a new type of processing equipment? Should a firm produce a new type of product? Most problems will fall under these headings. All we shall say about the latter is that it calls for a careful study of costs, the market, and probably some consumer acceptance testing.

The problem of appraising the economic feasibility of changing to new type of equipment may be explored. Will it pay? The approach here appears to be easy, but the answer is by no means easy. Calculate the expected increase in gross revenue per unit; from this subtract the expected operating costs per unit. If the remaining margin times the annual number of units produced is enough to pay the annual cost of the new equipment, the investment is economically feasible. The difficulties in obtaining an accurate answer arise at three main points.

First, the estimate of annual volume of output calls for a careful appraisal of the sufficiency of material supplies. Will farm production hold up to expected levels? Will new firms enter the field rapidly to compete for the supplies available to the plant? Also the probable level of demand for the product must be studied. If the product has good substitutes, how abundant will be their supplies? How about the impact of prospective consumer incomes on the level of demand for the particular product? Knowledge of the income-elasticity of demand for the product would be helpful here.

Second, estimating the annual cost of the proposed equipment presents the problem of using a proper depreciation rate. A higher rate will be in order if rapid improvements in the design and set-up of processing equipment is likely. The problem is difficult to solve with any precision, but it should be faced.

Finally, the estimate of the increase in revenues per unit has its own difficulties. What are proper market prices to use? It must be assumed a certain average level of product prices (in the period the equipment is to be paid for) or that the fluctuations in the level of product prices will be followed fairly closely with similar fluctuations in unit operating costs. Next, it should be determined how the price of the specific product is likely to deviate from the general group level. This point will be amplified with a timely illustration.

Suppose a cottonseed mill considers investing in a newly designed set of equipment that will lower the gossypol content of cottonseed meal. Such feed would be improved in the sense that it would be used more freely in livestock and poultry rations. The price premium might be expected to approximate the differential in selling price between current quality cottonseed meal and other oil meals. Would this premium be sufficient?

The answer depends largely upon two factors: the supply of cottonseed meal relative to other meals, and the over-all demand for protein feeds. A situation may be visualized in which a short supply of cottonseed meal and a generally strong demand for protein feed would cause cottonseed meal prices to be about equal to the other oil meals since there is a substantial area of use in which present-day cottonseed meal is just about as good.[2] This may not be the situation this year or the next, but it probably is the direction in which the industry is moving in the coming decade. There will be an increase in the demand for high protein feed with *no equivalent increase* in the size of the cottonseed crop.

The above conclusion may be modified by other factors, e.g., the cost of the necessary equipment may be made low enough to permit profitable operation despite a narrow premium for the improved product; or perhaps a way may be found to increase the volume of cottonseed mills, thus achieving lower unit costs of operation than would obtain at present.

The point of the above example is that firms must be careful in using current premiums in calculating the expected increase in returns from an improved product since these premiums are governed by economic forces that might change. This reasoning may be applied to many other areas in the fats industries. The unique factors peculiar to each situation should be examined to arrive at a good appraisal.

[2] The rapid growth of the mixed-feed industry in recent years probably has resulted in a greater rationality in users' evaluation of alternative sources of protein.

The Chemistry of Fats

B. F. DAUBERT, Department of Chemistry, University of Pittsburgh

A CHARACTERISTIC feature of fats is their complexity. No longer can we conceive of a fat as consisting of glycerol and three fatty acids for they are complex mixtures of mixed triglycerides of which the constituent fatty acids are both saturated and unsaturated. Indeed, the realization of the large number of possible combinations of glycerides in a fat serves to emphasize their complexity. Inherent problems of the molecular structure of the component glycerides of a fat have been a worthy and exciting challenge to the chemist, and although considerable progress has been made on the study of their composition through the application of such techniques as fractional distillation, fractional crystallization, selective hydrogenation, and chromatographic adsorption, developments during the past decade have indicated a quickened pace in the fundamental chemical study of these naturally occurring products.

In this brief discussion of the chemistry of fats attention in most respects must be centered on the chemistry of the fatty acids rather than on the glycerides. Many of the properties of the glycerides are a reflection of the properties of the fatty acids. Naturally occurring fats, in addition to containing predominantly triglycerides as the major constituents, contain phosphatides (triglycerides in which one of the three fatty acid groups may be considered as having been replaced with a phosphoryl choline group, lecithin, or a phosphoryl β-amino ethyl alcohol group, cephalin). Other minor constituents include sterols, pigments (carotene), antioxidants (tocopherols), and carbohydrate fragments. The latter are present in a few per cent or less and together with the phosphatides are removed to a greater or lesser degree in the refining process.

The complexity of the glyceride composition of a fat increases with the number of component fatty acids as it is well known that different fatty acid radicals combine with a single glycerol molecule.

Phosphatides. The phosphatides which are largely removed in the refining process of fats and oils occur to varying amounts in animal and vegetable fats, the latter containing by far the greater amount of phosphatide. The phosphatide content of animal fat is usually very low. The phosphatide in both animal and vegetable fat is usually associated and may be chemically combined with carbohydrate. The fatty acid composition, at least in vegetable phosphatides, approximates the composition of the oil in which they are found.

The two general classes of phosphatides occurring in vegetable fats are the lecithins and the cephalins, structures of which are indicated in Figure 1. The nitrogen-phosphorus ratio in both classes is usually 1:1.

Sterols. Sterols occur in both plant and animal fats. Those occurring in plants are called phytosterols and those in animals zoosterols. They comprise most of the unsaponifiable matter in a fat, the remainder consisting essentially of hydrocarbons (squalene, etc.).

The most extensively investigated animal sterol is cholesterol. The plant sterols occur in considerable

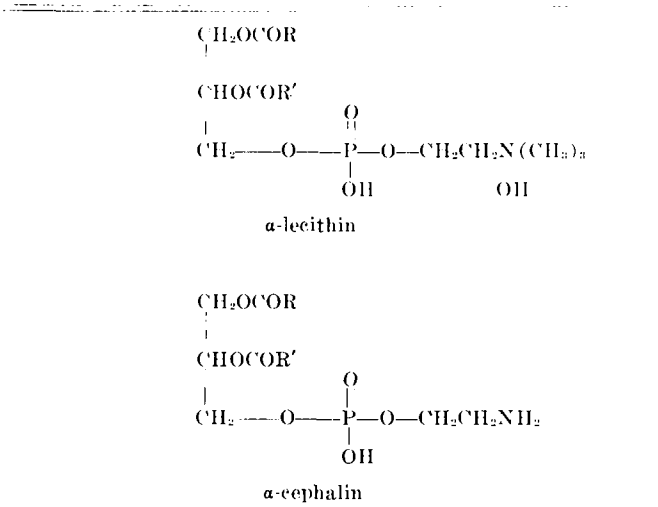


FIG. 1. Types of phosphatides.

numbers in nature; two of them, β-sitosterol and stigmasterol, are fairly well characterized.

Fatty Acids. The naturally occurring fatty acids, in the main, are divided into two general classes, the saturated and unsaturated. The saturated acids, characterized by the formula $C_nH_{2n-1}COOH$, are normal, monobasic, aliphatic acids and with but one exception (iso-valeric) contain an even number of carbon atoms. The unsaturated acids for the most part consist of 18 carbon atoms with one or more double bonds in the aliphatic chain. Both the saturated and unsaturated acids are structurally related.

The saturated fatty acids include lauric, myristic, palmitic, and stearic as the more important naturally occurring fatty acids. The more important unsaturated acids are oleic, linoleic, and linolenic acids. These groups of acids with but few exceptions occur to the greatest extent in most natural fats and oils. Tables I and II include, in addition to these acids, other saturated and unsaturated acids.

Isomeric Fatty Acids. Although it is not normal for saturated fatty acids to exhibit isomerism, unsaturated fatty acids show both positional (difference in position of double bonds) and geometric (*cis-trans* isomerism). Isomers of oleic acid (9,10-octadecenoic acid) which are known to be naturally occurring include petroselinic acid (6,7-octadecenoic acid) and vaccenic acid (11,12-octadecenoic acid). Elaidic acid, the *trans* isomer of oleic, does not occur in natural fats and oils, at least so far as I am aware. Several isomers of normal linoleic acid (9,12-octadecadienoic acid) have been reported to occur naturally, and it is well known that isomers of linolenic acid (9,12,15-octadecatrienoic acid) occur in natural fats.

However, although few isomeric fatty acids occur in nature, it is quite possible that a variety may be produced in processed fats and oils by (1) hydrogenation of monoethenoid, conjugated and non-conjugated polyethenoid fatty acids, (2) action of isomerization and heat, (3) debromination of tetrabromo-

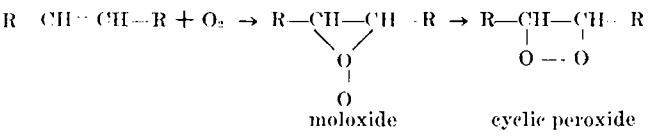
stearic acids, (4) catalytic dehydration of naturally occurring hydroxy fatty acids. Positional and geometric isomers may also be prepared artificially or synthetically.

The partial hydrogenation of unsaturated fatty acids or glycerides containing them usually results in a variety of isomeric acids. The amount and kind depend upon the nature of the original oil and the conditions of hydrogenation.

The two methods which are customarily used to determine the position of the double bond in the aliphatic chain are oxidation and ultraviolet absorption. Both methods however are somewhat limited. Neither method is satisfactory for distinguishing geometric isomers *(cis-trans)*. More extensive use however of infrared analysis has served to provide an adequate method for distinglishing *cis* from *trans* isomers. Fatty acids of *trans* configuration exhibit characteristic infrared absorption in the region of 10.3 μ.

Autoxidation. The spontaneous addition of atmospheric oxygen to the double bond system of the unsaturated fatty acids in a glyceride to form peroxides which later result in the formation of short chain products and thus rancidity in edible fats is differentiated from the purposeful addition of oxygen to highly unsaturated fatty acids to cause polymerization into useful products.

Since autoxidation is the major cause of rancidity, it is perhaps appropriate to discuss briefly some of the postulated mechanisms of this. The classical concepts of the reactions that occur during oxidative rancidity involve the initial addition of oxygen to an unsaturated carbon-to-carbon linkage and the subsequent formation of a cyclic peroxide. Staudinger believed that a highly reactive moloxide stage precedes the formation of the cyclic peroxide:



The active peroxide once formed presumably undergoes rapid decomposition with the simultaneous formation of new peroxide molecules. Several mechanisms have been postulated for the decomposition of these organic peroxides and initiation of a chain of reactions accompanying the development of oxidative rancidity. One involves a suggestion that the peroxide reacts with a saturated fatty acid chain by a process of dehydrogenation with the corresponding formation of a new double bond, which then peroxidizes and subsequently decomposes into short-chain saturated aldehydes and acids.

Perhaps a more complete understanding of the autoxidation process has resulted from the work of Farmer, who postulated a hydroperoxide as the first compound formed in the autoxidation of olefinic type substrates (e.g., unsaturated fatty acids). If the hydroperoxide theory is correct, then a reinterpretation of the autoxidative process must be made in the light of this theory. The hydroperoxide is formed presumably by a free radical mechanism of olefinic peroxidation. Secondary reactions subsequently lead to the production of scission products.

Important Chemical Characteristics of Fats

Saponification Value. Considerable information concerning the nature of a fat or oil can be gained from a knowledge of the saponification value. The saponification values of neutral glycerides and other esters of fatty acids vary with the nature of the fatty acids. Oils of high saponification number contain fatty acids of low molecular weight while the converse is true for oils containing high molecular acids. The use of the term saponification equivalent is preferred by many as an indication of the molecular weight of a single fatty acid or the average molecular weight of a mixture of fatty acids; the saponification equivalent in the case of glycerides is one-third of their molecular weight. If the saponification number is known, however, the saponification equivalent can be calculated as follows:

$$\text{S.E.} = 56{,}104 \ : \ \text{Sap.No.}$$

TABLE I

Saturated Fatty Acids

Name	Number of carbon atoms	Source with highest content		Other sources
		Source	%	
Caproic	6	Coconut	2	Butter, palm nut oils, etc.
Caprylic	8	Coconut	10	Butter, palm nut oils, etc.
Capric	10	Elm	50	Coconut, butter, palm nut oils, etc.
Lauric	12	Cawal-Kurundu	86	Laurel oil, spermaceti, babassu, palm kernel, etc.
Myristic	14	Nutmeg butter	77	Kombo, dika, ucuhuba
Palmitic	16	Japan wax	77	Animal and vegetable fats
Stearic	18	Bouandja (allanblackia)	57-63	Animal and vegetable fats
Arachidic	20	Rambutan tallow	35	Peanut oil
Behenic	22	Niam Xylia xylocorpa	14.2 17.3	Peanut oil, oil of Ben
Lignoceric	24	Coral tree	26	Peanut oil, rapeseed oil, cerebrosides
Carnaubic	24	.....	.....	Carnauba wax
Cerotic	26	.....	.....	Beeswax, wool fat, opium wax
Melissic	30	.....	.....	.....

TABLE II

Unsaturated Fatty Acids

Name	Carbon number	Double bonds	Source with highest content		Other Sources
			Source	%	
Crotonic	4	1	.....	....	Croton oil
Tiglic	5	1	.....	....	Croton oil
Oleic	18	1 (9)	Coula	95	Animal and Vegetable fats
Elaidic	18	1 (9)	.....	....	Hydrogenated fat? Does not occur in natural fat
Petroselinic	18	1 (6)	Parsley	76	Umbelliferae oils
Erucic	22	1 (13)	Nasturtium	82	Cruciferae oils
Linoleic	18	2 (9, 12)	Safflower	78	Linseed and cottonseed oils
Tariric	18		Tariri (Picramnia Sow)	95	.....
Linolenic	18	3 (9, 12, 15)	Perilla oil	70	Linseed oil
Elaeostearic	18	3 (9, 11, 13)	Tung oil	75-95	.....
Clupanodonic	18	4	.....	....	Japanese sardine oil
Arachidonic	20	4	.....	....	Animal fat, phosphatides

The S.E. to be of experimental value in determining molecular weights must be determined with care and precision.

Iodine Value. The simplest and most rapidly determined chemical constant for a fat or oil is its iodine value. It is a most valuable characteristic in fat analysis for it measures total unsaturation. It is highly accurate and gives near theoretical values except in cases of conjugated double bonds or triple bonds, or when double bond is near a carboxyl group. The iodine value will, as a general rule, lead in the most rapid manner to the identification of a fat or oil. One can certainly determine the class to which a given oil or fat belongs if the iodine value is known. Despite its usefulness however the absorption of hydrogen (hydrogen number) is perhaps the best indication of total unsaturation. The possibility of halogen substitution is always present in iodine value determinations and may lead to faulty results. The mechanical difficulties involved in the determination of hydrogen absorption however militates against its wide use.

Valuable indications of the nature of a fat or oil can be obtained from the Reichert-Meissl number for it is generally known that most naturally occurring fats and oils contain but small quantities of soluble volatile acids. It therefore follows that a relatively high Reichert-Meissl number would be a characteristic and possibly lead to information concerning the nature of the fat.

Methods available for identification and amount of specific fatty acids in a fat include thiocyanogen number (linoleic and linolenic acids), tetrabromide number (linoleic acid), hexabromide number (linolenic acid), diene number (conjugated acids). These methods, for various reasons, have largely been supplanted by the spectrophotometric procedure although it is claimed by many that the thiocyanogen determination, if carefully controlled, gives a more accurate indication of linoleic and linolenic acids, despite its empirical relationship, than the spectrophotometric procedure.

Acetyl value of a fat or oil is a valuable characteristic only if triglycerides containing hydroxy fatty acids are present, e.g., castor oil. The acid value, although a variable constant, is important because the extent of hydrolysis (deterioration) or oxidation can be followed by its determination. Therefore it is particularly useful in determining the quality or freshness of fats and oils.

The Composition of Fats

B. F. DAUBERT, Department of Chemistry, University of Pittsburgh

THE general scope of the problem of investigating the chemical constituents of the natural fats is now clear since it has been conclusively demonstrated that seed fats are mixtures of mixed triglycerides and that the occurrence of simple triglycerides is quite exceptional. It falls into two parts: 1. the identification and determination of the proportion of the fatty acids present, and 2. the elucidation of the manner in which these are combined with glycerol.

B. F. Daubert

At the present time the methods of that branch of analysis concerned with the determination of the fatty acid composition of fats and oils have attained an advanced state of sensitivity and precision; contributions to the evolution of the present day techniques have come from a number of sources, and the techniques themselves embrace a wide variety of separation procedures and analytical methods directly applicable to fatty acid mixtures.

Non-Solvent Crystallization. The higher melting fatty acids of a fatty acid mixture have been separated from the mixture by slowly chilling and filtering out the solidified portion.

Solvent Crystallization. a) *Separation of Fatty Acid Salts.* The separation of fatty acids from solid fatty acids through the difference in solubility of such salts as barium, magnesium, or lead salts was first accomplished nearly a century ago. Such methods are tedious and only successful to a limited extent. In all cases the methods are empirical, and a single fractionation yields only a partial separation, a number of operations being required for a good resolution.

b) *Separation of Fatty Acid Bromine Addition Products.* Bromination of linoleic acid yields, among other products, a solid tetrabromide insoluble in petroleum ether, and linolenic acid, a hexabromide insoluble in ether. These facts have led to procedures for the separation of these acids from mixtures, but the large percentage of other isomers formed and the complex mutual solubility effects largely vitiates these procedures.

c) *Separation of Fatty Acids.* Crystallization procedures at or near room temperature are not well adapted to separating most mixtures of fatty acids, for above 0°C. the common unsaturated fatty acids are liquids, infinitely soluble in such solvents as acetone and ether. Only in the comparatively recent past have crystallization techniques, at markedly lower temperatures, been employed. Low temperature solvent crystallization has been extensively used for the isolation of many naturally occurring fatty acids such as oleic, linoleic, linolenic, erucic, and ricinoleic. Elaborations of the procedure have served as foundations of analytical methods for the determination of the saturated acid content of fatty acid mixtures. Determinations of fatty acid solubilities and of mutual solubility effects at low temperatures are leading to the development of more effective crystallization procedures.

Fractional Distillation. The first important studies in the use of fractional distillation for the separation of fatty acids were made as early as 1880. The fractional distillation of methyl or ethyl esters of the acids has been considerably refined since that time by a large number of investigators. For accurate quantitative results it is necessary to obtain separate portions which contain not more than two adjacent homologous saturated esters and not more than two adjacent homologous unsaturated esters. For the latter fraction the percentage of saturated esters can be determined by oxidation of the unsaturated esters to alkali-soluble products. The saponification equivalent and iodine value of the original and the separated group together with the percentage of the latter provide enough data for calculating the composition of the total fraction in terms of known fatty acids. Four equations are obtained, sufficient to provide a solution for four unknowns.

In practice the procedure is usually, but not always, simplified by preliminary separation of the mixed fatty acids into saturated and unsaturated. In these cases where myristic and lower fatty acids are present, it is often possible to separate these by a preliminary partial ester distillation. Whenever lower fatty acids are present, e.g. butyric, a preliminary steam distillation of the mixed acids serves to remove them for separate examination.

Chromatography. Chromatographic separations, originally developed at the beginning of the 20th century, have only recently been successfully applied to the separation of fatty acids. Unsaturated fatty acids, saturated fatty acids, and branched chain fatty acids have been separated, using a flowing chromatographic method. Partition chromatography has been recently applied to the separation of normal saturated fatty acids from five to 19 carbon atoms.

Spectrophotometry. Studies of the ultraviolet absorption spectra of unsaturated fatty acids, both of the natural isomers and the conjugated isomers, have led to the development of methods for the direct determination of tetraenoic, trienoic, and dienoic acids in a fatty acid mixture. Determination of the iodine value of the mixture allows an extension of the method to the estimation of monenoic and saturated fatty acids.

In many instances, several or more of the above procedures have been used in combination to great advantage in the isolation of a single acid or the identification of the components of a mixture. The analytical work of Hilditch exemplifies a combination of the lead salt separation and fractional distillation; his extensive studies of the fatty acid compositions of many plants and animal fats have established correlations between fatty acid composition and species. The quantitative work of Baldwin and Longenecker clearly demonstrated the remarkable accuracy attainable in the analysis of a fatty acid mixture and its components by a combination of spectrophotometry and fractional distillation.

Glyceride Content of Fats. The analytical meth-

ods previously described have been widely applied, and the fatty acid compositions of many naturally occurring fats and glyceride oils are known; many properties of these substances can be successfully correlated with their fatty acid compositions. But this approach to the properties of fats and oils from the viewpoint of their fatty acid composition, although a valuable one in many respects, encounters its final limitations in the facts that the components of these materials are glycerides rather than fatty acids and that the characteristics of fats and oils are derived from the characteristics of the component glycerides.

It is apparent that the order of magnitude of difficulty attending the separation and determination of glycerides is much greater than that concomitant to the separation and determination of fatty acids. Adjacent members in homologous or analogous series of glycerides differ from each other much less in characteristic physical and chemical properties than do adjacent members of similar series of fatty acids because of the factor of approximately three separating their molecular weights. Furthermore many of the procedures proper to fatty acid analyses cannot be applied to glyceride analysis because they possess features which would lead to the destruction of the glycerides. Prominent examples of unapplicable procedures are salt formation and fractional distillation in the range of ordinary vacua, the one involving glyceride destruction through hydrolysis, the other through polymerization and thermal cracking. Only since 1927 has the study of the component glycerides of fats and oils been placed on a quantitative basis. Since then a number of separations and analytical procedures have been developed and applied. They lead for the most part to the elaboration of glyceride mixtures simpler than the original or to analytical figures in terms of closely related glycerides, and in only a few cases have single compounds been separated or analytical data in terms of single compounds been obtained. However the occurrence in various fats of simple triglycerides—trilaurin, trimyristin, tripalmitin, triolein, trilinolein, trilinolenin, trierucin, triricinolein, trielaeostearin, and traces of tristearin—have been authenticated. Of the mixed triglycerides only the 2-oleyldistearin, of kokum butter, cocao butter, and the rare allanblackia fats and 2-oleyldipalmitin of Stillingia tallow and piquia fats have been authenticated. There is also considerable evidence that 2-palmityl oleylstearin is contained in lard.

One of the first quantitative tools applied to glyceride analysis was the oxidation procedure developed by Hilditch. It allows the estimation of those glycerides possessing only saturated acids. The glyceride mixture is oxidized in acetone with potassium permanganate; all ethylenic leakages are split and the carbons oxidized to carboxyl groups. The alkali soluble azelaoglycerides can be separated from the unaffected trisaturated glycerides.

Complete and partial hydrogenation procedures are also used to study the glyceride composition. In general, however, the exact sequence of events in the hydrogenation of a complex mixture of glycerides of different degrees of unsaturation is not known. Thus the margin of error in both types of hydrogenation studies is rather large, and they are not favored for analytical purposes at the present time. Hilditch says, ". . . . (hydrogenation) is a procedure which should be used with caution and indeed avoided where possible. It has proved of considerable use in the earlier stages of the study of glyceride composition, but the subsequent advances in pre-resolution of mixed glycerides by crystallization have made its employment less necessary."

Molecular distillation has been applied to many oils but the process, while capable of separating free fatty acids, odorous and flavoring materials, sterols, and vitamins from the oils, does not accomplish any significant fractionation of the glycerides. The predominance of oleodilinolenin and dilinoleolinolenin in linseed oil has been established by chromatography. In addition an impure trilinolenin has been isolated from linseed oil by the same technique.

Solvent Partition. The employment of binary liquid-liquid extraction systems for the separation of components of oils has been tried; high iodine value fractions have been separated from soybean, corn, cottonseed, and linseed oils using the system oil-methanol. The only slight solubility differences exhibited between the predominant glycerides of these oils and the complex mutual solubility effects found to exist impose limitations on this type of separation as far as isolation of single glycerides or even radically simpler mixtures is concerned.

Non-solvent crystallization is not very useful for glyceride separation. On the other hand solvent crystallization for the separation of unchanged glycerides has been of advantage and falls naturally into two phases. Prior to 1936 the primary aim was the isolation of pure glycerides from fats and oils with little attention being focussed on the evaluation of the entire glyceride structure of a particular fat as a whole; these studies were conducted in the range of temperature from 0° to room temperature. In 1936 however crystallization procedures were applied not towards isolating single compounds but rather towards separating the entire complex fat into a number of fractions simpler in their composition; chemical studies for further information could then be applied to the individual fractions, the relative simplicity of the fractions facilitating the interpretation of the chemical data. The method has been applied to a number of fats employing temperatures below 0°C. This technique of low temperature precipitation of the glyceride components of an oil from a dilute solution of the oil or fat, utilizing no physical agencies that would change the glyceride components of the oil, involving no chemical treatment of the glycerides, and possessing the ability to bring about a marked separation of the glycerides, is the most promising procedure yet developed for the resolution of a glyceride mixture into its components or markedly simpler mixtures.

This brings us to the glycerides themselves. The fat or oil triglyceride mixture may be regarded as broken down into glyceryl residues and fatty acid residues, and an inquiry has been instituted to determine what scheme of fatty acid distribution predicts the manner in which the fatty acid residues are actually found distributed among the positions on the glyceryl residues available for esterification. The inquiry possesses additional interest in that all features of the distribution scheme actually found must be paralleled by features in the enzyme systems responsible for the glyceride synthesis.

TABLE I

Comparison of Experimental With Calculated Glyceride Structures

	Ln Ln Ln,1	Lo Lo Lo,1	Ol Ol Ol,1	S S S,1	Ln Ln S,2	Ln Ln Ol,2	Ln Ln Lo,2	Lo Lo S,2	Lo Lo Ol,2	Lo Lo Ln,2
Mono-Acid Triglyc. Distribution	6.15 g.	596	230	147	0	0	0	0	0	0
Random Distribution	0.0003	223	12.5	3.24	0.02	0.03	0.07	164	257	6.96
Even Distribution	0	0	0	0	0	0	0	291	524	0
Partial Random Distribution	0	8.0	0	0	0	0	0	332	485	0.50
Experimental Distribution	0	8.9	0	0	0	0	0	335	482	0
	Ol Ol S,2	Ol Ol Lo,2	Ol Ol Ln,2	S S Ol,2	S S Lo,2	S S Ln,2	S Ol Lo,3	Ol Lo Ln,3	S Ol Ln,3	S Lo Ln.3
Mono-Acid Triglyc. Distribution	0	0	0	0	0	0	0	0	0	0
Random Distribution	23.9	98.0	1.02	15.3	39.9	0.41	125	5.34	1.30	3.40
Even Distribution	0	0	0	0	0	0	146	15.5	0	3.00
Partial Random Distribution	1.69	70.0	0.50	4.16	17.5	3.20	40.8	1.00	10.5	2.94
Experimental Distribution	3.60	72.7	0	0.18	16.8	4.10	41.5	0	11.8	3.19

The number of glyceride types possible from n fatty acids depends on the degree of distinction made.

Let

N_1 = number of glycerides, optical isomers distinguished = n^3

N_2 = number of glycerides, position isomers distinguished, but not optical isomers = $(n^3 + n^2)/2$

N = number of glycerides, neither position nor optical isomers distinguished = $(n^3 + 3n^2 + 2n)/6$

Schemes of Fatty Acid Distribution. The oldest scheme, the monacid triglyceride scheme, long proven invalid and of interest only historically, is the simplest possible and states that only monacid triglycerides are formed; thus all palmitic acid in a fat would be esterified as tripalmitin. Here the quantitative calculations are obvious. All experimental work on both plant and animal fats indicates this idea to be in error; the reality is nearly the reverse since experiment demonstrates simple monacid triglycerides formation to be the exception rather than the rule.

Random Distribution. The scheme of random distribution states that the fatty acids are distributed among the various positions of the glycerol molecule in the manner that would be expected from considerations of probability alone; simple continuous relationships exist between the number of glycerides present and between fatty acid concentrations and glyceride concentrations. Hence an oil or fat in which the fatty acids are distributed randomly possesses quantities of all possible triglycerides derivable from the fatty acids present.

The total possible chemically distinguishable glycerides = possible triacid triglycerides + possible diacid triglycerides ($a = a^1$) + possible diacid triglycerides ($a = \beta$) + possible monacid triglycerides = $(n^3 + n^2)/2$. For example, two fatty acid species result in an oil containing six glyceride species while an oil containing four fatty acid species results in an oil containing 40 glyceride species. The random scheme results in a more complex fat than does any other scheme.

Even Distribution. The scheme of even distribution arose from the experimental observation that monacid triglycerides in natural fats and oils are actually rather rare. Both previously mentioned schemes of distribution allow the occurrence of monacid triglycerides; the random scheme, in fact, indicates that a fatty acid existing in a large percentage is represented to a substantial degree by a monacid triglyceride formation and that even an acid existing in only a small percentage is present in some amount as monacid triglyceride. The even distribution hypothesis limits the types of glycerides possible. Every glyceride molecule must possess one molecule of the particular fatty acid before any glyceride can possess two, and every glyceride must possess two before any glyceride can possess three. Geometrical considerations of the even case show that a concentration greater than 33⅓% is necessary for diacid glyceride formation and that a concentration greater than 66⅔% is necessary for monacid glyceride formation. In even distribution not all conceivable glycerides are expected. Even distribution, as may be seen, greatly reduces the number of total glycerides.

It should be emphasized that the even system, though evolved primarily from considerations of monacid triglycerides, affects the proportion of all types of glycerides existing in a fat and gives a composition entirely different from that of the random scheme.

Partial Random Distribution. The partial random scheme represents something of a compromise from the relatively rigid conditions of the pure even system and derives from the fact that monacid triglycerides, although much less prevalent than the random system suggests, occur more frequently than the pure even system allows. The partial random system, in effect, has many characteristics in common with the even system, but it deviates from the even system in that it decreases the critical concentrations of acid required for diacid and monacid triglycerides formation from 33⅓% and 66⅔% to lower values. Obviously many partial random systems exist. The minimum fatty acid concentration for monacid triglyceride formation in the partial random scheme has been set as low as 50 to 55%, with a corresponding reduction made in the requirement for diacid triglyceride formation. The partial random scheme as used in a recent study of corn oil placed the critical fatty acid concentration necessary for monacid triglyceride formation below 59.0% and above 20.9% and the concentration necessary for diacid triglyceride formation below 20.9% but above 0.56%. Hence linoleic acid (59.6%) can occur either once or twice, or three times. Oleic acid (23.0%) can occur either once or twice and the same is true of saturated acid (14.7%). Linolenic acid (0.6%) can occur only once.

In Table I is shown a comparison of glyceride structures for corn oil calculated for the above schemes and determined by analyses of fractions obtained by low temperature fractional crystallization of the oil in acetone.

Mechanism of Glyceride Formation. It is reasonable to assume that glycerides are largely formed from carbohydrates. This is suggested by the sharp decline of carbohydrates and the rise of the glyceride content in ripening seeds.

Processing of Oil Seeds and Nuts by Hydraulic and Mechanical Screw Press Methods

R. P. HUTCHINS, The French Oil Mill Machinery Company, Piqua, Ohio,
Hydraulic Processing and Continuous Screw Presses

Summary

OIL seeds and meat scraps are processed to produce crude oil and high protein feeds by the following methods: (In all methods there is an initial cleaning, weighing, storing, and meats preparation preliminary to the production of raw material suitable for subsequent oil separation.)

1. Crushing, cooking, forming, and pressing in hydraulic box presses
2. Crushing, cooking, forming, and pressing in hydraulic cage or curb presses
3. Preparation and pressing in continuous mechanical screw presses
4. Preparation and solvent extraction
5. Preparation, pre-pressing, and solvent extraction

A brief description and illustrations of the first three processes are included in this discussion.

R. P. Hutchins

The hydraulic processing of oil seeds using box presses in which each 16 pounds of material are handled individually by labor is clearly obsolete in these times of efficiency in engineering and high labor costs. A somewhat better case can be made for cage press processes, especially on materials that are highly abrasive and corrosive or of a nature that presents difficult problems in solvent extraction.

It seems obvious that hydraulic box press operators should convert to either continuous presses or solvent extraction. Continuous presses have several advantages over extraction:

1. Lower initial investment
2. Simpler operation
3. Lower operating costs
   a) Less labor and supervision
   b) Lower steam usage
   c) No solvent loss
4. No special safety problems

Only in power cost, maintenance cost, and value of products does solvent extraction usually have an advantage.

For high oil seeds such as flax, peanuts, copra, and similar materials, pre-pressing in mechanical screw presses followed by extraction is the most economical method of obtaining maximum oil yields. For intermediate oil content seeds, such as cottonseed meats, although direct extraction is feasible, it is probable that present mechanical press plants will find it economical to go to pre-pressing followed by extraction. On such seeds new plants using continuous presses can be safely installed without fear of losing out economically to solvent operation.

Discussion

Oil seeds can be processed to separate the oil from the high protein meats by five processing methods. These methods are indicated in Figure 1. The seeds

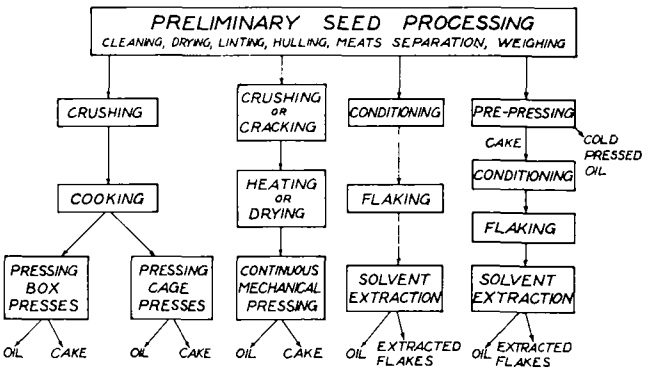


Fig. 1. Methods of obtaining crude oil from vegetable seeds and nuts.

are first brought into the plant and treated according to the nature of the material. The usual processes are cleaning, drying, delinting (as regards cottonseed), hulling, meats separation, and weighing.

In the hydraulic method of processing, the meats are then crushed in vertical rolls, cooked to coagulate the protein and obtain the proper moisture and temperature, and then pressed under hydraulic pressure. There are two kinds of equipment for pressing seeds: the box presses in which each 20 pounds of material are wrapped in hair cloth and carried manually to the press, and the cage press machinery in which the meats are introduced into the large presses without individual handling, and pressed. In both processes it is necessary to strip the press cloths from the cakes before they are ground into meal.

In the continuous mechanical press process the meats are sometimes crushed or cracked and sometimes fed directly to the presses. Most material is also heated or dried and then fed to the continuous press. The fourth process is the solvent extraction method and the fifth is pre-pressing of high oil seeds, followed by solvent extraction.

In pre-pressing the same continuous press is used but speeded up for very large capacity, and most seeds can be handled directly by the presses without preliminary heating or drying with the result that a high quality cold pressed oil is obtained. This fifth method is almost a universal system in that any oil seed, as far as I know, can be handled satisfactorily by this process.

Hydraulic Operation. The hydraulic method of processing in box presses is used extensively in this country only in the cottonseed industry. Most of the equipment business is in repair parts, extra capacity, or foreign sales.

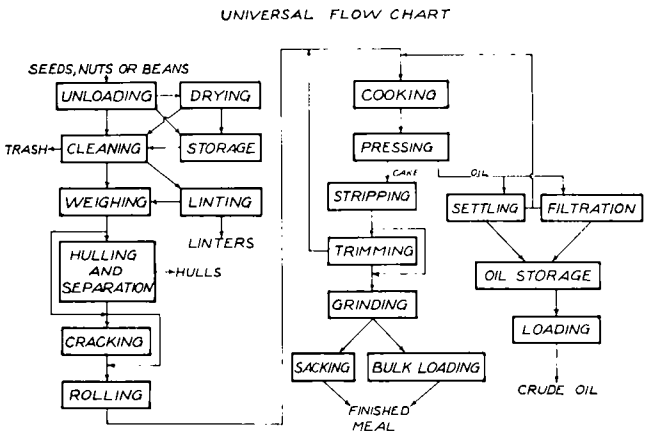


FIG. 2. Hydraulic processing of oil seeds and nuts.

Figure 2 shows a more detailed flow sheet for box press or cage press operation. This chart is made up with cottonseed chiefly in mind but is applicable to any oil seeds.

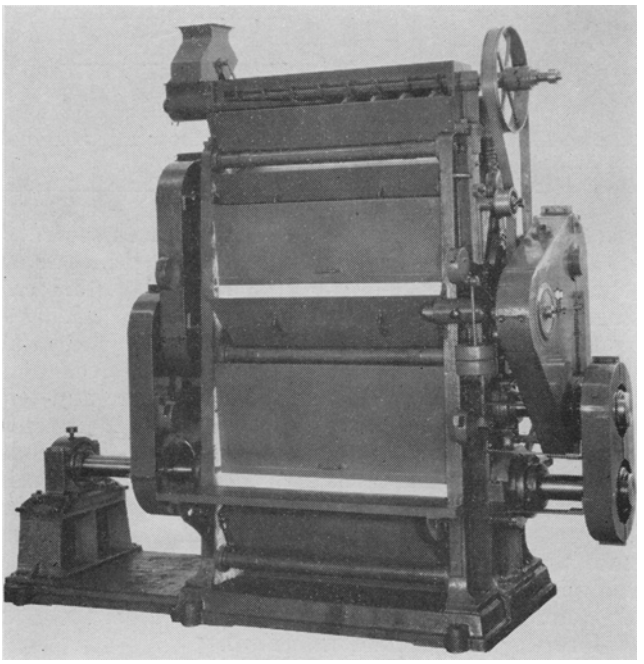


FIG. 3. French stack flaking roll.

After the meats are separated from the hulls, they are usually rolled in vertical crushing rolls as shown in Figure 3. Figure 4 shows the construction of these rolls, which reduce the meats to flakes of .095 to .014 inch thick. The flakes are then conveyed to a vertical stack cooker made up of multiple kettles which can be seen in the center of Figure 5. The meats are usually humidified in the top kettle in order to improve oil quality, and then the moisture is reduced in successive stages in the cooking until they are brought out at about 5½% at the bottom. The temperature of the top kettle will usually be held between 175 and 195°F. and gradually raised through the cooker until the seeds are discharged at 220 to 240°F. The total cooking time is usually between 70 and 120 minutes. The meats are formed into cakes and wrapped in hair cloth and inserted into the box presses.

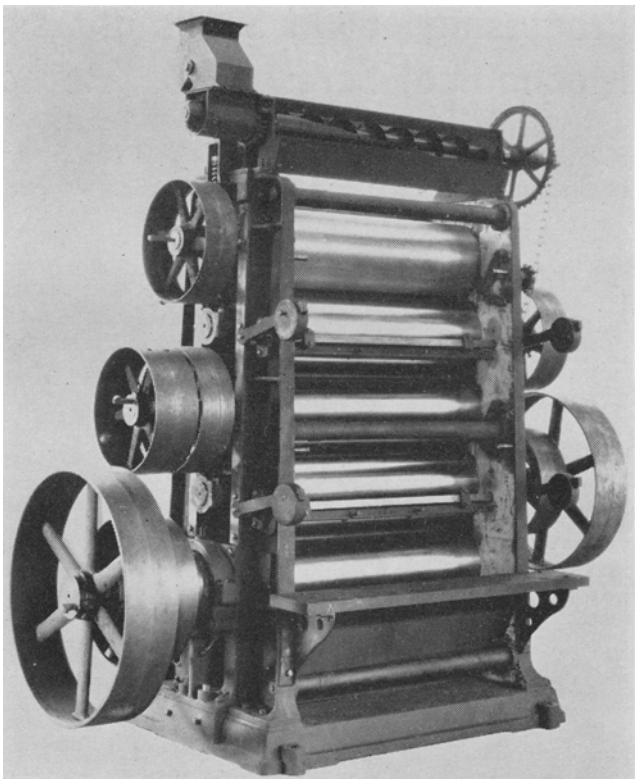


FIG. 4. Interior of stack rolls.

A cage press is pictured in Figure 6, which shows an installation in Ceylon. Seeds are treated similarly up to and including the cooking process, where the cakes are formed into layers in huge presses, given a preliminary pressing in the first low pressure cage, and then transported by trucks running on rails to the finishing presses.

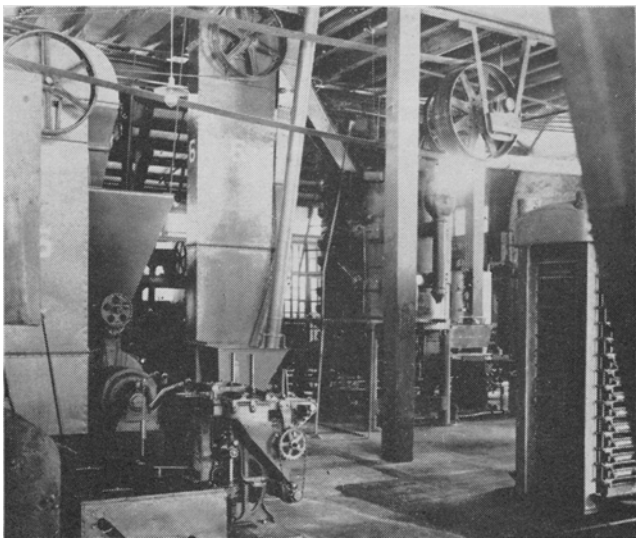


FIG. 5. Hydraulic press room showing cooker, former, presses, and cake trimmer.

The hydraulic process of crushing seeds has high labor costs and seems to be outmoded. This will be deeply regretted by almost every one who had a part in the industry as there will never be a more colorful and interesting process. It is a rough and tough oper-

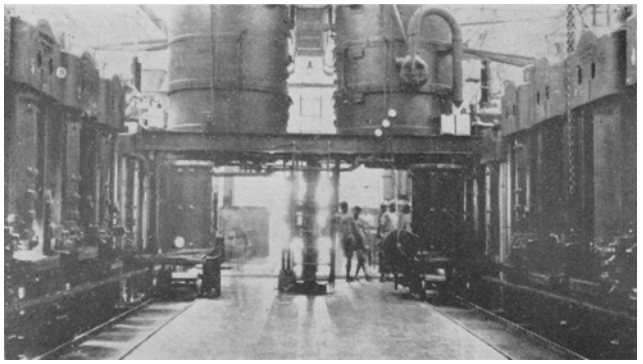


FIG. 6. Cage press installation in Ceylon.

ation that requires of all personnel engaged in it an exceptionally strong back and a strong mind.

Those of us who got into this industry later found it a gold mine in regard to opportunities for technical improvements. Many such changes still can be profitably applied in hydraulic plants by proper application of humidification before cooking, moisture control during cooking, close supervision of the manual techniques of forming and press charging, and in many other places.

The hydraulic processing operation appears to be obsolete, but there remain two other methods, and the combination of them, as replacements.

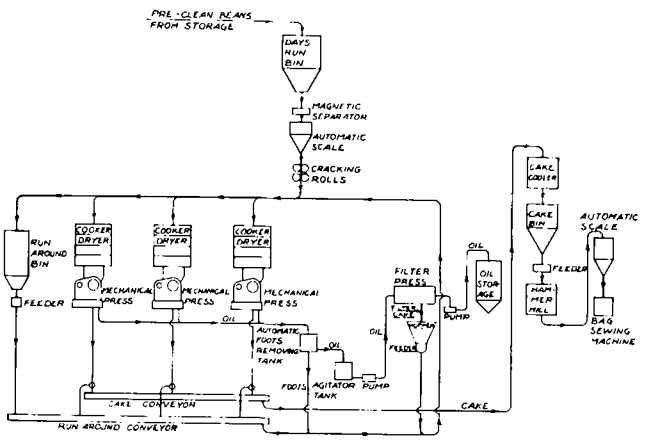


FIG. 7. Flow sheet for continuous mechanical screw pressing.

Continuous Screw Press Operation. The mechanical screw press process has overwhelming advantages over hydraulic box press operation, and it also has a number of advantages over solvent extraction. Figure 7 is a flow chart for a continuous press operation as applied to soybeans. Other oil seeds are handled similarly, with a somewhat different preparation. Soybeans are cracked and sometimes flaked before going to the cooker dryers. The oil goes to a continuous settling tank or is put over a vibrating screen and then filtered. The foots and filter press cakes are sent back to the presses. The cake is cooled and ground into finished meal. In setting up a screw press plant one must have adequate and well designed auxiliary equipment, such as the run-around bin with feeder, and feeder provision for foots and filter press cake which will feed the material very uniformly to the presses. The most important operating principle in running mechanical screw presses is uniformity, both in the kind of material and the amount of material sent to the presses. The value of uniformity cannot be stressed too strongly. It is frequently the difference between efficient, profitable operation and inefficient operation.

For most efficient operation soybeans should be heated to about 290°F. Other oil seeds require lower temperatures, as low as 200° for copra, 220° for flaxseed and cottonseed, and 230 to 240° for peanuts. The moisture of the material going to the press will run as low as 1½% for soybeans and up to 3% for most other materials.

A French mechanical screw press is shown in Figure 8. This unit has a vertical cooker dryer to heat and dry the material. Figure 9 shows a V. D. An-

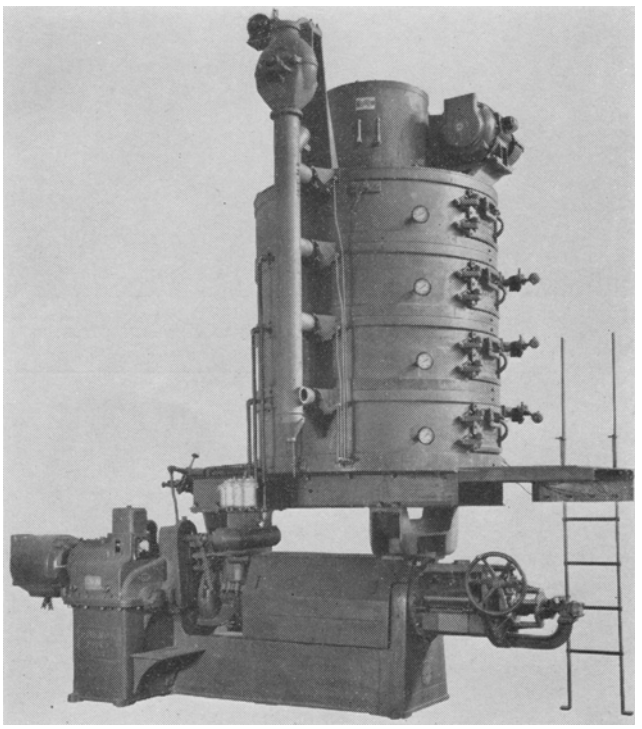


FIG. 8. Four-high cooker dryer and four-section mechanical screw press.

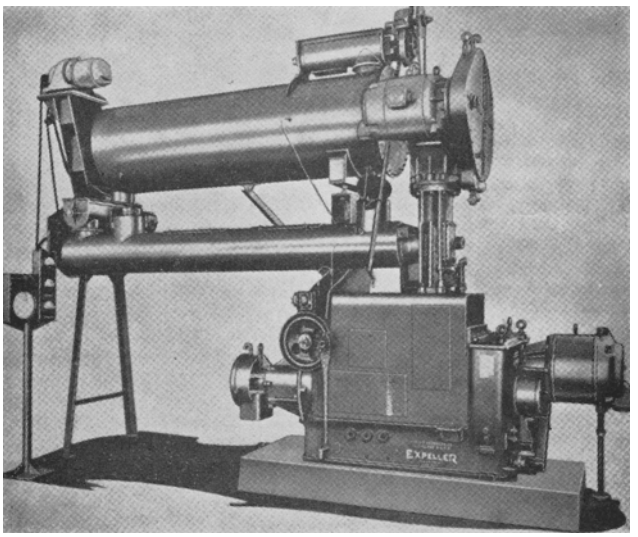


FIG. 9. Twin motor super duo expeller with 36" cooker. (The V. D. Anderson Expeller Co., Cleveland, Ohio.)

derson expeller with a horizontal cooker. (There are only two manufacturers of continuous mechanical screw presses for oil seeds in this country.) The two machines perform the same operation in that the oil seeds are first heated and the protein coagulated so as to reduce foots, and the oil separated from the solids by the application of high pressure. Figure 10 shows the barrel of the French press, which has a straight line flow. The feed worm runs at a higher speed than the main shaft and helps to apply the initial pressure to the material and to start the flow

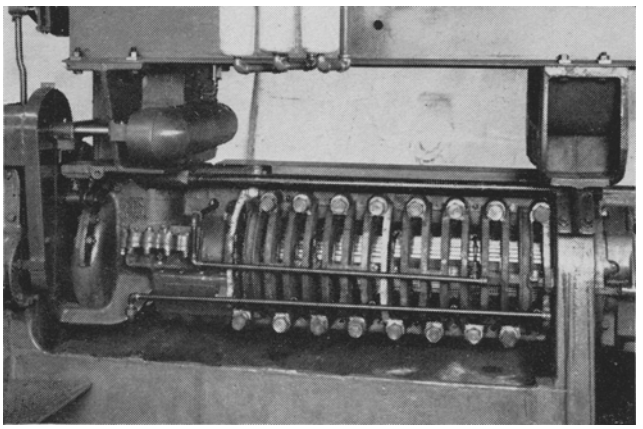


FIG. 10. Drainage cage of French mechanical press.

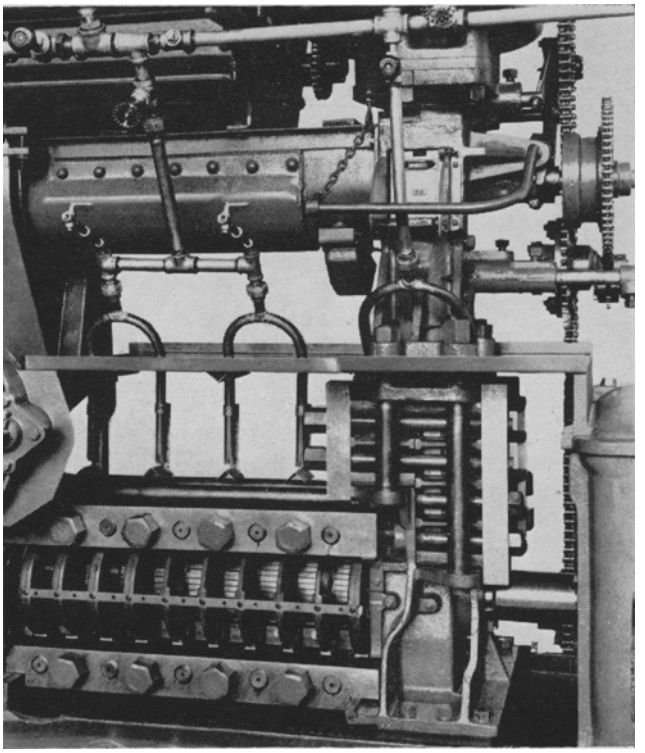


FIG. 11. Drainage cage of Anderson expeller.

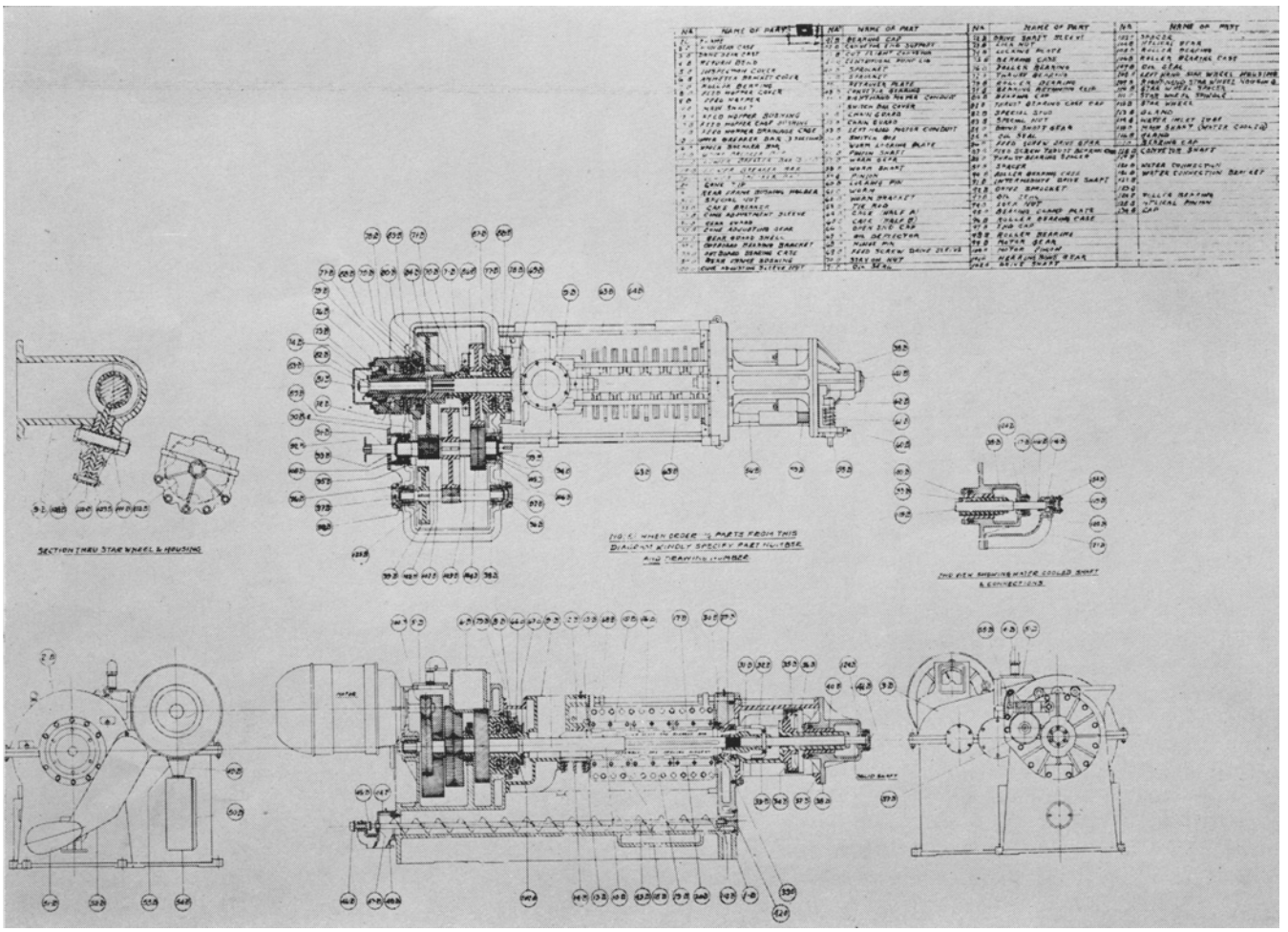


FIG. 12. Sectional view of French press.

of oil which is most easily removed. On the main shaft worms and collars build up to the maximum pressure toward the discharge end to get the last possible amount of oil separated. Both machines have a choking arrangement at the discharge, which also helps to apply the final pressure.

The Anderson expeller barrel is shown in Figure 11. This machine has a feed worm usually separately motor-driven at right angles to the main shaft. In general, the operation is quite similar in that the low pressure is applied in the feed worm and the final high pressure is applied through worms and collars on the main shaft.

Figure 12 shows a sectional view of a French press and illustrates the heavy duty construction of all gears, bearings, and other parts which is necessary for this type of machine.

This type of high pressure operation results in a great deal of abrasive wear, and all oil seeds present more or less of a corrosion problem. It is a false economy, recognized by all good processors, to allow these machines to wear excessively. Efficient operation requires periodic maintenance work, involving the replacement of worn parts. Great strides have been made in the manufacture of the parts subject to the greatest wear, and use of hard alloys has been developed to a high degree.

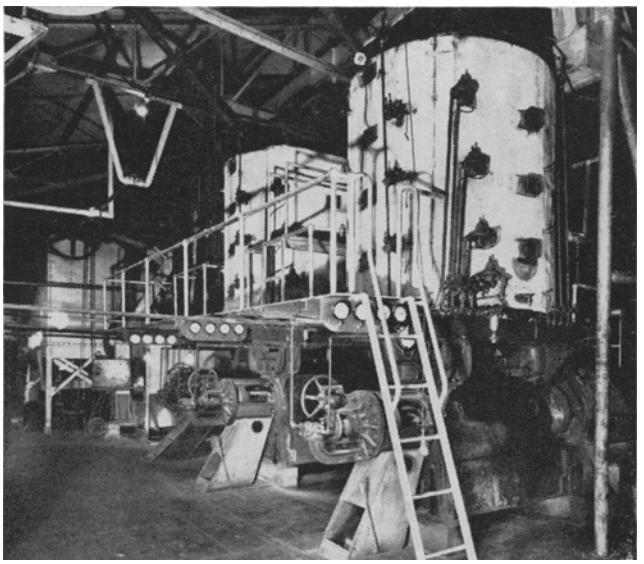


FIG. 13. Mechanical screw press installation.

Figure 13 is a view of a mechanical press mill. There are many mills in operation in this country with 16 and 24 machines usually arranged in two lines, and one mill has about 48 machines. This is a unique characteristic of oil milling practice in the United States as a result of the availability of large quantities of one seed. This permits large capacity mills to be set up for the most efficient operation on one oil seed and contrasts with the practice in other countries where it is usually necessary to produce machines that can handle a variety of oil seeds.

Since hydraulic operators in this country should convert to either mechanical screw pressing or solvent extraction, it seems desirable to present a list of the respective advantages and disadvantages of these two processes. Mechanical screw presses have a lower initial investment, are simpler to operate, require less labor (not as high type labor) and less supervision, have lower steam usage, no solvent loss, and no special safety problem. The solvent extraction process has slightly lower power cost, lower maintenance cost, and higher product value since the price of oil has practically always been more than meal, and solvent extraction results in a higher oil yield.

FIG. 14. Pre-pressing flaxseed on mechanical screw presses.

It seems probable that a small operator, located in a favorable area where freight rates operate to his advantage, might be much better off with mechanical screw presses. He would certainly have much less of an operating problem. It is my view that operation of a solvent plant at less than 50 tons per day is not advisable. The technical supervision which should be available for solvent extraction operation cannot be justified for a smaller plant.

Pre-Pressing Operation. Mechanical screw presses are being used extensively for pre-pressing high oil seeds, followed by solvent extraction. Figure 14 shows a line of presses which are pre-pressing flax seed down to 18 to 20% oil prior to extraction. For pre-pressing a mechanical screw press operates at high speeds and high capacity, pressing out the easily expelled oil; the seeds usually require little, if any, pre-treatment, resulting in a very high quality cold pressed oil. For soybeans direct extraction is certainly advisable for operators who consider solvent extraction. Cottonseed, in the intermediate range of oil content, can be extracted directly quite satisfactorily, but it may work out advantageously for a plant having mechanical presses already to convert them to pre-pressing service, followed by solvent extraction, when they wish to obtain this additional oil. For flaxseed, copra, sesame, peanuts, and all the other high oil bearing materials, the greatest economy will be obtained by a combination plant wherein the oil content of the seeds is reduced to 18-20 per cent before extraction.

Current and future developments are certain to make further great strides in the efficiency of operating mechanical screw presses, from which the oil seed processing industry will benefit.

The Theory of Solvent Extraction

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A COMPLETE analysis of the practice of solvent extraction would require the equivalent of a text on the unit operations of chemical engineering. The unit operations involved are materials handling, size reduction, size separation, drying, flow of fluids, heat transfer, extraction, evaporation, stripping, filtration, and sometimes adsorption. However, whereas the handling of most of these operations is fairly conventional, the extraction operation which is the heart of the complete process requires equipment of special design and theoretical analysis not yet to be found in textbooks. This paper will be devoted entirely to a discussion of the extraction operation.

The extraction of soluble material from a solid matrix has had relatively few applications. Examples are counter-current washing as practiced in the manufacture of caustic from soda ash and lime, leaching of soluble ores, leaching of soda ash from black ash in the manufacture of paper pulp, and the extraction of sugar from beets. Superficial examination of these examples will explain why it is impossible to devise a single theory of extraction. The first is a case of simple washing from the surface of a finely divided granular solid, the second involves leaching from an impermeable heterogeneous matrix finely divided soluble particles which can only be reached by fine grinding. In the third case the soluble material is uniformly distributed throughout a permeable homogeneous matrix and the mechanism of extraction is possibly one of true diffusion. The extraction of sugar from beets takes place by dialysis.

Total Extractibles

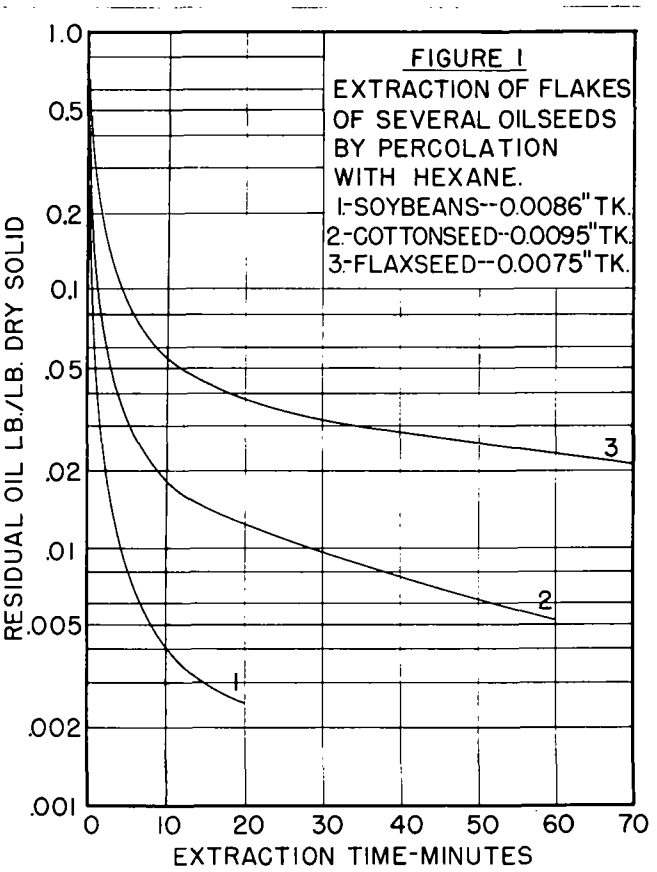
Before it is possible to discuss extraction from oil seeds, it must be clearly established what it is that is being extracted. It would simplify the task considerably if it were possible to say that we are concerned with the extraction of a single chemical substance from a non-extractible solid of uniform composition. However we are dealing with a product of nature which is subject to considerable variation so that the definition of extractibles is not precise. The various factors described below affect the per cent total extractibles by as much as 1%, which is an important consideration in view of the fact that commercial extractors are designed to produce meal containing 0.5% residual "oil."

The factors affecting the total extractibles are:

1. *The Solvent.* Even among the solvents recognized as the specific for glycerides, such as trichlorethylene and the commercial paraffins, there is a decrease of about 1% in total extractibles among trichlorethylene, heptane, hexane, and petroleum ether at their boiling points, in that order. In addition to glycerides the materials extracted are phosphatides, non-saponifiables, and pigments.
2. *Temperature of Extraction.* Although not clearly established there is some evidence that the total extractible with any one solvent is a function of temperature of extraction.
3. *Moisture Content of Sample.* It has been reported (1) that a reduction in moisture content without heat treatment from 8 to 5% may decrease the total extractibles from soybeans by as much as 1%. This is related to the increased removal of phosphatides from the sample of high moisture content.
4. *Heat Treatment History of Sample.* Heating generally increases the total extractibles. This is of especial importance to the supplier of extraction equipment who must guarantee the residual oil content of the meal since it is found in practice that heat treatment subsequent to extraction increases the extractibles by as much as 0.3%. It is customary to guarantee the residual oil content of extracted soybean meal sampled after complete desolventizing, but prior to toasting.

The A.O.C.S. has recognized these factors and set up a standard analytical method (2) for oil using a Butt extractor, which specifies the solvent, pretreatment of sample, the extraction time, reflux rate, etc. The pretreatment specified includes drying to about 2% moisture by heating in an oven for 2 hours at 130°C. This has been found to give a maximum yield of extractibles. The standard method also specifies that the sample must be reground at an intermediate point in the extraction, thus recognizing that the seed substance is not very pervious to the solvent.

The situation was well summed up in 1943 by Bull (3), who said, "The wide variation in results for lipid content indicates that the lipids removed cannot be considered as either triglycerides alone, or total lipids, but an empirical value given by a rigidly controlled procedure. It is apparent that methods are needed to determine the triglycerides and total lipid content of soybeans and soybean meal."



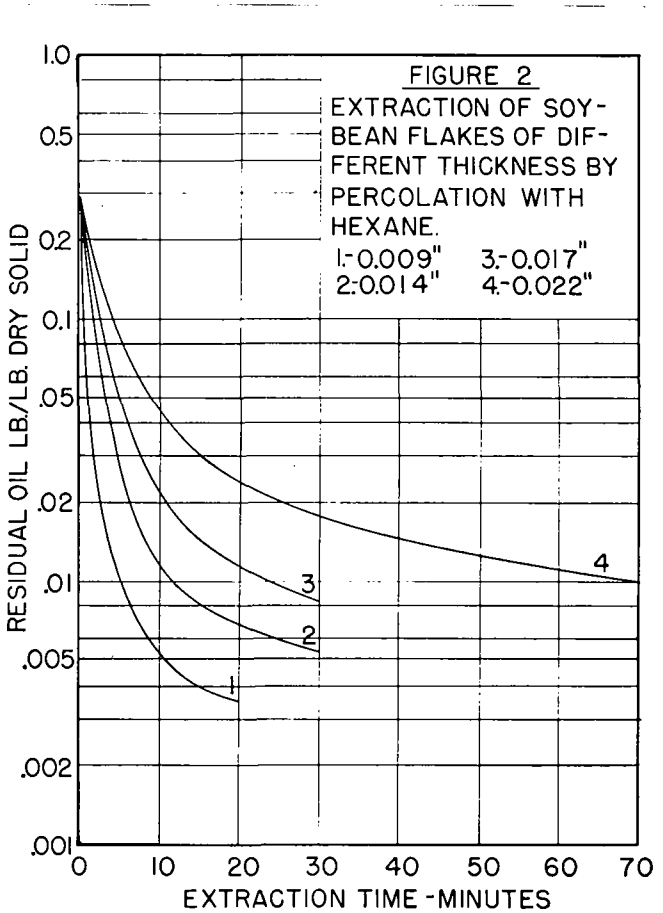
Distribution of Extractibles

It is well known (4) "that the oil removed initially is of higher quality than the smaller proportion which is extracted with difficulty in the final stages of the contacting operation." In an analysis made in the Blaw-Knox laboratory a 10-lb. sample of flakes was extracted with hexane down to 0.25% residual in 13 successive steps. The first cut included all the extractibles down to 2% residual while the other 12 cuts constituted the fraction from 2% down to 0.25% residual. While the first cuts were light orange in color and otherwise normal, the quality deteriorated until the material corresponding to 0.25%-0.50% fraction was a dark red-brown, very viscous, only slowly soluble in hexane, and had a bad odor. The first cut had 0.36% free fatty acids and a refining loss of 6%. The combined cuts corresponding to 0.25%-1.1% residual had 5.0% free fatty acids and a refining loss of 81.5%.

In a similar experiment Bull and Hopper (5) tested the fractions for iodine number, thiocyanogen number, unsaponifiable matter, and phosphatides. The most marked difference was found in the phosphatide content, which varied from 1.25% in the first fraction to 18.6% in the fraction corresponding to 0.41%-0.56% residual.

Rate of Extraction

Any work on the rate of extraction in order to be useful must recognize the limitations imposed where what is being extracted is so poorly defined. In order to get consistent results it is better to perform the analysis for total extractibles with the same solvent and at the same temperature as the experiments on rate rather than use the A.O.C.S. method.



In the paragraphs that follow typical data on rate of extraction are presented. The data have been selected to demonstrate the most important variables that affect the rate in commercial operation. The qualitative conclusions to be drawn from these data are useful to those concerned with plant operation, without regard to any theory of extraction. However the data are examined more critically in the section on mechanism of extraction.

It will be noted that all the data are concerned with the extraction of flakes, prepared ordinarily by successive steps of cracking or cutting the seed, conditioning the cracked seed by adjustment of moisture content and temperature, and rolling between smooth rolls to produce flakes of controlled thickness. The advantage of flaking is that it produces thin particles which can be rapidly extracted without at the same time making troublesome fines. The practice of flaking as a method of preparation for extractions is, with very few exceptions, the only one used in this country at the present time. For this reason the discussion is limited to the extraction of flakes prepared directly from the seed. Where the other methods of preparation are used, as for example forepressing (7) of high oil content seeds, the conclusions may not apply.

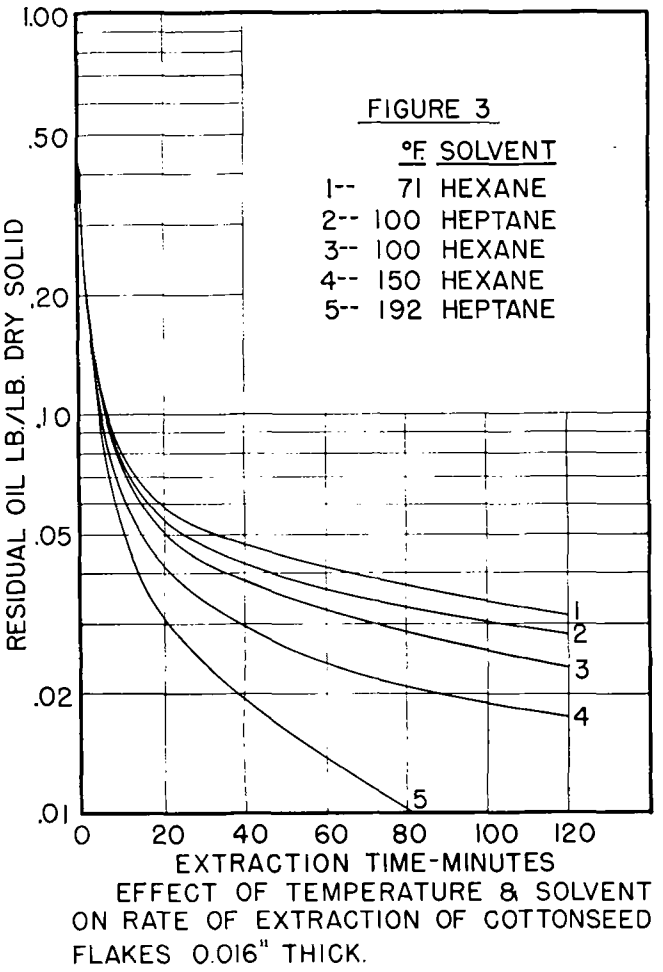
In Figure 1 typical extraction rate data for flakes have been plotted. Soybean, cottonseed, and flaxseed flakes of approximately the same thickness were extracted with hexane at the boiling point by percolation. The data is plotted on semi-logarithmic coordinates as residual oil vs. extraction time.

Three significant generalizations can be made from Figure 1 that have been substantiated by considerable data. First, there is a great difference in the rate of extraction of flakes made directly from different oil seeds, soybeans being one of the most easily extracted of the common oil seeds. Second, the bulk (about 80%) of the oil is extracted rapidly, but the last of the oil is extracted slowly and with increasing difficulty. Third, as demonstrated in the case of flaxseed, for all practical purposes some of the oil cannot be extracted at all without grinding.

Effect of Flake Thickness: In Figure 2, the extraction rate curves of soybean flakes of different thickness extracted by percolation with hexane have been plotted. That flake thickness has a profound effect on extraction rate is apparent.

Effect of Temperature: The study of the effect of temperature of extraction on rate is complicated by the possibility that the total extractible varies with temperature. Practically, however, the performance of an extractor is judged by the A.O.C.S. method so there is justification for measuring the effect of temperature against a standard analysis. In Figure 3 data are presented for extraction of cottonseed with hexane at three different temperatures, the analysis for total extractibles having been made by the A.O.C.S. method, using hexane. There is a significant change in extraction rate with temperature, which cannot be overlooked in plant practice.

Effect of Solvent: The effect of solvent on rate is complicated by the fact that the total extractible differs with the solvent. For research purposes it is desirable to measure the rate of extraction against



EFFECT OF TEMPERATURE & SOLVENT ON RATE OF EXTRACTION OF COTTONSEED FLAKES 0.016" THICK.

total extractible with the same solvent, but practically the solvent is judged by analysis of the meal produced by the A.O.C.S. method.

The use of the heptane fraction instead of hexane as a solvent is feasible, especially where cold condenser water is not available. In Figure 3 data are presented for the extraction of cottonseed with heptane at two temperatures, the analysis for total extractibles having been made by the A.O.C.S. method using hexane. The extraction at 100°F. was made for comparison with hexane at the same temperature. It will be noted that heptane extracts slightly more slowly than hexane at the same temperature. However the use of heptane makes possible operation at higher temperatures, and comparison of rates at their respective boiling points shows that heptane extracts far more rapidly than hexane.

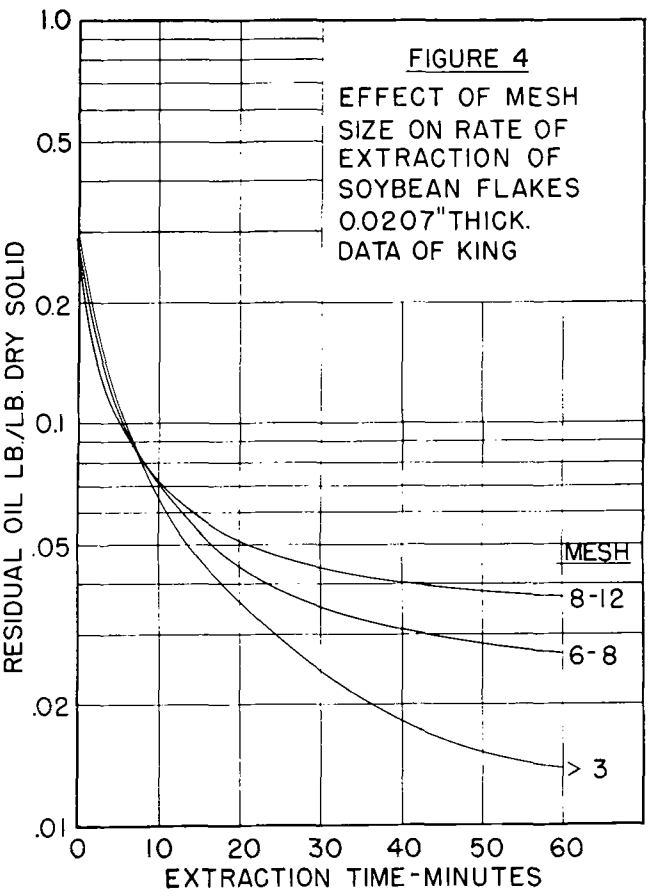
Effect of Flake Size: The flake thickness is not its only significant dimension. When first made, the volume of the flake is that of the cracked bean from which it is made so that the mesh size of a flake of given thickness is a measure of that of the original cracked bean. If the distortion of the seed structure caused by the flaking operation affects the extraction rate, then it can be expected that large flakes will extract more rapidly than small flakes of the same thickness since the large flakes have suffered the greater distortion.

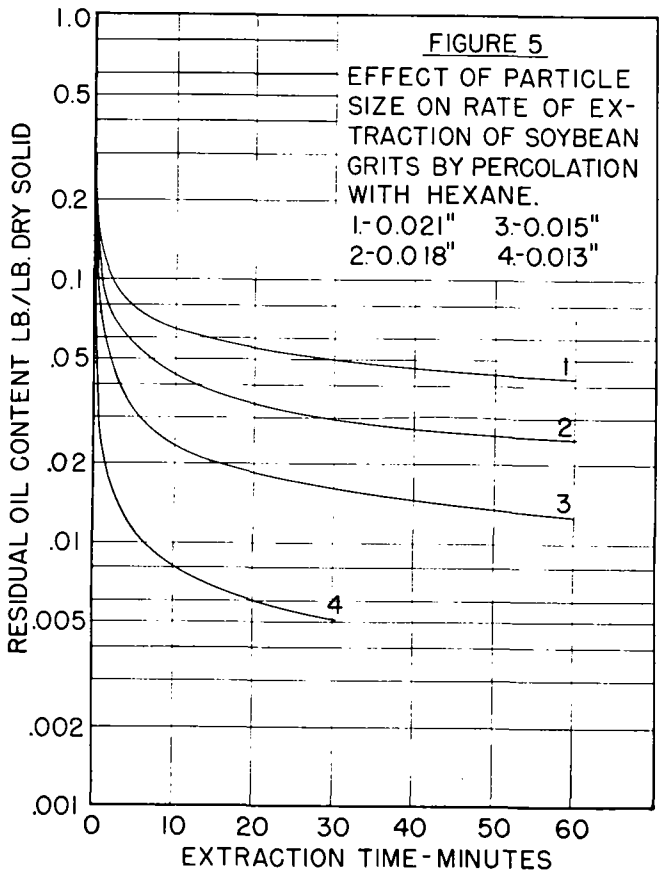
This is borne out by the data of King (6), presented in Figure 4. Soybean flakes, all of the same thickness and prepared from the same batch of cracked beans, were separated by screening into several fractions of different mesh size. The fractions were extracted with trichlorethylene. There is a significant increase in extraction rate as the flake size is increased.

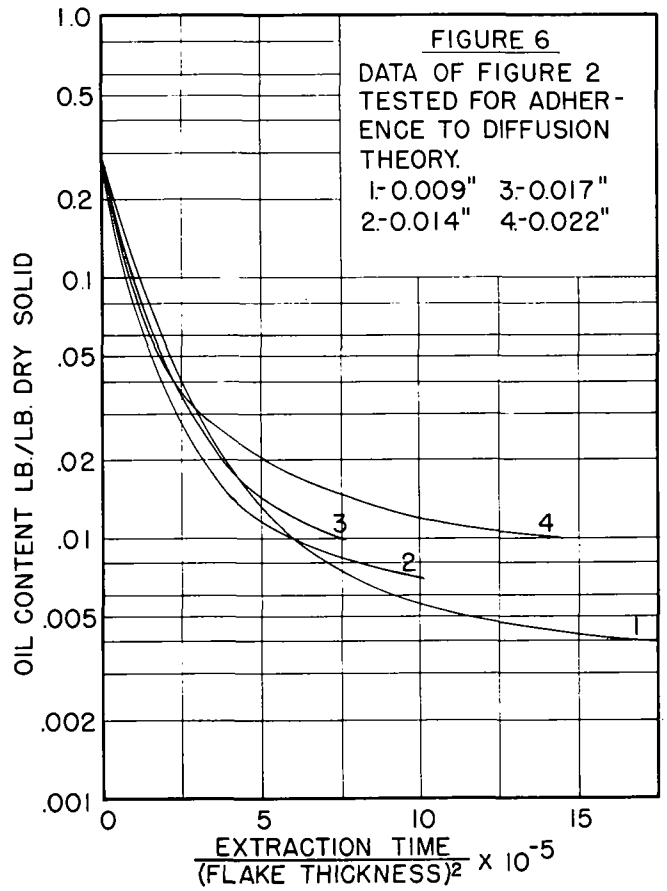
The Mechanism of Extraction

The general nature of the curves of Figure 1 has been explained (8) on the basis that after flaking the oil is distributed in three fractions: oil at the surface of the flake, loosely held; oil in the capillary spaces formed by ruptured cells which is removed with difficulty; and oil in unruptured cells, probably not recoverable commercially without regrinding. This theory has no experimental confirmation based on microscopic examination of flakes. In fact, Woolrich and Carpenter (9) showed that the cells of cottonseed flakes 0.007" thick were practically unbroken by the rolling operation. Since cottonseed cells are about 0.001" in diameter, the broken cells at the surface of the flake could hardly account for the 80% of the oil which is easily extracted with solvents.

In order to measure the effect of flaking on the rate of extraction, carefully sized grits were prepared by grinding and screening, and then extracted by percolation with hexane. The average diameters of the grits chosen were roughly the same as the flake thicknesses of Figure 2, so a comparison can be made. The curves for grits (Fig. 5) and flakes have the same general character. There is a large easily extracted fraction of oil in the grits, which have not been subjected to forces which might rupture cells. The easily extracted fraction is apparently characteristic of unruptured cells. Small grits (less than





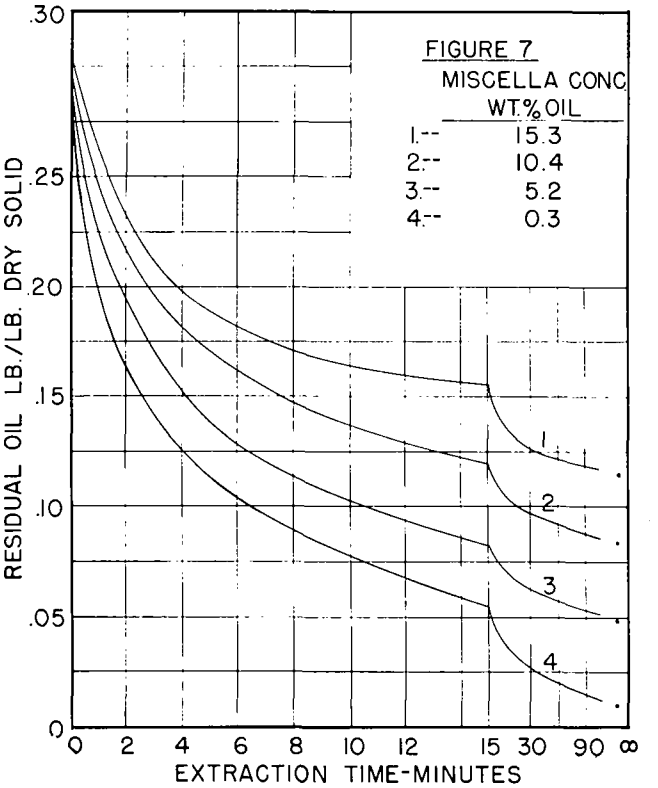


0.01") extract more rapidly than flakes of the same thickness, as would normally be expected if the flaking operation did not change the seed structure. However the flaking operation does make available for extraction oil which in the larger grits is practically unextractable.

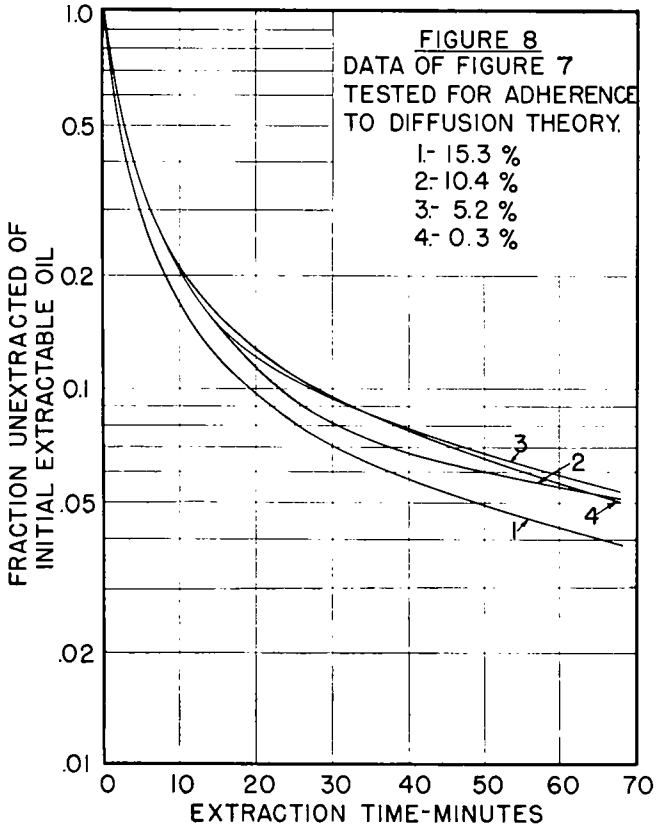
Flakes are porous, and in the course of extraction the pores fill with solvent which cannot be removed by centrifuging. In the case of soybeans 22% of the volume of unextracted flakes is occupied by the oil and 19% by air (6). Based on the porous nature of the flakes, two entirely different extraction mechanisms may be postulated. These are the familiar theory of molecular diffusion, and, less familiar, the idea that the rate of extraction is determined by the rate of solution of undissolved oil. These mechanisms are defined and examined in the following paragraphs.

The theory of molecular diffusion assumes that the solid is homogeneous and that the solvent (or partial miscella) used for extraction enters the voids to form with the oil originally in the flakes a miscella of uniform concentration throughout the matrix. As extraction proceeds by diffusion of the oil a concentration gradient is set up within the matrix from a maximum at the center of the flake to the concentration of the extracting solution at the surface. At infinite time the concentration of the miscella within the matrix is uniformly equal to that of the extracting solution.

Where the extraction of thin slabs takes place by diffusion, a plot of residual oil vs. time on semi-log



EXTRACTION OF SOYBEAN FLAKES 0.0207" THICK WITH SEVERAL TRICHLORETHYLENE MISCELLA CONCENTRATIONS. DATA OF KING (6)



paper is expected to have a characteristic shape. After an initial curvature at the beginning of extraction the curve becomes a straight line after about 40% of the oil is extracted.

It is apparent that the extraction rate curves for the flakes cannot be explained by the simple diffusion theory since the point of maximum curvature occurs when about 90% of the oil has been extracted. However, it was shown by Osburn and Katz (10) that such curves can be explained by the diffusion theory if it is assumed that there are two kinds of structure characterized by a high diffusion coefficient and the remainder being held in a structure from which it is extracted with great difficulty.

Another requirement of the diffusion theory is that a single curve should result when unextracted oil is plotted against time divided by flake thickness squared for flakes of different thickness. In Figure 6, the curves of Figure 2 have been replotted in this way. It will be seen that while the easily extracted oil conforms approximately with the theory, increase in flake thickness results in unavailability of the last of the oil greater than would be predicted for diffusion.

Diffusion theory also requires that if the fraction of extractible oil still unextracted is plotted against time, all the data for flakes of the same thickness should fall in a single curve, regardless of the concentration of the extracting solution. Figure 7 is taken from the excellent data of King (6). It gives the extraction curves for 0.0207" thick soybean flakes extracted with trichlorethylene solutions at four different concentrations. These curves have been replotted in Figure 8 as E, the fraction unextracted, vs. time. The agreement with theory is fair.

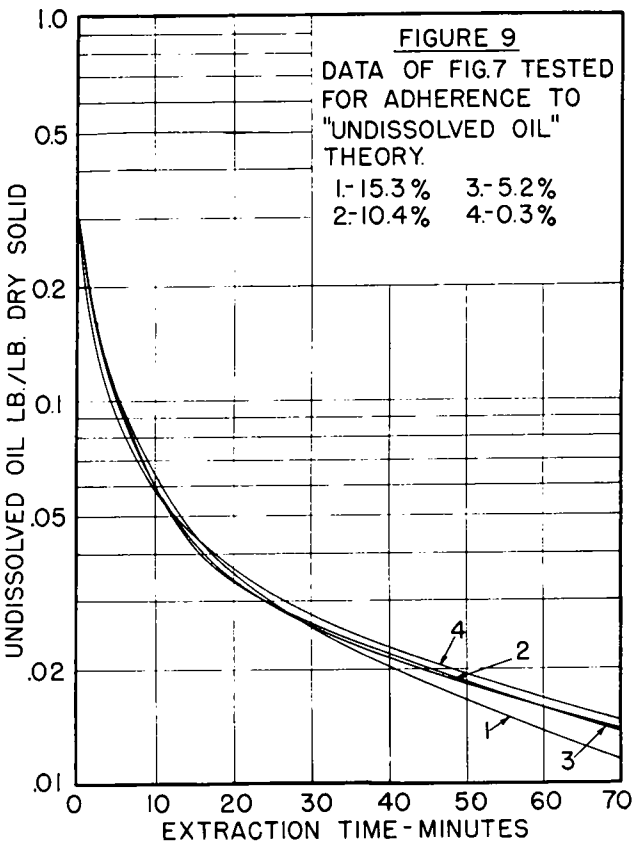
The "undissolved oil" theory assumes that the oil acts like a slowly dissolving material, the rate of solution of which is independent of miscella concentration. This theory is supported by the fact that there are slow-dissolving constituents in the extractibles which may inhibit the solution of the oil, as pointed out by Goss (4). The theory also assumes that the diffusion through the cell walls is rapid compared with the rate of solution of oil so that the miscella in the voids has the same concentration as the extracting solution.

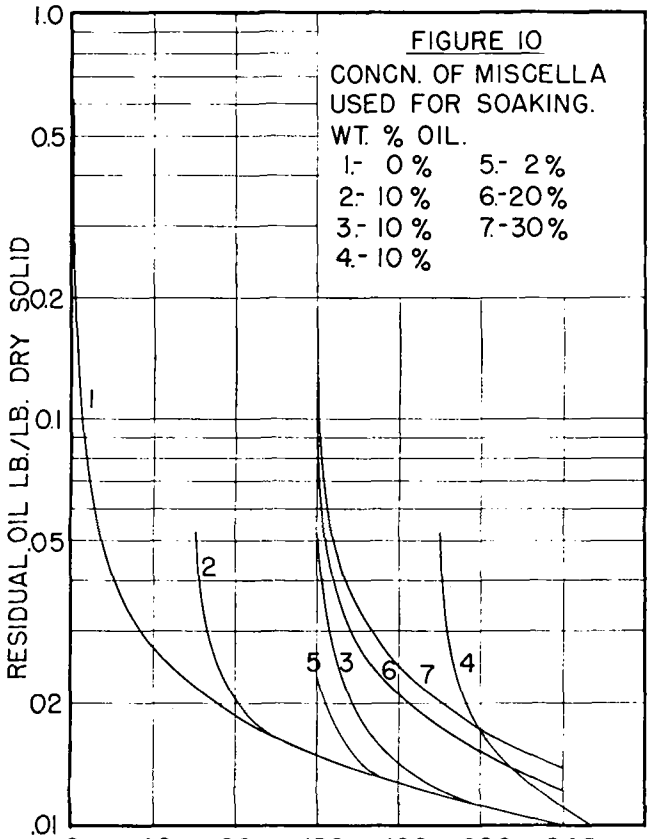
The data of Figure 7 can be used to test the idea that the rate of solution of undissolved oil is independent of miscella concentration. In Figure 9, the data of Figure 7 have been replotted as "undissolved oil" vs. time. It will be noted that, with an agreement better than that of Figure 8, the undissolved oil is a function only of time and not of concentration of extracting solution.

The experimental work reported so far does not make possible a distinction between the two mechanisms. In order to make this distinction, the following experiments were performed:

Cottonseed flakes 0.016 inch thick were extracted by percolation with hexane. Three samples of flakes from the same batch were soaked with 10% miscella for periods of 60, 120, and 180 minutes, respectively, and then extracted by percolation with hexane. Three other samples of flakes from this same batch were soaked for 120 minutes in miscella of 2%, 20%, and 30% concentrations, respectively, and then extracted with hexane by percolation. The data for these experiments are presented in Figure 10.

If the mechanism of extraction is one of diffusion (or dialysis), it would be expected that even after long soaking in miscella the subsequent extraction with hexane would take place slowly, at a rate ap-





proximately independent of soaking time, and determined by the concentration of the miscella used for soaking. On the other hand, if the rate of solution of the oil determines the extraction rate, it would be expected that in the extraction with hexane following soaking the soaking miscella would be rapidly washed out of the flakes at a rate independent of soaking time or miscella concentration, leaving as residual oil the same amount as was found for the same total extraction time with hexane.

Examination of Figure 10 shows that extraction takes place by both mechanisms simultaneously. Although the rate of extraction subsequent to soaking is slow and dependent on miscella concentration, it is significant that the curves all become tangent to the curve for extraction without soaking. This indicates that the solution of the difficultly extracted material is a slower process than the diffusion of dissolved oil so that the former eventually determines the extraction rate.

Summary

1. The study of the extraction of oil seeds is complicated by the fact that the total extractible material is variable in quantity and composition, depending on the solvent and other factors.

2. Composition of the extracted material changes as the extraction proceeds, from nearly pure glycerides in the first fraction to fractions containing increasing amounts of slowly soluble non-glyceride material.

3. The rate of extraction is determined by flake thickness, temperature, solvent, and mesh size of flakes as formed.

4. Mechanism of extraction appears to be a combination of diffusion, dialysis, and the solution of slowly soluble extractible material. The latter is sufficiently important that it determines the size of commercial extractors.

REFERENCES

1. Report of the Soybean Analysis Committee, Oil and Soap, *16*, 129 (1939).
2. Report of the Soybean Analysis Committee, Oil and Soap *21*, 305 (1944).
3. Bull, W. G., Oil and Soap *20*, 94 (1943).
4. Goss, W. H., Oil and Soap, *23*, 348 (1946).
5. Bull, W. G., and Hopper, T. H., Oil and Soap, *18*, 219 (1941).
6. King, C. O., Katz, D. L., and Brier, J. C., Trans. Am. Inst. Chem. Engrs., *40*, 533 (1944).
7. Goss, W. H., Oil and Soap, *23*, 241 (1946).
8. Boucher, D. F., Brier, J. C., and Osburn, J. O., Trans. Am. Inst. Chem. Engrs., *38*, 967 (1942).
9. Woolrich, W. R., and Carpenter, E. L., "Mechanical Processing of Cottonseed," University of Tennessee Press, Knoxville, Tenn. (1935).
10. Osburn, J. O., and Katz, D. F., Trans. Am. Inst. Chem. Engrs., *40*, 511 (1944).

The Mechanics of Solvent Extraction

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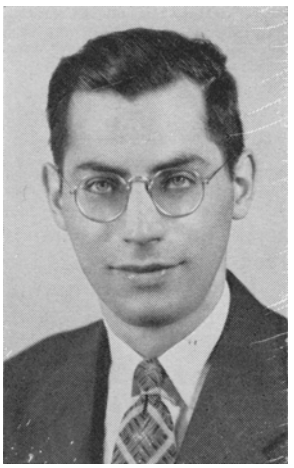
IN the preparation of a paper on the mechanics of solvent extraction two interpretations of the subject are possible. Strictly speaking, solvent extraction includes the steps of leaching the oil from the solid residue and subsequent recovery of solvent-free oil and meal. In practice, the operator or designer of a solvent extraction plant is concerned with all the steps from seed selection and storage to grinding finished meal and refining finished oil.



George Karnofsky

This concern does not arise merely from the fact that the numerous operations between raw seed and finished products are carried out in continuous series or on the same premises. The more basic reason is that the operations cannot be separated into neat categories since each step has its effect on some subsequent step. For example, an extraction process may meet every requirement for successful operation except that it produces a meal containing excessive fines; or a solvent may be available that reduces the cost of extraction, but the oil cannot be refined.

A commercial solvent extraction process, by the second interpretation, is one that produces marketable products from raw seed at a competitive cost for initial investment and operation. Based on cost alone, batch extraction of oil seeds is ruled out in this country. There are several successful continuous processes in active competition. To describe each of them adequately, with the proper background of European experience, would take more space than is available. For this reason only a brief discussion of the complete process will be presented, based on a generalized block flow diagram. The unit operation of extraction will be studied in detail, with emphasis on design and operation of the various extractors. For those desiring more complete information about the practice of solvent extraction a supplementary reading list is appended.

Block Flow Diagram

The processing steps shown in Figure 1 are characteristic of all solvent extraction plants. They can be classified under the broad headings of seed storage and cleaning, preparation for extraction, extraction, desolventizing of extracted solids, meal finishing, miscella clarification and desolventizing of miscella.

Seed Storage and Cleaning. Proper selection and storage of seed are essential if the products are to be of high quality. Proper cleaning of the seed may make the difference between operation uninterrupted for many weeks and operation plagued by minor shut-downs. Since warm, moist protein quickly forms hard masses, which plug equipment and conveyors, one shut-down generally causes several more. Not only does down-time reduce production, but it is during periods of irregular operation that plants using hydrocarbon solvents are hazardous.

Preparation for Extraction. The proper preparation of the seeds for extraction is perhaps the most important operation in the process. In any case the seed must be reduced in size so that at least one dimension is about 0.01″ in order to make the oil available for extraction in a reasonably sized extractor. The size reduction can be accomplished by either of two methods, the choice of which determines the rest of the process.

The first, and most obvious method, is to grind the seed in the simplest manner, say in 5-high rolls such as are used for cottonseed. This method of preparation produces an extractible material with a large range of particle size distribution and a large percentage of extreme fines. The extractor must be specially designed to handle such a feed; provision must be made to clarify the miscella; and the meal produced must be agglomerated to make it salable. The saving in the cost of the preparation system may be more than offset by the additional cost of the extraction equipment. In Europe this method was not used. However in this country there are at least two plants that are operating in this manner on high oil-content seeds.

The second, almost universal method, is to prepare precisely-sized flakes from the seed by rolling between accurately-spaced smooth rolls. In the case of soybeans the beans are cracked into eighths in

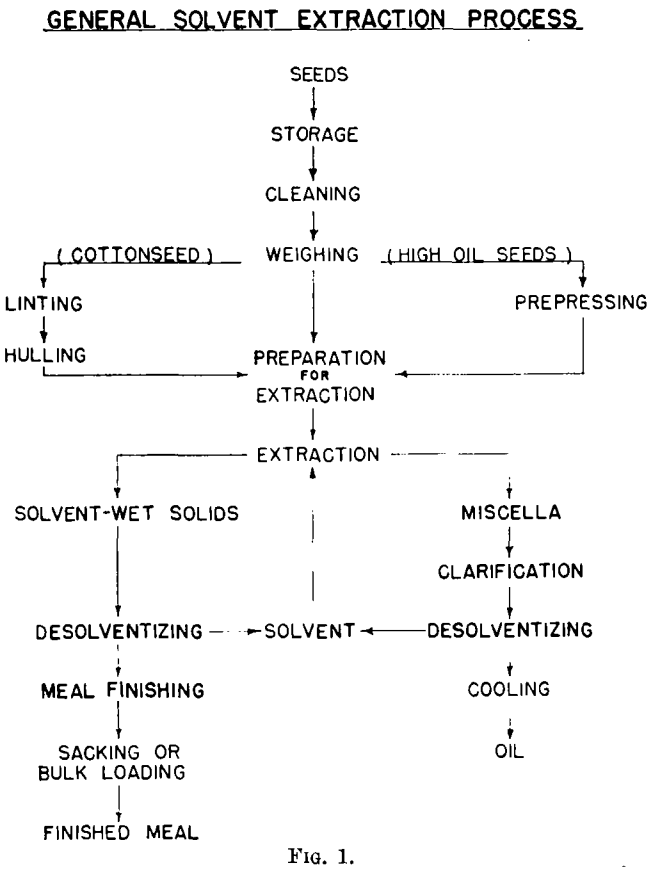


FIG. 1.

2- or 3-pair high corrugated rolls, then heated to temperatures between 140 and 170°F., and the moisture content adjusted to 10-11% prior to flaking. In the case of high oil-content seeds, from which strong flakes cannot be prepared directly, the seeds are prepressed in a screw press to a residual oil content of 10-20%, and the press cake carefully conditioned prior to flaking. The advantages of flaking are:

1. Precise control of flake thickness. The rate of extraction decreases rapidly as flake thickness increases, so that optimum extraction requires flakes of uniform thickness.
2. Minimum fines in miscella and meal.

Extraction. In the extractor the oil is leached from the prepared seed to yield, on the one hand, a solution of oil in solvent, called "miscella," and on the other, extracted solids containing a small amount of residual oil and considerable solvent "hold-up." The miscella and solids are desolventized in subsequent processing steps.

Superficially, the criterion of good extraction is the percentage of residual oil in the desolventized meal. For soybeans the trade now expects a guarantee of 0.7% residual or less. For cottonseed and flaxseed, which are more difficult to extract and for which there is still little commercial experience, a guarantee of 1% residual is more likely.

Desolventizing the Extracted Solids. The solids leaving the extractor must be freed completely of residual solvent. This is generally done applying indirect heat to vaporize the solvent followed by direct steaming to remove the last traces.

Meal Finishing. This includes steps required to convert the solvent-free meal into a marketable product. These include toasting in the case of soybeans, moisture content adjustment, grinding, agglomerating, pelletizing, etc. The finishing steps required are determined by the nature of the extraction process employed.

Miscella Clarification. This is generally required to remove fines from the miscella prior to distillation. The magnitude of this step varies with the extraction process, from simple straining or filtration when soybean flakes are extracted in a percolation-type extractor to elaborate centrifugal clarification where a finely-ground material is extracted in an immersion-type extractor.

Desolventizing the Miscella. The miscella is concentrated by evaporation followed by direct steaming to remove the last of the solvent. Most vegetable oils must be processed for a minimum time at low temperature in order to prevent deterioration of the color of the oil and fouling of heat transfer surfaces.

Classification of Extractors

A good extractor must meet the following specifications:

1. It should extract substantially all the oil from the prepared seed, using an economical solvent ratio. (Solvent ratio is the ratio of solvent fed to seed fed to the extractor.) In soybean practice a ratio of one pound of hexane to one pound of flakes is standard.
2. It must be mechanically strong, capable of continuous operation for many months without maintenance.
3. It must operate simply and automatically.
4. It should cause a minimum of particle size reduction in the solids.
5. It should produce a miscella of maximum clarity possible, depending on the nature of the feed.

There are two types of extractors, the immersion-type and the percolation-type. In the immersion-type the solids are agitated in the solvent while in the percolation-type the solvent is run through fixed beds of solids. In each of these the contacting between solvent and solids may either be continuous or stage-wise, with partial draining of the solvent from the meats between stages. In all cases the flow of solvent and solids is made as nearly counter-current as possible.

Each type has application where it has peculiar advantages. The percolation-type requires that the solids form a porous bed through which solvent can flow. This limits its application to well-prepared flakes or sized particles whereas the application of the immersion-type is not limited. However where the percolation-type can be used, it has the advantages of producing clear miscella by the filtration through the bed characteristic of its operation; of permitting adequate drainage by gravity, within the extractor, of the solvent in the extracted flakes; and of causing little reduction of particle size. The immersion-type generally requires auxiliary miscella clarification and auxiliary means for draining solvent from the extracted solids, such as drain boards, squeezers, and centrifuges.

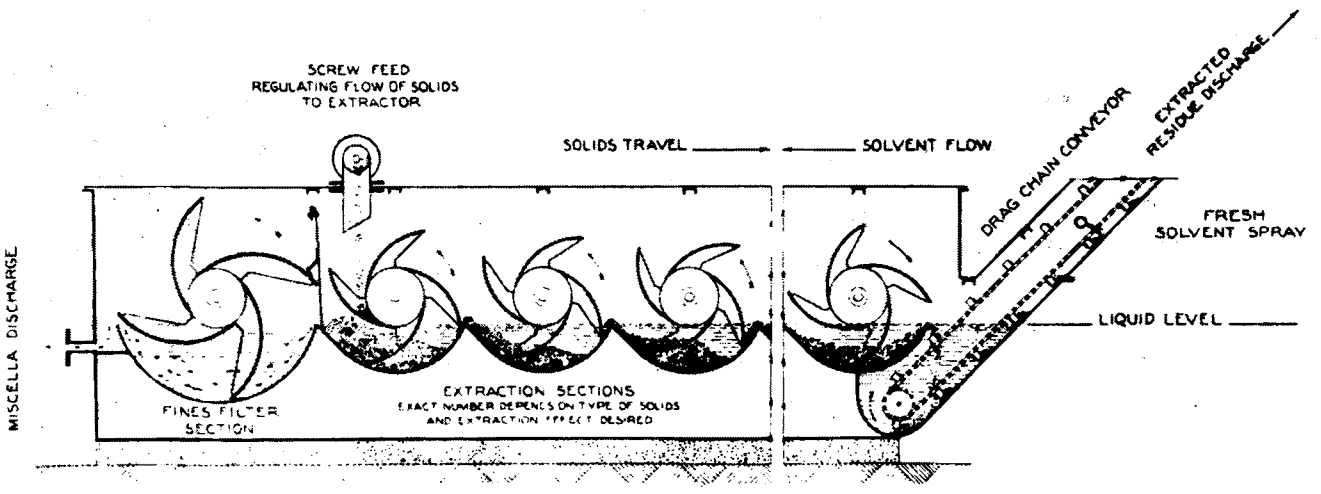
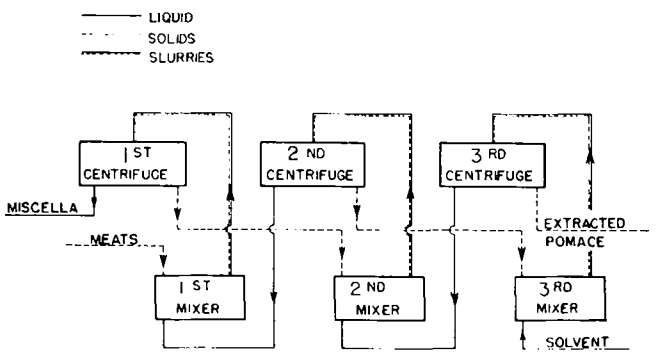


FIG. 3. Sectional view showing operation of Kennedy patented-continuous counter-current extractor

In practice the distinction between the two types of extractors is not sharp since an effort is made in the design of several of the immersion extractors to establish a bed and so gain the advantages of percolation. This will be apparent from the descriptions of extractors that follow.

The extractors described are those in use in this country. There are many extractors described in the patent literature and several used successfully in Germany which are not included. In listing the extractors, an effort has been made to describe first those that are of the immersion-type and last those of the percolation-type.



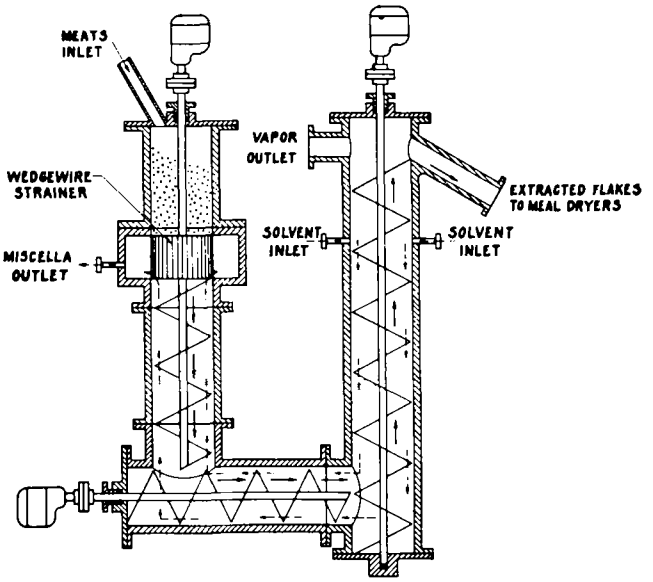
CENTRIFUGAL EXTRACTION SYSTEM

FIG. 2.

The Centrifuge Extraction System. This system, shown in Figure 2, is designed particularly to handle finely ground material. It is a continuous, counter-current stagewise operation, in which each stage consists of a mixer and a continuous solid-bowl centrifuge. The solvent ratio required depends on the number of extraction stages. This extraction system gives well-drained extracted solids and miscella of maximum clarity possible with a ground feed, although the miscella needs further clarification. It is now being used for the extraction, without prepressing, of flaxseed.

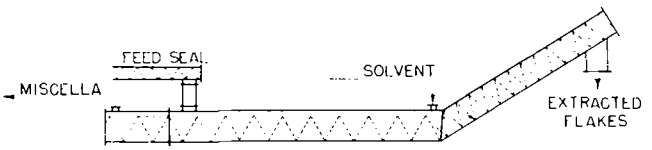
Horizontal Cell Extractor. The only immersion extractor of this type in commercial use is the Kennedy, shown in Figure 3. This is a counter-current, stagewise system in which each stage is a horizontal cell through which solids are conveyed by a paddle-wheel. The paddles are designed to squeeze the solids as they leave the cells in order to reduce the holdup of solvent and thereby reduce the number of extraction stages required. The miscella is clarified by trapping the fines against a filter wheel, but auxiliary miscella clarification is generally required. This system is now applied to the extraction of cocoa beans and cottonseed.

The Screw Conveyor. Although this is the most simple type of extractor, it has had only limited application in this country. The Hildebrandt extractor, Figure 4, was extensively used in Germany for soybeans, and there are two installations in this country. For successful operation, careful flaking is required to avoid excessive fines in the miscella and to prevent choking with fines in the horizontal leg while at the same time maintaining a dense bed of flakes in the columns. A recent attempt to apply this extractor to the direct extraction of cottonseed ended in failure.



U-TUBE EXTRACTOR

FIG. 4.



DETREX EXTRACTOR

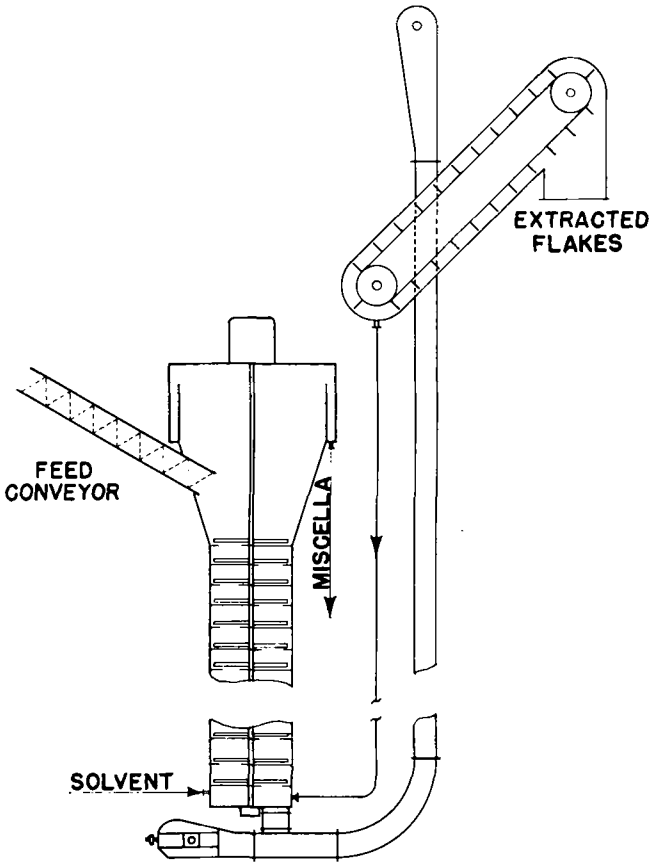
FIG. 5.

The Detrex extractor, Figure 5, has been applied on a small scale in soybean plants, using trichlorethylene as the solvent. The success of this extractor is in part due to the fact that the flakes have the same density as the trichlorethylene miscella so that there is intimate contact between the flakes and solvent. Miscella is removed through a screen scraped by the conveying element, and the flakes are drained by removal with an inclined screw conveyor.

Vertical Column Tray Extractor. There are three systems using this type of extractor: the Allis-Chalmers, Anderson, and Bonotto systems. The feed enters at the top of the column and falls by gravity past partial trays counter-current to rising miscella. These extractors share in common the problems of removing clear miscella and well-drained solids, and the tendency of the miscella, becoming more concentrated and therefore heavier as it rises through the column, to flow backwards.

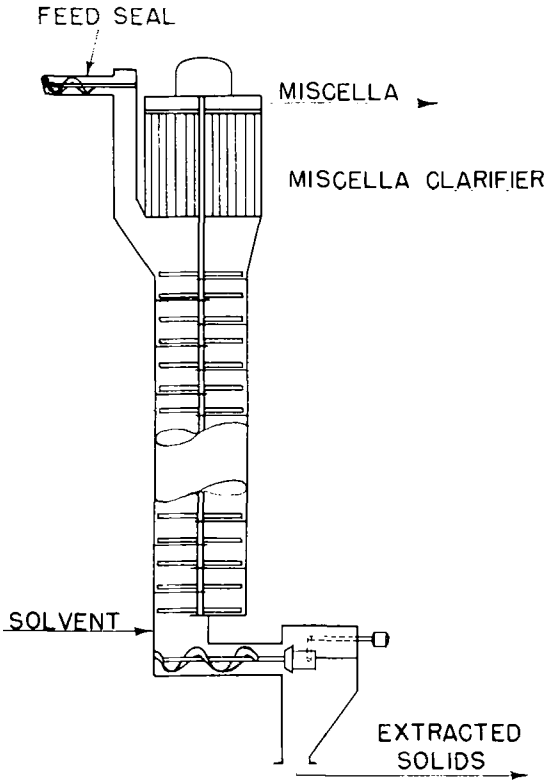
The Allis-Chalmers extractor (Figure 6) has stationary trays, each with a sector-shaped opening through which miscella and solids pass, and a rotating center shaft to which are fixed paddles that sweep the solids off the trays. Miscella leaves through an enlarged settling section at the top, and flakes are removed at the bottom by a Redler conveyor which carries them above the liquid level for drainage. Auxiliary miscella clarification and flakes drainage are generally required.

The Anderson extractor (Figure 7) is similar to the Allis-Chalmers. The miscella is removed at the



ALLIS CHALMERS EXTRACTOR

FIG. 6.



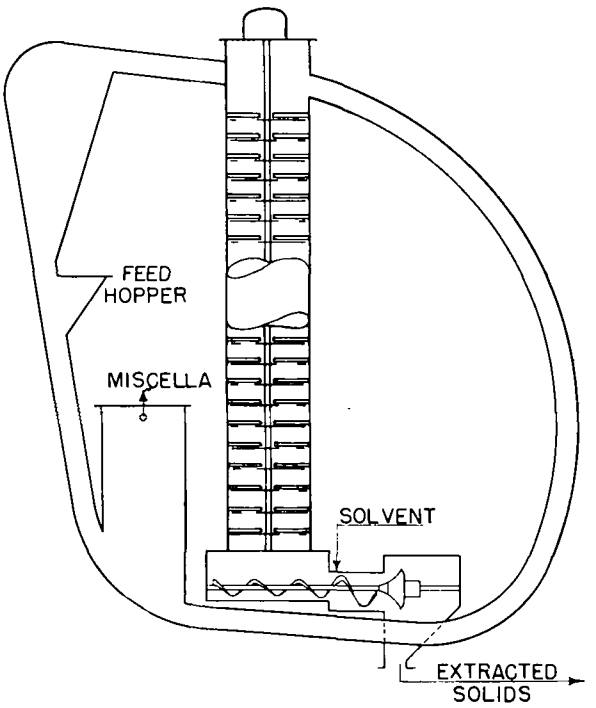
ANDERSON EXTRACTOR

FIG. 7.

top through an ingenious settling chamber in which the miscella is held in long, narrow tubes to reduce convection currents. The flakes are removed at the bottom through a cone-plug squeezer which supports the liquid column and reduces the solvent holdup in the flakes. The flakes are conveyed away from the squeezer to the desolventizer by a Redler conveyor which extends above the liquid level in the extractor so that in case of mechanical failure of the squeezer the contents of the extractor are not dumped.

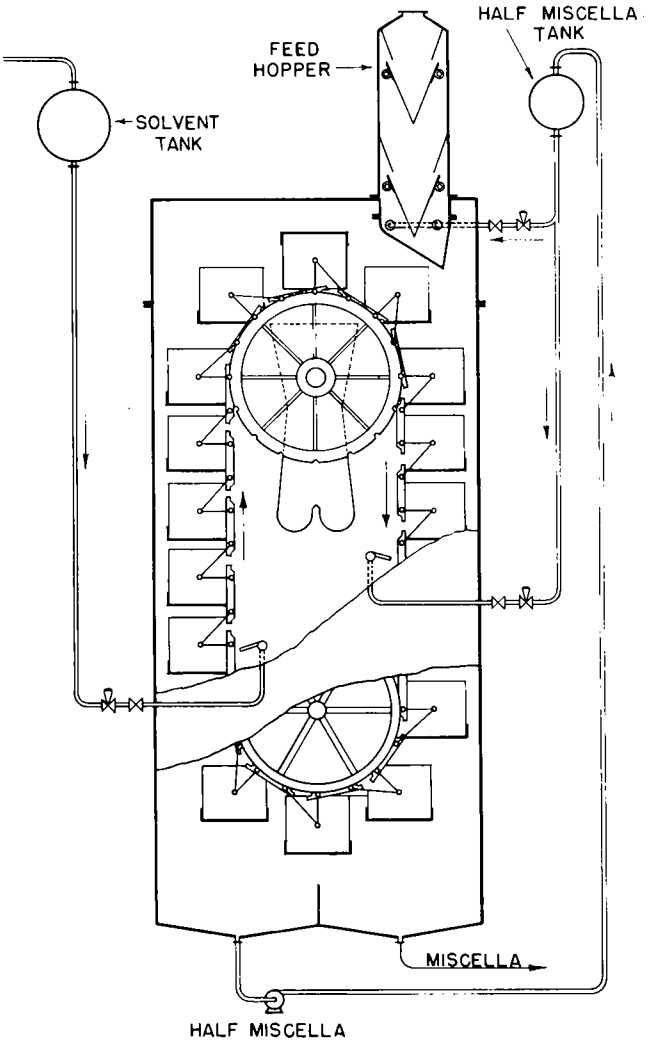
The Bonotto extractor (Figure 8) has rotating trays and stationary paddles. It is claimed for this extractor that it runs full of solids, through which the liquid percolates in a rotating spiral path. The flakes fall vertically, without agitation, and are removed at the bottom through a squeezer. The partial miscella is drawn off countercurrent to the entering flakes through a run-around Redler, in which the greater part of the extraction takes place.

The Basket Extractor. The Basket extractor (Figure 9) is the most widely used for soybeans despite the fact that it is a bulky, complicated machine. Its major advantages are that it produces, without auxiliary equipment, clear miscella and well-drained flakes. Flakes enter the extractor through a cam-operated double-gate hopper which serves both as a volumetric feeder and vapor seal. The baskets move around the closed circuit and are inverted as they pass over the head sprocket to dump the extracted flakes. Fresh solvent from a gravity-flow tank is sprayed, through a cam-operated valve, into each basket in turn part way up the ascending column. The flakes in the baskets above the solvent feed point drain by gravity. The solvent percolates down



BONOTTO EXTRACTOR

FIG. 8.



BASKET EXTRACTOR

FIG. 9.

through the ascending flakes to collect as half-miscella at the bottom, from which it is pumped to a tank above the extractor. The half-miscella flows by gravity through cam-operated valves to the descending baskets, through which the liquid percolates, collecting at the bottom as full-miscella.

To get good extraction in the basket extractor requires careful flake preparation and extractor operation. The solvent will channel through a poorly prepared bed of flakes. To overcome this, three expedients are used:

1. Control the porosity of the flakes by careful cracking and flaking, followed by reduction in flake size, if necessary.
2. Provide a liquid re-distributor on the bottom of each basket.
3. Inject the solvent into the baskets in a sufficiently short interval so that the bed is flooded, guaranteeing uniform distribution of liquid. The flake bed will then itself maintain the distribution.

The descending side of the extractor is especially subject to channeling since there is considerably less full-miscella than half-miscella, and the horizontal area of the basket is based on half-miscella flow. This can be overcome by recirculation of full-miscella through the descending baskets.

The Rotocel Extractor. The Rotocel (Figure 10)

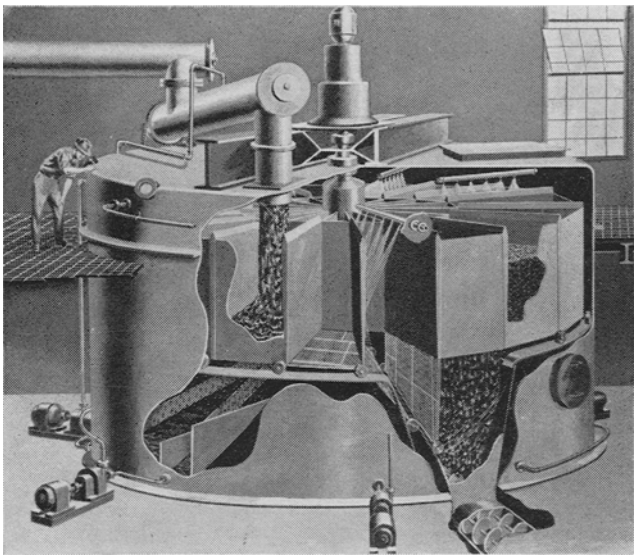


FIG. 10. Artist's drawing of Rotocel extractor.

is a percolation-type extractor, in which the flakes move in a horizontal plane counter-current to the solvent, which is advanced by pumps. The flakes are fed continuously, as a slurry in miscella, to sector-shaped cells of a horizontal rotor. The flakes are supported in each cell by a perforated, screened door, which at the proper time opens over a discharge hopper to dump the extracted, drained flakes. As the flakes move around the circular path, they are flooded by successive miscella washes of gradually decreasing concentration. The liquids draining from the cells collect under the rotor in stage basins from which they are pumped by stage pumps. The flakes are finally sprayed with fresh solvent, then permitted to drain by gravity before they are discharged from the cells. The final miscella is filtered through an established bed of flakes before it leaves the extractor.

The Rotocel extractor retains the advantages of the basket extractor while improving on some of its weaknesses. The major advantages of the Rotocel are that it does not demand the tall building required by the basket extractor and that it is more flexible in operation, requiring less control of preparation and a lower solvent ratio.

In the basket extractor sufficient solvent must be fed to get good hydraulic action on the flakes. Although the amount of solvent required to percolate down through the baskets may be reduced by decreasing the porosity of the bed of flakes, this results in poor drainage from the extracted flakes so that the desolventizing load is shifted from miscella evaporator to flakes desolventizer without reduction in solvent ratio. In the Rotocel the amount of liquid pumped by the stage pumps is independent of the solvent input rate and can be controlled to maintain flooding in the cells without close attention to the porosity of the bed. Drainage of solvent from extracted flakes moving in a horizontal plane is more complete than from flakes moving vertically as in the basket extractor.

SUPPLEMENTARY READING

Bilbe, C. W., Chemical Engineering, *55*, 99 (1948).
Bonotto, M., Oil and Soap, *23*, 297 (1946).
Goss, W. H., Oil and Soap, *23*, 241, 348 (1946).
Kenyon, Kruse, and Clark, Ind. & Eng. Chemistry, *40*, 186 (1948).
MacGee, A. E., Oil Mill Gazetteer, August (1947) p. 17.
Markley, K. S., and Goss, W. H., Soybean Chemistry and Technology, Chemical Pub. Co. (1944).

Rendering

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RENDERING, as it shall be used in this paper, has to do with the separation of the fat from the fatty or adipose tissue of land animals grown and slaughtered for meat. The paper will be further limited to rendering of the edible adipose tissue from swine, cattle, goats, and sheep for the production of lard and tallow.

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Meat has been a human food for thousands of years, and the use of fat from land animals in cooking human food extends back to antiquity. But it was at a much more recent date that fats became an article of commerce. Cattle, swine, and sheep were brought to North America from Europe in the last decade of the 15th century and on several occasions during the early part of the 16th century. These animals were the forebears of the domesticated meat animals of our colonial and more recent times. They, with the wild animals native to this country, furnished the meat and fat for the early settlers.

The early meat packers in the United States were farmers who began preserving meat by packing it in salt; this meat came not only from cattle and swine but also venison and bear. These operators, in the words of a popular song, "by doing what comes naturally" built packing-houses which were just enlarged farm slaughtering establishments.

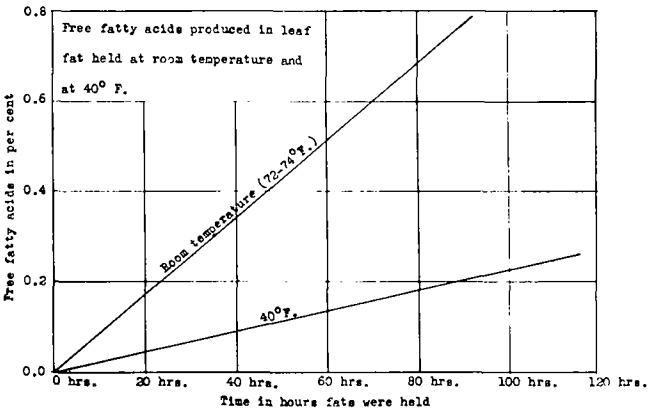
Around the middle of the 17th century a considerable quantity of salt pork and beef was sent to Boston to help supply that city with meat for the table. As cities grew, more packing-houses were formed to supply them with fresh meat. Many of the packing-houses served only their own community, but some of them salted meat and shipped it to other cities.

Centralized slaughter and selling of fresh meat was a more or less seasonal business until natural ice was employed to keep the meat from spoiling. The era of natural ice refrigeration was followed by the development and use of artificial refrigeration. The first mechanical refrigerator was installed in a packing-house in Chicago in 1880. The transportation of fresh meats from packing centers to the large eastern cities was a problem which was not solved until the late 1870's with the industrial development and general use of the refrigerated railroad cars.

The fatty tissue from meat animals which is not a part of the carcass or which is trimmed off from it in preparing the carcass for market is the raw material from which lard and tallow is rendered. The total amount of this fatty tissue taken from the cattle, sheep, and swine commercially slaughtered for meat in the United States, varies somewhat from year to year; but for the year 1947 these fats yielded 2,427,000,000 pounds of lard and 182,000,000 pounds of edible tallow, oleo oil, and oleo stearin.

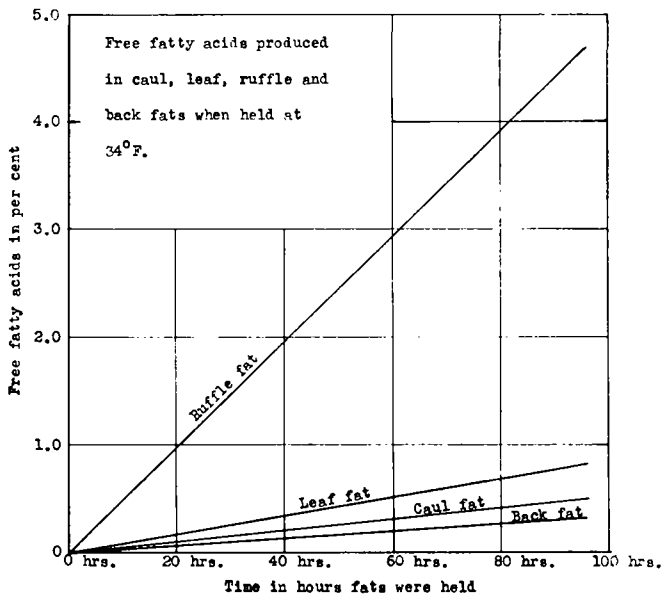
In rendering fatty tissue for the production of lard and tallow, in addition to obtaining maximum yield of fat, the processor must also strive to produce a light-colored fat with a minimum of free fatty acids and good keeping quality. To accomplish this the fats must be rendered as soon as possible after the animals are slaughtered. The amount of free fatty acids an animal fat contains is a good indication of whether the fats were properly handled before they were rendered. This is true because associated with all fatty tissue are fat splitting enzymes which, as soon as the animals are dead, start to hydrolize the fat with the formation of free fatty acids and glycerine. However to avoid misinterpreting a free fatty acids determination, the method used in rendering the fats should also be known. The visceral fats are hydrolyzed more rapidly than the carcass fats when held at the same temperature so it is especially important that the fats from the killing floor be rendered without delay. If they cannot be rendered promptly, they are chilled quickly and held at as low a temperature as economically feasible.

The rate at which fats are decomposed by enzymes and the effect of temperature on the rate of hydrolysis are shown in the following charts:



The fatty tissues to be rendered are usually delivered to the tank house in one of two ways. Either the fats are accumulated in trucks or buggies and wheeled to the rendering department and dumped into the rendering tanks; or in houses where the killing and cutting floors are directly above the rendering tanks, the raw fats are sent to the tanks through gravity chutes.

When the amount of raw killing and cutting fats is sufficient to fill several rendering tanks, they are rendered separately; but when the total amount of raw fat is small, it is all put together in a tank and rendered at one time. Killing fats are the visceral fats and other fatty tissues which are taken from the carcasses on the killing floor. Cutting fats are the skeletal fats which are trimmed from the chilled car-



casses when they are dismembered on the cutting floor for sale and/or processing. These fats include back fat, ham and shoulder trimming, etc.

As would be expected, the rendering of the vast quantity of fatty tissue necessary to produce over 2,600,000,000 pounds of lard and tallow is done in many establishments, ranging in size from the small abattoir to the large packing-houses. The number of these plants is large, and there is wide variation in the estimates found in the trade journals. The 1947 United States Census of Manufacturers lists over 2,000 different commercial plants rendering edible fats.

Open Kettle Rendering

Like all early industries expanding from scratch, the scientific background for enlarging the equipment was governed by the "rule of thumb," so open kettle rendering equipment was the first to be used in packing-houses. It was just an enlargement of what had been used on farms. Thus the first commercially rendered lard and tallow were made from fatty tissues cooked in open iron kettles, which were heated directly with wood fires. As centralized slaughter increased in volume and packing plants built boilers to supply the plants with steam under pressure, the rendering tanks were jacketed and heated with steam. The open wood fires became a thing of the past. Then later, to facilitate more even cooking and less scorching of the fat, the tanks were also equipped with mechanical stirrers. Insulated equipment of this type is in common use in many plants at the present time.

In plants where more than one rendering process is used, open kettle rendered fats are produced only from the fatty tissues that are most easily rendered. For example, open kettle rendered lard is made from leaf fat, which contains about 95% fat, or a mixture of leaf fat and back fat. Back fat contains about 90% fat. In many small plants however all the fresh fats are hashed and rendered in an open kettle.

The common operating procedure is to turn the steam into the jacket and then start hashing the fatty tissue, letting it drop directly into the tank. This operation is continued until the kettle is completely charged. After the tank is filled, the rendering period may be considered in two parts. During the first period most of the water in the tissues is rapidly boiled away. And so long as there is an excess of water present, there is practically no danger of burning the fat and there is very little temperature rise even though full steam is maintained in the jacket.

The second part of the rendering operation begins after most of the water has been removed from the tissues and the temperature of the fat in the kettle rises slowly. When this point is reached, the steam pressure in the jacket is reduced to prevent burning; and a short time before the cook is completed, it should be completely shut off. The maximum cooking temperature should not be more than 240°F. The cook is finished when the cracklings are dry enough to be satisfactorily pressed. There is no entirely satisfactory method for determining when this point has been reached, but there are three things which must be considered in arriving at the proper end of the cook: 1. the fat must be cooked long enough to produce a good yield, 2. the cracklings must be dry enough so they can be satisfactorily pressed, and 3. cooking must not be continued so long at a high temperature that the rendered fat will get dark-colored and possibly burned.

Under normal conditions it requires about three hours to cook a batch of fat. The exact cooking time depends of course on the size of the tank, the steam pressure in the jacket, and the quality of the fat. When in the judgment of the operator the cook is done, the contents of the kettle are dropped into a strainer box with perforated bottom. The cracklings are retained in the box, but the liquid fat runs through the perforated bottom into a receiving tank. The hot fat is next freed from fine cracklings by straining it through two or more thicknesses of cheesecloth and then run into a storage tank, from which it is packaged without further treatment. Open kettle rendered lard is almost always sold without decolorizing or filtering.

Although there are still many small companies making open kettle rendered lard and tallow and a few larger ones making some open kettle rendered products for specific purposes, the total volume of open kettle rendered fat is relatively small when compared to the total production of edible animal fats in the U. S.

Steam Rendering

More than 80% of all edible fats are steam rendered. This process is sometimes called wet rendering. It consists of heating directly with live steam the fresh fats contained in closed cone-bottomed, usually uninsulated, steel tanks. The tanks are made in various sizes, but they are usually made so the depth is about twice the diameter. The tanks are equipped with a charging door, a vent line and safety valve on top, draw-off cocks on the side, steam inlets in the lower part of the cone, and a quick opening gate valve on the bottom of the cone for dumping the tankage and tank water.

Ordinarily a plant is equipped with enough steam rendering tanks so they are used only once a day. However during the busy season some packers use their rendering tanks twice in 24 hours.

The unhashed fats are charged into the tank until it is filled to about three feet from the top. The charging door is then closed and live steam turned into the tank through the steam inlets near the bottom of the tank while the vent line on the top of the tank is

open wide. The vent on the top of the tank is left open until all the air in the tank has been replaced with steam. The vent is then closed and a steam pet cock attached to the top of the tank opened and left open throughout the cooking period. After the vent line is closed, the steam pressure in the tank gradually builds up until the pressure in the tank is equal to the pressure in the steam line.

The pressure at which fats are cooked varies between 30 and 60 pounds gauge. The tendency at present is to cook at a higher pressure than formerly. When the cooking pressure is increased, the cooking time is shortened. Apparently it does not make much, if any, difference on the yield or the quality of the rendered fat whether the fatty tissues are cooked at 40 or 60 pounds pressure, providing the cooking time is adjusted accordingly. Depending on the size of the tank and the cooking pressure, tanks are usually cooked for 3 to 6 hours after full pressure has been built up in them.

Although the size of pieces of fatty tissue that are charged into a steam rendering tank receives very little if any consideration, the length of the cooking time can be greatly affected by hashing the fats. Batches of cutting fats requiring three hours to cook at 47 pounds steam pressure can be completely cooked in one hour when the tissues are put through a sausage grinder equipped with a one inch plate. Data which illustrate this are shown in Tables I and II:

TABLE I

Steam Rendered Non-Hashed Fats

Test No.	Size of Charge Lbs.	Length of Cook	Per Cent F.F.A. In Lab. Rendered Fat	Per Cent F.F.A. In Lard After Settling	Lard Yield %	Lard Stability A.O.M. Method
7B	14059	3 hrs.	0.36	0.55	80.4	6 hrs.
8B	14650	3 hrs.	0.23	0.41	72.5	5 hrs.
9B	12916	3 hrs.	0.31	0.57	76.3	6 hrs.
10B	14083	3 hrs.	0.30	0.67	74.8	6 hrs.
11B	14279	3 hrs.	0.23	0.45	85.5	6 hrs.
		Average.....	0.29	0.53	77.9	5.8 hrs.

This rendering process is the simplest of any of the methods used for separating fats from the fatty tissues. Any and all kinds of fatty tissues can be successfully rendered in a steam tank without any special precaution or change in method of operation. Fool-proofness is a big point in its favor because most fats are rendered at night when operational darkness abounds and supervision is minimal — conditions which make for processing mistakes that are seldom seen and less frequently reported. The large amount of water present in the tank with the fats makes it impossible to burn the fat and about the only thing over-cooking will do is to increase the free fatty acids beyond that which is necessary. All the time while the fat is under pressure in the rendering tank, free fatty acids are slowly being formed and the rate at which the fat is being hydrolized, under any set of conditions, is quite uniform. A few years ago a study was made on the rate free fatty acids were formed when cutting fats were steam rendered at 47 pounds pressure. Under the conditions of these experiments the rate at which free fatty acids were produced in the rendering tank when the tank was at full pressure, was approximately 0.06% per hour.

TABLE II

Steam Rendered Hashed Fats

Test No.	Size of Charge Lbs.	Length of Cook	Per Cent F.F.A. In Lab. Rendered Fat	Per Cent F.F.A. In Lard After Settling	Lard Yield %	Lard Stability A.O.M. Method
4	9884	1 hr.	0.27	0.36	.....	.....
5	9690	1 hr.	0.22	0.31	.....	.....
6A	9884	1 hr.	0.27	0.36	.....	6 hrs.
7A	9690	1 hr.	0.22	0.31	76.2	5 hrs.
8A	12512	1 hr.	0.22	0.30	76.2	4 hrs.
9A	12511	1 hr.	0.31	0.42	83.6	5 hrs.
10A	12620	1 hr.	0.28	0.42	83.4	6 hrs.
11A	13430	1 hr.	0.37	0.48	71.3	5 hrs.
		Average.....	0.27	0.37	78.1	5.2 hrs.

The data in Table III show the rate at which the free fatty acids are formed during the rendering operation.

To conclude the cook the steam is turned off and the vent line is partly opened. If the pressure in the tank is reduced too rapidly, the tank water boils up vigorously and may form an emulsion with the rendered fat. This emulsion is difficult to break, and the settling time is greatly lengthened even though fine salt is sprinkled on the surface of the fat in the rendering tank. After the tank water has separated, the clear fat is run off through a draw-off cock on the side of the tank provided for this purpose. Rendering tanks are usually equipped with two draw-off cocks, placed about 18 inches apart. All the fat is usually drawn off through either one or the other of these cocks. To make this possible water is run into the bottom of the tank, which lifts the fat to a position so it will all run out. The fat as it leaves the rendering tank is run through a separator which removes most of the water that may have been carried over from the tank with the fat. From the separator the fat is run into a shallow tank equipped with steam coils, in which it is further settled and dried. From this tank the fat may be transferred to storage or it may be bleached and packaged.

Steam rendered fats have a characteristic odor and flavor. And although the comparison is not exact, the odor of the fat resembles the odor and flavor of boiled meat from the same species of animals. For example, the flavor and odor of steam rendered lard approaches that of boiled pork.

Prime Steam Lard is a Board of Trade term which means steam rendered lard that has been settled and dried but which has not been bleached or filtered. A bleached or filtered lard is not acceptable for trade on the Board. Until a few years ago Prime Steam Lard was the only lard that could be bought or sold on the Board of Trade. But in July 1946 the Board acted favorably on requests by a number of manufacturers of dry rendered lard that their product be accepted as a commodity for sale on the Board. This action went into effect in July 1947 so that now both Prime Steam Lard and Dry Rendered Lard may be bought and sold without discrimination on the Board of Trade.

Dry Rendering

After the steam jacketed tank had been put in use in packing-houses and vacuum equipment became available, the two were combined and applied to the rendering of animal fats. The tank used for making dry rendered lard and tallow is known as a dry melter. It consists usually of an insulated horizontal

TABLE III

F.F.A. Produced During Rendering
Samples Taken at Hourly Intervals

Test No.	Per Cent F.F.A. in Laboratory Rendered Fat	Per Cent F.F.A. After Heating Up Plus 1 Hr. Cook	After 2 Hrs. Cook	After 3 Hrs. Cook	After 4 Hrs. Cook	After Pressure Was Removed	After Settling
1	0.21	0.33	0.38	0.44	0.52	0.55	0.56
2	0.25	0.33	0.36	0.45	0.51	0.56	0.58
3	0.26	0.32	0.38	0.45	.....	0.52	0.54
9B	0.31	0.36	0.42	0.46	.....	.....	0.57
10B	0.30	0.33	0.36	0.46	.....	.....	0.67
11B	0.23	0.27	0.32	0.37	.....	.....	0.45
Average	0.26	0.32	0.37	0.44	0.51	0.54	0.56

steam-jacketed cooking tank with charging door, vent line, vacuum line, discharging door, and sampling device. It is also equipped with a mechanical arm agitator extending the length of the tank to stir the material while it is being cooked; this keeps the surface of the shell clean to insure good heat transmittance from the steam in the jacket to the contents of the tank and prevents darkening of the rendered fat.

Dry melters are made in various sizes so one can be purchased which will handle up to about 12,000 pounds of fat per charge. And the turn over time on a dry melter is approximately four hours.

There is no limitation on the type of fats that may be rendered in a dry melter and the fats may or may not be hashed. But since small pieces of fat always render more quickly and uniformly than large pieces, many operators hash the fats as they are charged into the melter.

Dry melters may be and are operated in a number of different ways. For example, cooking may be done under pressure, at atmospheric pressure with the vent open, or under vacuum. And the cook may be finished at atmospheric pressure or under vacuum. No matter what operating procedure is used, the temperature of the fat must not get too high. If rendering is done at too high a temperature, the fat will darken and possibly be scorched. The steam pressure in the jacket is controlled so the temperature in the tank, except when the initial cooking is done under pressure, never gets above 240°F. There is no satisfactory way to know when a tank is cooked. The temperature of the fat in the tank does not necessarily give an accurate indication of the moisture content of the cracklings. If 240°F. is reached before the cracklings are dry enough to press, the steam pressure in the jacket is reduced and the cook continued. The cook is considered done when a sample of cracklings, drawn from the tank through a sampling pipe by the operator, feels dry enough to press without squirting from the press when the pressure is put on them. To find the end point, samples of cracklings are taken every 10 or 15 minutes towards the end of the cook. If the tank is over-cooked, nothing can be done about that. A good experienced operator can judge the dryness of the cracklings quite closely, but a less experienced person may run into a lot of trouble, both with respect to yield of fat and also with pressing the cracklings. The cook is terminated when, in the judgment of the operator, the cracklings are dry enough to press. When this point is reached, the vacuum is broken on the cooker and the discharge door opened slowly, permitting the contents of the melter to flow into a tank made with a perforated false bottom which retains the cracklings and allows the fat to drain through. The fat is then either strained through cheesecloth and packaged; or it may be bleached and/or just filtered and packaged.

Dry rendered fat resembles open kettle rendered fat in many ways. It has low free fatty acid, good stability, and a flavor and odor resembling open kettle rendered fat.

Other Rendering Processes

Neutral Lard and Oleo-stock. Neutral lard is made by gently heating hashed leaf or a mixture of leaf and back fat in an open water-jacketed kettle provided with a paddle agitator. The temperature is maintained at 126°F. until there is a separation of lard and fiber. This separation is aided by sprinkling fine salt on the surface of the lard from time to time. As soon as the clear lard begins to separate, the agitator is stopped so the lard can further separate from the tissue. After the tank has settled, the clear lard is siphoned off and run through two or more layers of cheesecloth. To make sure that it is free of moisture it is held for several hours at about 120°F. and then barreled. Practically all neutral lard is used in the manufacture of oleomargarine.

The material left in the rendering tank after the neutral lard is siphoned off is known as neutral bottoms. It contains quite a large percentage of lard so it is transferred to a steam rendering tank and further rendered along with fresh fats.

Oleo stock is made in much the same manner as neutral lard. The hashed beef fats are heated in an open water-jacketed tank provided with mechanical agitation. Rendering is done at 155°F. Fine salt is sprinkled over the fat to coagulate the wet fibers and permit the clear fat to separate. The melting operation is usually completed in about two hours. When separation begins to take place, the agitator is stopped and the tank settled for about an hour, longer if it is necessary to get good separation. After settling, the oleo stock is siphoned off through several layers of cheesecloth into a settling tank and dried. Oleo stock is the material from which oleo oil and oleo stearin is made. The material left in the rendering tank after the oleo stock has been removed is only partly cooked, so it is transferred to another tank and further rendered.

Drip Rendering. This process gets its name from the way the rendering tank resembles a drip coffee pot. The rendering tank is divided into two sections, one above the other. They are provided with strong stirrers driven by a motor through a reducing gear placed under the tank. The sections are separately steam jacketed so they can be heated one at a time or both together. Both sections are connected through a common vapor line to a good vacuum pump or

steam ejector. The raw fat is charged into the upper chamber, the charging door closed, and heat and vacuum applied. The fat, as it separates from the tissue, runs through perforated plates placed in the bottom of the upper chamber and into the lower section in which it is refined, bleached, and dried.

The theory on which this rendering procedure is predicated implies that the fat as it is rendered from the fatty tissue by dripping into the lower chamber is immediately separated from the cracklings. In practice however a considerable amount of fine cracklings also passes through the perforated plates into the refining compartment so the anticipated advantage of the process is at least partly nullified. Nevertheless by the use of a rather large amount of sodium bicarbonate and activated carbon a light-colored, low free fatty acid and mild-flavored fat is produced.

Continuous Rendering. There are a number of continuous rendering plants in Europe. And within the past few months a Danish continuous rendering plant, known as the Titan process, was put in operation in Canada for processing edible fats. The plant has a rated capacity of 3,000 pounds of fat per hour and the fats pass through the plant, from hasher to clear dry lard or tallow, in less than 15 minutes.

This is a steam process in which the fats, after hashing in a steam-jacketed grinder, pass through a pre-heater and into a cooker where they are further heated with live steam. The comminuted fats are almost completely rendered in the few minutes while they are in the cooker, and the rendering is completed when the pressure is taken off the hot slurry of fat, fiber and tank water as they leave the cooker. The sudden release of pressure disintegrates the fatty cells which had not been ruptured by heat and also breaks up the tissue.

The larger pieces of tissue in the slurry are separated from the fat and water in a rotating drum and then pressed. The rendered fat is completely separated from the tank water and fine fiber by two centrifugations. Nearly all the water and fiber are removed from the fat in the first centrifuge, and the remaining water and fine suspended matter are removed in the second. The fat from the second centrifuge is clear and free from water so it may be put in storage or packaged for sale without further treatment.

Lard produced by this process is reported to have a mild flavor, with low free fatty acids and good keeping quality.

Circulation Rendering. A circulation rendering procedure was developed about 20 years ago for rendering inedible fats and is in use in several plants of the company which developed it. Essentially it is a dry rendering unit operating under vacuum and using exhaust steam in the heat exchanger.

The material to be rendered is hashed and circulated through a heat exchanger with a rotary pump until it is rendered. Above the heater is a large flash chamber in which the water is evaporated. The vapor is drawn off the flash chamber through a separator into a barometric condenser. Vacuum is maintained with a steam ejector. When dry, the mixture of fat and cracklings are pumped to a settling tank. After the tank has settled, the supernatant fat is siphoned off and the cracklings are pressed either in an expeller or in a hydraulic press.

The Use of Enzymes in Rendering

Four or five years ago a patented process which uses a proteolytic enzyme concentrate was announced as a material aid to the rendering of fats from animal tissues. The use of these enzymes does not take the place of a standard rendering procedure, but the patent claims that if the hashed tissues are treated with the enzymes and then rendered in the usual way, the cooking time will be reduced 30 to 70% and the yield will be increased by about 7.5%. The process also claims the production of a fat with improved flavor, less free fatty acid, and better keeping quality.

There has been considerable interest in this adjunct to commercial rendering, but there are no data available on how much success has been had with its use in commercial plants.

Rendering in the Presence of NaOH

More recently, in December 1948, another patented process for rendering edible fats appeared. In this procedure the hashed fatty tissue is digested with a specified amount of alkali. Under the temperature of the patent, 180-190°F., the alkali digests the non-fat tissue solids but does not promote an appreciable amount of fat hydrolysis. After digestion, 30 to 60 minutes, the mixture of fat and digested tankage is run into a centrifuge in which the fat is separated from the aqueous digestion liquid. The fat is then washed free of soap with water and dried. After drying, it is ready for storage or further processing. No data are available to show whether the process is commercially feasible.

Two other procedures have been tried experimentally to separate fat from animal fatty tissue. These probably should be mentioned although there are no data or even claims available to indicate what might be expected from them. 1. The application of infra-red rays for heating a layer of comminuted fat spread out on a belt conveyor which could be passed under a bank of infra-red lamps, similar to the arrangement used commercially for baking cookies, has met with some small-scale success, but data on the experiments are not available for our use. 2. Experiments on cooking fats have been made with high frequency equipment, similar to that used in the plywood industry for melting the adhesive between the layers of wood before pressing. And although the fat can be separated from the tissues by this procedure, there are no data available for evaluating the process.

So much for processes. Now a word about processing trends in the industry. There is an increased interest by the smaller packers in dry rendering edible fats. This is especially true with packers who dry render the inedible fats and who do not have evaporation equipment to recover the dissolved protein compounds in tank water. The use of dry melters assists some packers with their sewage problems and at the same time yields more high-grade tankage, which is in demand as an animal feed at a good price.

A further interest in dry rendering edible fats may be expected if the conductivity apparatus which is being developed for continuously determining the moisture in the cracklings in a dry melter without removing them from the tank is successful and sufficiently rugged to meet tank room operation.

At a time when industry is adapting its processes to continuous operation wherever possible, the continuous rendering of edible animal fats will undoubtedly

be given more thought and serious consideration in the United States. With the improved and efficient heat exchangers which are now available, comminuted fats can be quickly heated to effect complete separation of fat and fiber. The resulting slurry can then be put through a centrifuge to separate the fat from the tankage and tank water. Interest in continuous rendering has lagged because the cost of continuous rendering equipment is considerably more than the expenditure necessary for the tanks used in batch rendering. However, with the application of newer ideas on design, there may be a saving in steam, room space, etc., which will make the continuous method competitive. In this case, continuous rendering units can be expected to replace some of the batch plants now in use.

Batch Against Continuous Refining of Vegetable Oils

B. H. THURMAN, Consulting Chemical Engineer, New York City

ALL crude vegetable oils contain non-glyceride constituents commonly known to be impurities, in addition to free fatty acids. Jamieson and others have identified by painstaking analysis a large number of these:

Minor Constituents of Vegetable Oils

Proteoses
Peptones
Phytosterols
Phytosteroline
Inosite phosphates
Phospholipins
Resins
Mucilaginous substances
Carbohydrates—Raffinose, Pentosans
Pigments—Xanthophyll, Carotin, Chlorophyll

B. H. Thurman

Others have found iso flavone glycosides included with pigments, and saponins have also been isolated.

A noticeable odor of ammonia can be easily recognized when caustic soda solution is added to many crude cotton oils in batch or kettle refining. I have detected methane, a mercaptan, hydrogen, and amino nitrogen from cotton oil soapstock in the escaping vapors during high pressure digestion. It is certain that phosphorus compounds and nitrogen are carried away from the seed by the oil during expression.

The major portion of these components are emulsifiers or stabilizers in the presence of alkalies, and it is difficult to remove them without excessive entrainment of the more valuable glycerides. Because the largest portion is phosphatidic, it is practical to remove a considerable amount by precipitating with water and centrifuging or settling out. But the refiner knows by experience that this water treatment, called degumming, does not prepare the glycerides or remaining treated oil for deodorizing into a stable palatable oil. He must alkali-refine even though degumming may be repeated until only a mere trace of phosphorus is left. For some unknown reason crude or degummed oils will have strong undesirable flavors if deodorized at temperatures above 350°F. Unfortunately oils deodorized at 350°F. or lower will be bland in flavor but unstable and revert to some of the original crude flavor. Of course water treatment alone will not remove sufficient pigments to meet color standards.

Therefore up to now an alkali treatment had to be given and an excess used over that to neutralize the free fatty acid. This excess combines with these minor constituents, including color, and makes a heavy emulsion with the soap from neutralized F. F. A. and water from the caustic solution, entangling valuable neutral oil. This mass when settled out or separated is a cheap by-product known as soapstock and represents the refining loss.

There is an added improvement apparent in furfural and propane refining, liquid-liquid, to promise some hope of eliminating alkali refining, but my associates and I are convinced that these oils also should be alkali-refined to compare with the best quality of palatable oils marketed. If hydrogenation is also employed, there is a better possibility of eliminating alkali refining.

FOR years the well known refining kettle or batch method was used to mix in the alkali solution with the crude oil, agitate, heat, and separate into a two-phase oil and soapstock condition whereby the latter would settle freely and compact tightly to eliminate entrainment of neutral oil. It also was necessary to avoid over-heating the mass to prevent the neutral oil from saponifying on account of an excess of alkali and causing steam formed from the water and the gas-like ammonia set free by the caustic to expand and tend to float the soapstock particles and beat them back into the oil and fail to gravity settle. All this technique was necessary and took pains and experience and was costly due to entrainment and saponification of neutral oil. At times salt or sodium silicate of soda were added to the batch to bring about better separation of soapstock and oil and compact settling. But the best experience and technique failed to surmount the inefficiency of batch refining.

For this reason years of research and experimenting were spent by numerous ones trying to perfect a better method. It remained for Benjamin Clayton to develop a caustic soda continuous refining process which saved up to 30% of the refining loss incurred by batch refining. His patents were issued about 12 years ago. The main features of improvement were mixing in the course of seconds compared to minutes and heating to temperatures so much higher than feasible in the kettle. The soapstock particles melted together better, and the viscosity of the neutral oil was reduced, thus permitting faster separation of

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For this reason years of research and experimenting were spent by numerous ones trying to perfect a better method. It remained for Benjamin Clayton to develop a caustic soda continuous refining process which saved up to 30% of the refining loss incurred by batch refining. His patents were issued about 12 years ago. The main features of improvement were mixing in the course of seconds compared to minutes and heating to temperatures so much higher than feasible in the kettle. The soapstock particles melted together better, and the viscosity of the neutral oil was reduced, thus permitting faster separation of

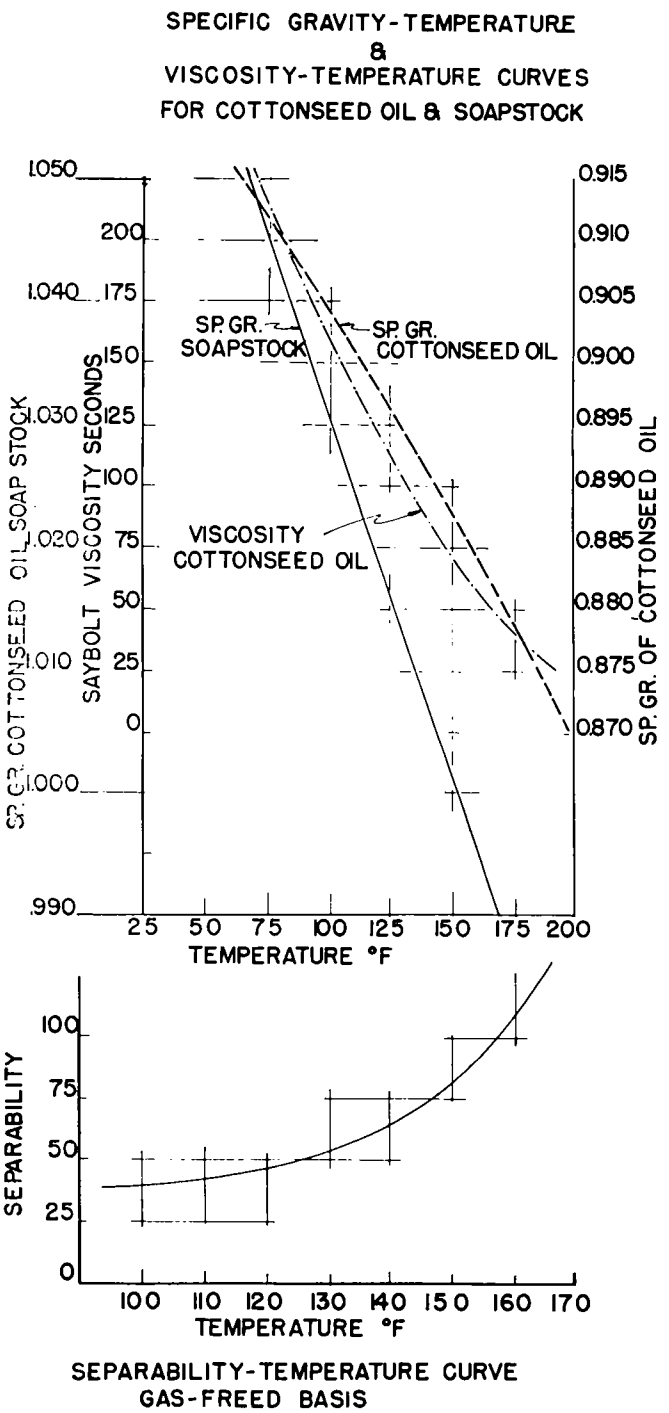
soap particles from the oil phase. A centrifuge was employed for separation so that no long time exposure between oil, free caustic, and soapstock particles was necessitated as in the kettle, sometimes for over an hour, and a more compact oil-free soap by-product resulted in a sizeable economic saving. Other advantages were saving in refining building space and making control of the operation much more automatic, thus avoiding operators' inexperience and carelessness. It made practical the refinement of oils with excessive amounts of F. F. A. and impurities. This process was quickly adopted by refiners throughout the United States and in many countries abroad (1).

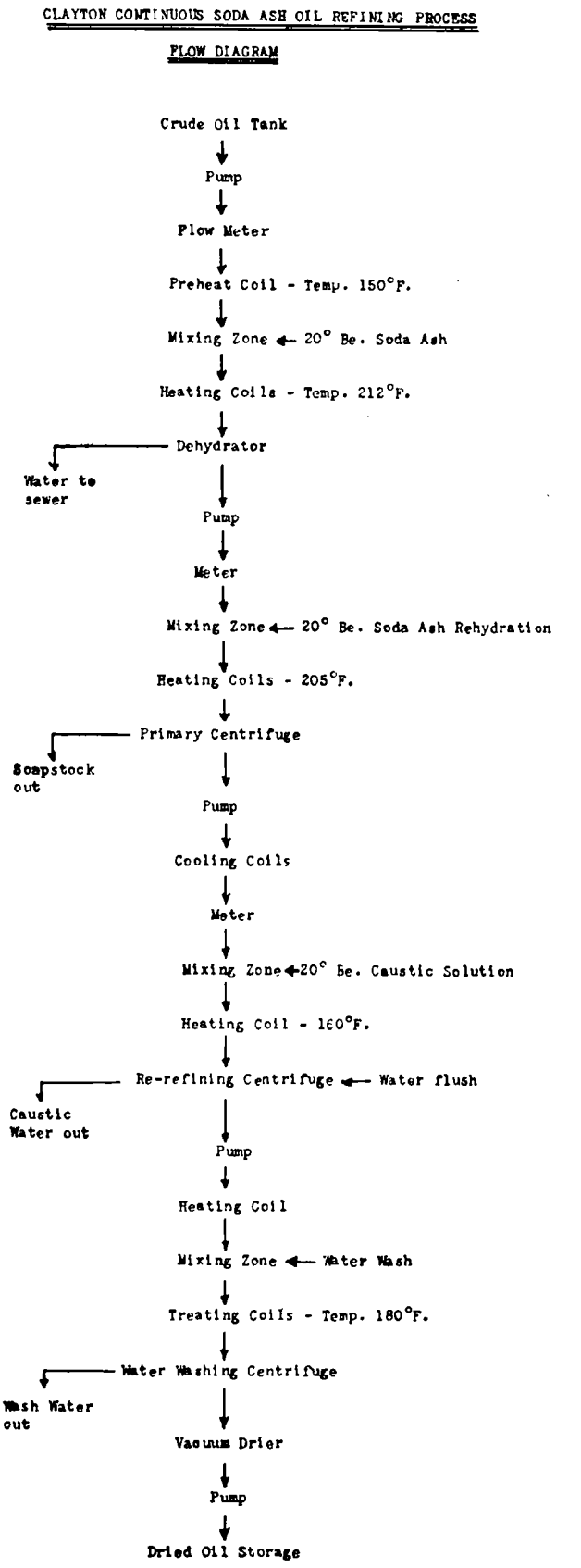
A word about the methods used for measuring in the laboratory the quality and refining loss of a crude oil is pertinent (2). The methods and the equipment are similar to the batch kettle method. This method employed caustic soda of varying strengths, no other alkali could be used successfully. Long time exposure to the caustic, soapstock, and oil is unavoidable, also a temperature range under 150°F., which causes too little change in oil and soap viscosity to effect best separation of oil from soap and prevent neutral oil saponification. The large batch cannot usually be manipulated as well as the laboratory can as to temperature on both oil and soapstock.

While the continuous caustic refining method overcame many difficulties in the laboratory and batch method, there remained a gap between that and theoretical refining loss (3, 4). This theoretical determination is called the Wesson Loss, also the Absolute Refining Loss. Briefly, it consists of combining caustic soda with the F. F. A. and minor constituents of a crude oil which is first dissolved in petroleum ether. Then 50% alcohol is added to dissolve the soapstock in a bottom liquid layer, and the neutral refined oil remaining in the petroleum solvent is blown off, evaporated, and weighed, the difference being impurities and F. F. A. The cup test loss is usually about double the theoretical loss on most vegetable oils other than the coconut family type. This prompted Benjamin Clayton to develop an entirely new and novel continuous process, known as the Soda Ash Oil Refining Process (5). For the first time soda ash was employed successfully as a refining agent. It consists of a system of mixing in concentrated soda ash solution (20° Be.), heating to 210°F., dehydrating under vacuum or evaporating off the water and carbon dioxide and other gases, then rehydrating with 20° Be. soda ash solution (just enough to make the soapstock break out from the neutral oil and not form an emulsion and be fluid enough to slide quickly along the walls of the centrifugal bowl), then mixing in flow a small percentage of 20° Be. caustic soda solution, centrifuging, washing and drying the resultant refined oil. This process saves about 45% over the batch kettle method and about 25% over the caustic continuous method and often comes within ½% over the theoretical loss, which is so close to the theoretical that little is left to gain by solvent refining liquid-liquid.

Such oils as peanut, soya, and corn often can be refined without the caustic step following soda ash neutralizing while cotton and linseed cannot be, on account of the different types of color pigments on which soda ash has little effect, necessitating caustic soda. There are times when the former oils contain an excessive amount of glycosides, both the sterol and iso flavone type, and perhaps other matters on which soda ash is not as effective as caustic soda (6).

THE advantages of the soda ash method are obvious. A non-saponifying agent is added to neutralize, the emulsion is broken by high temperature and evaporation; then rehydrating with a concentrated solution, thus not forming an emulsion, and heating to a temperature of more than 200°F., makes very effective centrifugal separation due to viscosity reduction on both the oil and soapstock. At 200°F. the viscosity of the soapstock is a semi-fluid, and at lower temperatures it resists any flow but changes from a solid mass to a semi-fluid around 180°F. If such a temperature were used in the kettle or even continu-





ous caustic method, separation would be very difficult.

The viscosity of the oil at 100°F. is 35 centipoises; at 200°F., it is 6.5 centipoises, and undoubtedly all particle settling follows the principle of Stokes' Law, which is dependent directly on particle size and inversely as to the viscosity of the medium through which the particle travels or settles. One of the most accurate instruments for determining particle size in micron dimensions employs this principle of settling plotted against time which is proportional to particle size. Another factor favoring the continuous process is the use of centrifugal force to increase settling out and packing the soapstock particles to prevent neutral oil entrainment by increasing gravity several thousand times. The time exposure of the excess caustic to neutral oil is reduced to a minimum, thus lowers saponification loss.

It is well known that neutral vegetable oils greatly resist saponification. In the soda ash process no saponifying agent is used until after the F. F. A. are removed. This permits the use of a strong alkali, caustic soda in the second step of the soda ash process, which causes practically no saponification but greatly reduces color and residual impurities.

It is not practical to use soda ash in the batch operation because of foaming and the impossibility of thoroughly neutralizing the F. F. A. of the oil. This reagent apparently only completely neutralizes under pressure and elevated temperatures that are not practical in batch operation. It is evident from this that the batch process never equalled the continuous methods both as to economy or quality.

Official rules for laboratory refining of vegetable oils in order to determine their quality both as to refining loss and color usually call for varying the excess and the strength of the caustic soda solution. Because vegetable oils of any given type vary, a burden is placed upon the refiner using the batch method likewise to carefully determine, prior to adding caustic soda in the factory batch operation, the suitable excess and strength of solution for the lowest refining loss and best color of the oil. In the continuous soda ash refining method practically all oils are refined with a 20° Baumé soda ash solution both for neutralization and rehydration. The caustic refining step in this process likewise can invariably use one strength of caustic soda, preferably 20° Be. Because the operation of this process is continuous, a refiner can determine the amount of solution to add in the first few minutes of the refining operation and adjust the quantities in accordance with rapid laboratory tests and determine if sufficient refining agent has been added, thereby checking the metering and proportioning device supplying the alkali reagents. It is also possible and practicable by making a laboratory analysis on the soapstock from this process to calculate the refining loss to an accurate degree in comparison to the theoretical or absolute refining loss and to check closely with actual scale weights as to refined oil yield and soapstock produced.

Laboratory methods for these procedures are as follows:

Refining, Unincorporated Method for Determining Total Alkalinity in Oil and Alkali Mixtures to Calibrate the Proportionometer

Procedure:

Ten grams of the oil and alkali mixture are weighed into a 4 oz. oil sample bottle. About 25 to 35 c.c. warm water is added and sufficient methyl orange indicator is used to produce a definite yellow cast to the solution. The solution is titrated with $\frac{N}{10}$ acid, shaking the bottle vigorously after each addition

tion of acid. The titration is continued until the end point has been reached which is indicated by an orange or orange-red color.

Calculations:

$$\text{Percent total alkalinity as } Na_2CO_3 = \frac{\text{Titre} \times .0053 \times 100}{\text{Wgt. of sample}}$$

$$\text{Percent total alkalinity as NaOH} = \frac{\text{Titre} \times .004 \times 100}{\text{Wgt. of sample}}$$

Process Control Calculations

$$\text{Percent } Na_2CO_3 \text{ to neutralize F.F.A. in crude oil} = \frac{\text{F.F.A.}}{5.3}$$

Percent excess Na_2CO_3 = % Na_2CO_3 in dehydrator oil − % Na_2CO_3 to neutralize

$$\text{Percent 20° Be. } Na_2CO_3 \text{ delivered by proportioner} = \frac{\%\ Na_2CO_3 \text{ in dehyd'tor oil} - \%\ Na_2CO_3 \text{ in crude oil} \times 100}{15}$$

Rehydration Calculations

A = Percent Na_2CO_3 in oil mix to primary centrifuges
B = Percent Na_2CO_3 in dehydrator oil
C = Percent Na_2CO_3 in soda ash solution (20° Be. = 15)

$$\text{Percent 20° Be. Soda Ash solution rehydration} = \frac{A\text{-}B \times 100}{C}$$

Caustic Wash Calculations (Re-refining Step)

A = Percent Alkalinity as NaOH in oil mix to secondary centrifuges
B = Percent Alkalinity as NaOH in oil from Primary
C = Percent NaOH in Caustic solution (20° Be. — 14.4%)

$$\text{Percent 20° Be. Caustic Wash} = \frac{A\text{-}B \times 100}{14.4}$$

Refining, Unincorporated Clayton Soda Ash Soapstock Method of Analysis to Determine the Refining Loss

Moisture:

Two to three grams of soapstock are weighed into a tared 50 c.c. beaker containing a small stirring rod and about 10-15 grams of coarse sand. After stirring well to coat the surface of the sand with the soap, the beaker is dried for 3 hours in a moisture oven at 105°C. During the drying period, the soap is stirred occasionally to promote complete drying. The beaker is cooled in a dessicator to room temperature and weighed.

$$\text{Percent moisture} = \frac{\text{Loss in total weight} \times 100}{\text{Weight of sample}}$$

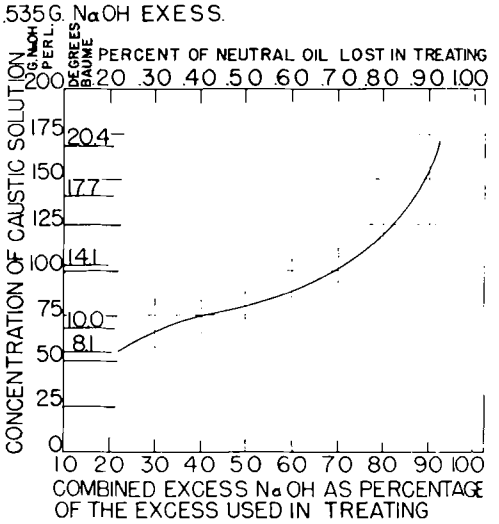
Free Oil:

Twenty c.c. acetone is added to the beaker containing the residue from the moisture test and stirred well to dissolve the free oil into the acetone. The acetone is filtered, preferably through a Gooch crucible into a 1" x 8" test tube placed inside a suction flask. The Gooch crucible has previously been prepared with asbestos and washed with acetone. Three additional washes of 15 c.c. acetone each are made of the residue in the beaker and filtered into the test tube. The Gooch crucible is finally washed with a small amount of acetone, and the filtrate contained in the test tube transferred to a tared 150 c.c. Soxhlet flask and the acetone evaporated on a steam bath. The flask is dried for 1 hour in a drying oven at 105°C., cooled and weighed.

$$\text{Percent free oil} = \frac{\text{Weight of oil in flask} \times 100}{\text{Weight of sample}}$$

Some charts are given to show the effect of strength of caustic, the time of contact, and the temperature in relation to the amount of caustic combined with the glycerides, which result in a loss of neutral oil. One curve shows the specific gravity and viscosity, temperature relation of cottonseed oil and caustic soda soapstock, also the increase separability corresponding to rise in temperature.

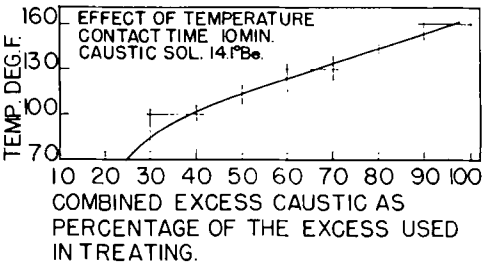
VEGETABLE OIL REFINING
EFFECT OF CONCENTRATION OF CAUSTIC SODA SOLUTION ON THE SAPONIFICATION OF COTTONSEED OIL. 350G. OF OIL (.075% F.F.A.) AGITATED FOR 10 MIN AT 130°F. WITH CAUSTIC SODA SOLUTION EQUIVALENT TO .535G. NaOH EXESS.

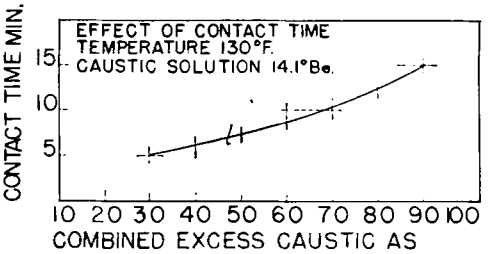


REFERENCES

1. A. E. Bailey, Industrial Oil and Fat Products.
2. Am. Oil Chemists' Soc. Official and Tentative Methods.
3. The Composition of Crude Cottonseed Oil; A Summary by G. S. Jamieson and Walter F. Baughman. Cotton Oil Press *4*; 3, 85 (July, 1920) and *6*, 48 (Oct., 1920).
4. M. Mattikow, Oil & Soap *19*, 83-87, No. 5 (May, 1942).
5. M. Mattikow, Oil & Soap *19*, 83-87, No. 5 (May, 1942).
6. M. Mattikow, J. Oil Chemists' Soc. *25*, 200-203 (June, 1948).

VEGETABLE OIL REFINING
EFFECT OF TIME OF CONTACT AND TEMPERATURE ON THE SAPONIFICATION OF COTTONSEED OIL. 350G. OF OIL AGITATED MECHANICALLY WITH AN AMOUNT OF 14.1°Be' CAUSTIC SODA SOLUTION EQUIVALENT TO APPROX. .535G. OF NaOH EXESS. (FATTY ACID CONTENT OF OIL .075%) CENTRIFUGING 90 MIN. AT 6000RPM AND 130°F.





Solvent Refining and Fractionation of Fats and Oils

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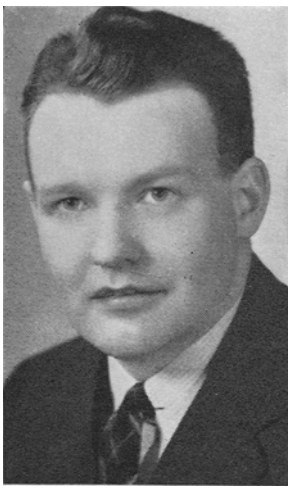
THE refining or fractionation of fats and oils by means of solvents has been practiced in various forms for a long time, but numerous improved processes have been introduced in recent years. Examples include furfural extraction, which has been described by Gloyer (4) and by Kenyon and Gloyer (5), the use of propane as a selective solvent, as in the Solexol process (1), and continuous crystallization from solution by means of the so-called "Emersol" process, which has been reported by Demmerle (2).



W. H. Goss

In the present paper the actual details of operation and equipment design will not be discussed since adequate descriptions already appear in the literature. Instead some interesting aspects of the theories involved and the potential effectiveness of these new methods will be discussed. First of these is the extent to which the glycerides are mixed in a naturally-occurring oil, soybean oil for example, and what the possibilities are of being able to separate these components into fractions. Then comparisons will be made between liquid-liquid extraction, distillation, and crystallization.

Glyceride Structure

The naturally-occurring fats and oils are glycerides of a number of fatty acids whose composition and characteristics are rather well known. In Table I are listed the fatty acids occurring in soybean oil, which is an excellent example to consider when discussing this subject, together with some of the distinguishing features of the individual acids. These acids are combined with glycerine in a mixed manner, and typical examples of the mixed glycerides occurring in soybean oil are as follows:

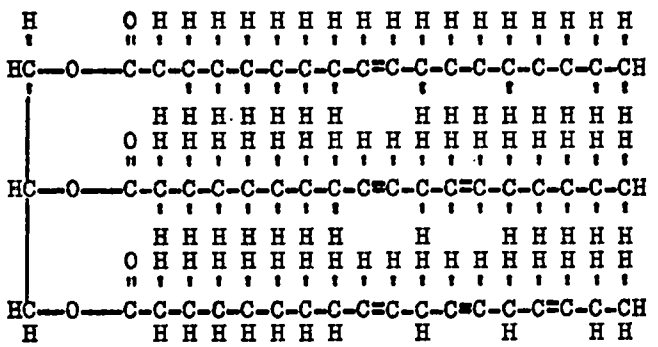
TABLE I

Characteristics of Common Fatty Acids

Acid	Number C Atoms	Number Double Bonds	Molecular Weight of Triglyceride	Iodine Value of Triglyceride
Palmitic	16	0	807	0
Stearic	18	0	891	0
Oleic	18	1	885	86
Linoleic	18	2	879	173
Linolenic	18	3	873	262

linolenic	—linoleic	—linolenic
linoleic	—linoleic	—oleic
saturated	—oleic	oleic

The complete formula for a typical molecule of this type, namely, oleolinoleolinolenin is as follows:



Discussions of glyceride structure usually concern the three common hypotheses for the mixed condition occurring in natural glycerides, namely, the "maximum" distribution, "random" distribution, and "simple triglyceride" distribution. The last named, although we know it does not exist in natural products, is of practical interest nevertheless because it is almost identical with the distribution occurring in the mixed methyl esters obtained by the methanolysis of oil.

Figure 1 is a graph showing the calculated extents to which glycerides of various types occur in a soybean oil having the fatty acid composition shown in the upper right corner. The results are shown for all three assumptions of distribution, namely, maximum, random, and simple triglyceride. In each case blocks have been drawn to indicate what percentage each type of glyceride represents of the total glycerides in the oil, the iodine value of the type of glyceride represented by each block being plotted against the percentage of that particular triglyceride. The glycerides are considered from the standpoint of the number of double bonds in the entire molecule. As an illustration, oleolinoleolinolenin, the example shown above, contains 6 double bonds and has an iodine value of 173. A glyceride containing 1 saturated, 1 oleic, and 1 linoleic acid possesses 3 double bonds and has an iodine value of 86.

The distribution calculated in accordance with the "maximum" hypothesis is shown by solid lines, there being three different types containing 6, 5, and 3 double bonds respectively. According to this method of calculation, there are about 40% of glycerides containing 6 double bonds and nearly 50% having 3 double bonds, the remainder being glycerides with 5 double bonds.

Provided this calculated composition is used, it is possible to determine the greatest amount of separation that could be achieved with respect to iodine value between two fractions if a theoretically perfect fractionating device were employed. The maximum difference in iodine value between the extract and raffinate obtained in liquid-liquid extraction, for ex-

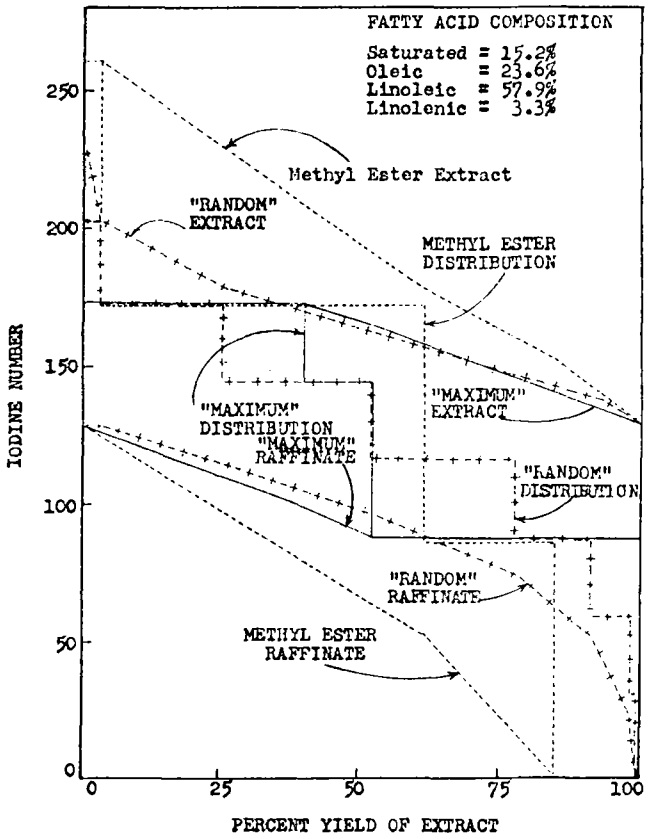


FIG. 1. *Hypothetical glyceride compositions in a typical soybean oil.*

ample, if the extraction apparatus could be made to perform perfectly, is determined by integrating the respective areas under the "blocks" to the left and to the right of a vertical line drawn to represent the percentage yield desired in the respective fractions. Such calculations have been made for various assumed yields in order to obtain the two solid lines designated "maximum raffinate" and "maximum extract."

A similar set of curves, i.e., blocks to represent the distribution and curves to represent the theoretical extract and raffinate, has been entered in the chart also for "random" distribution and for "methyl ester" (or simple triglyceride) distribution, the former being depicted as a series of plus marks and the latter as dotted lines.

These curves are of value as a guide to determining how efficient a given fractionating apparatus or process actually is although they are subject to some uncertainty because we do not know which of the preceding hypotheses is most applicable in the cases of most common fats and oils. There is considerable evidence however that the actual distribution in soybean oil is something between that estimated in accordance with the "maximum" theory and that calculated according to "random" distribution.

In Figure 1 the maximum difference in iodine value theoretically realizable between the extract and raffinate derived from the particular soybean oil under consideration varies with the percentage yield of the two products. In the cases of both the random and maximum hypotheses however the average theoretical difference in iodine value is about 70 units, and this degree of separation is approximately that foreseen as the ultimate goal in any process of fractionation which operates directly on the triglycerides without effecting some kind of ester-ester interchange. In the case of methyl esters the maximum separation is about 130 iodine value units.

Action of Selective Solvents

In liquid-liquid extraction, which is one of the most interesting types of fractionation, it is necessary to utilize a solvent which exhibits at least some immiscibility with the oil being processed. There are many such solvents of course, and furfural is one of the most common. It is possible to predict with considerable accuracy whether a given liquid will display immiscibility with soybean oil by applying Freeman's (3) rule. According to this principle, each functional group in the molecule under consideration is assigned a certain arbitrary number. Hydroxyl, for example, is given 3 points, and an ether linkage is credited with 1 point. If the summation of all these points, as assigned the various functional groups in the molecule, exceeds the number of carbon atoms, the liquid probably will be only partially miscible with soybean oil at ordinary temperatures.

The solubility relationships existing in systems consisting of soybean oil and such liquids have been investigated for a large number of selective solvents, and there are many methods used for depicting the data graphically. The triangular phase diagram is a common one. A typical example is shown in Figure 2,

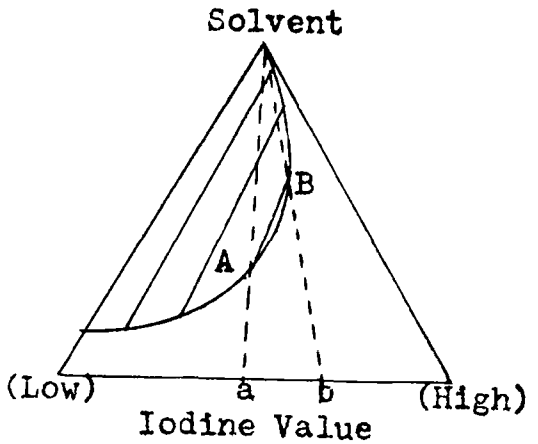


FIG. 2. Triangular representation of phase relationships.

in which the upper apex represents 100% selective solvent and the base line represents iodine value, ranging from low values at the left to high values at the right.

The area within the curved line represents the region of two-liquid immiscibility, and the compositions of raffinates and extracts in equilibrium with each other are represented by the ends of tie-lines, such as points A and B, which are for the raffinate and extract respectively. By projecting these points from the solvent apex to the base line, it is possible to determine the iodine value of the oils in these two phases, as shown by points a and b. The selectivity of a given solvent can be judged approximately by the difference in iodine number represented by these two points, which is, as a matter of fact, the difference

in iodine value obtained when soybean oil is subjected to a single batch extraction in a separatory funnel, followed by isolation of the oil content in the resulting phases. In the case of furfural this difference is about 14 units. Sulfur dioxide is more selective, and propane is less selective with respect to unsaturation.

The difference in iodine value, or in some analogous characteristic, between the oil in two phases at equilibrium frequently is called the "driving force" since it is the tendency of the system to approach these equilibrium conditions which causes the fractionating device to function. The driving force exists in all the systems which can be used for fractionation. In liquid-liquid extraction it is the difference in composition between the respective portions of the material being fractionated when they exist at equilibrium in two conjugate liquid phases. In crystallization it is the difference between the compositions of the crystals and the material dissolved in the solvent in equilibrium therewith. In distillation it is the difference in composition between a liquid and the vapor in equilibrium with it.

Application of Liquid-Liquid Extraction as a Laboratory Tool

The method of applying liquid-liquid extraction and some of its fundamental principles can be illustrated by drawing an analogy between this process and distillation. There are two types of rectification used for separating, by distillation, mixtures of liquids having boiling points not far apart. One of these is continuous rectification, by which process a continuous stream of raw material is fed into some point intermediate between the top and bottom of a rectifying column. A distillate is condensed at the top and in part returned as reflux, and a stream of stillbottoms is withdrawn beneath the column. The other is known as "batch fractional distillation" and consists in the removal, fraction by fraction, of the progressively less volatile components of a mixture of liquids. The liquids are contained in a distillation flask, which is surmounted by a fractionating column, with some arrangement for effecting reflux at the top.

There is an interesting analogy between continuous rectification by distillation and continuous fractionation by liquid-liquid extraction. In Figure 3 the right-hand diagram is the simplified flow sheet of a continuous rectification column in which raw material, such as stock for the production of gasoline, is introduced at some point intermediate between the top and bottom of a fractionating column. Heat is applied at the bottom, and vapors leave at the top to be condensed by the removal of heat. The condensate is divided into two streams, one of which is the distillate, and the other is returned to the top of the column as reflux. This liquid percolates downward through the column in close contact with the rising stream of vapors so that the gas and liquid phases can interchange their respective heats of vaporization or condensation, and the process results in the enrichment of the overhead stream with respect to the lower boiling constituents. The high-boiling materials are withdrawn at the bottom.

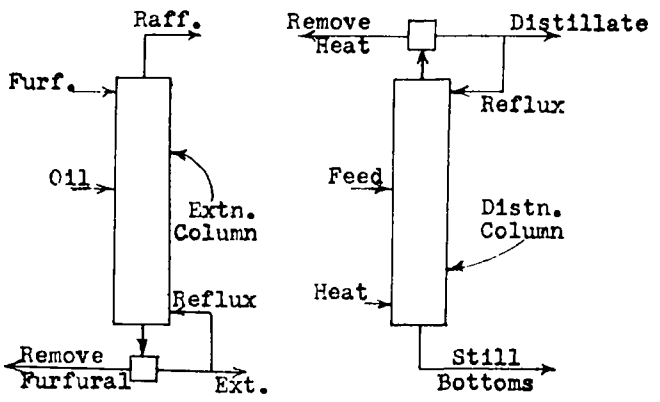


FIG. 3. Analogy between continuous liquid-liquid extraction, with reflux, and continuous rectification.

The left-hand diagram in Figure 3 is the exact analogy in liquid-liquid extraction as applied to the continuous fractionation of fats and oils by means of furfural. The raw material, namely, a vegetable oil such as soybean oil, is introduced into a vertical fractionating column at some point between the top and bottom. In this case however the apparatus is upside down from that shown in the right-hand side of the diagram applying to distillation. Instead of introducing heat at the bottom of the column, as in distillation, furfural is fed at the top of the liquid-liquid extraction column, and it runs downward counter-currently to a rising stream of oil. The oil and furfural are only partially miscible, and the latter is considerably the more dense. The furfural dissolves part of the oil, converting it from the undissolved state, much as heat converts hydrocarbons from the liquid to the vapor state in the case of fractionating hydrocarbons by distillation.

At the bottom of the liquid-liquid extraction column the furfural is withdrawn containing an appreciable quantity of dissolved oil, the furfural is separated from the oil in evaporating equipment, in a manner quite analogous to the removal of heat from the overhead vapors in the case of distillation, and the resulting oil is divided into two streams, one of which is known as the "extract." The other part is returned to the base of the column as reflux, just as a part of the distillate is returned at the top in distillation. The undissolved portion of the oil, which is known as "raffinate," is withdrawn at the top of the extraction column.

Only a few of the points of direct analogy between liquid-liquid extraction and distillation have been mentioned and shown in Figure 3, but practically every detail encountered in the operation of an extraction column can be compared directly with its analogue in distillation; and the latter field has been subjected to much more thorough study from an engineering standpoint than has extraction. For this reason it frequently is desirable, when contemplating some new problem encountered in liquid-liquid extraction, to ascertain how the corresponding situation is dealt with in distillation. Such reasoning invariably leads to a proper solution of the extraction problem.

The analogy between distillation and extraction can be carried further, especially its application to batch operation, and leads to the consideration of interesting possibilities for employing extraction as a laboratory tool. Figure 4 is similar to Figure 3 except that the arrangements of extraction and distillation equipment, shown diagrammatically, are

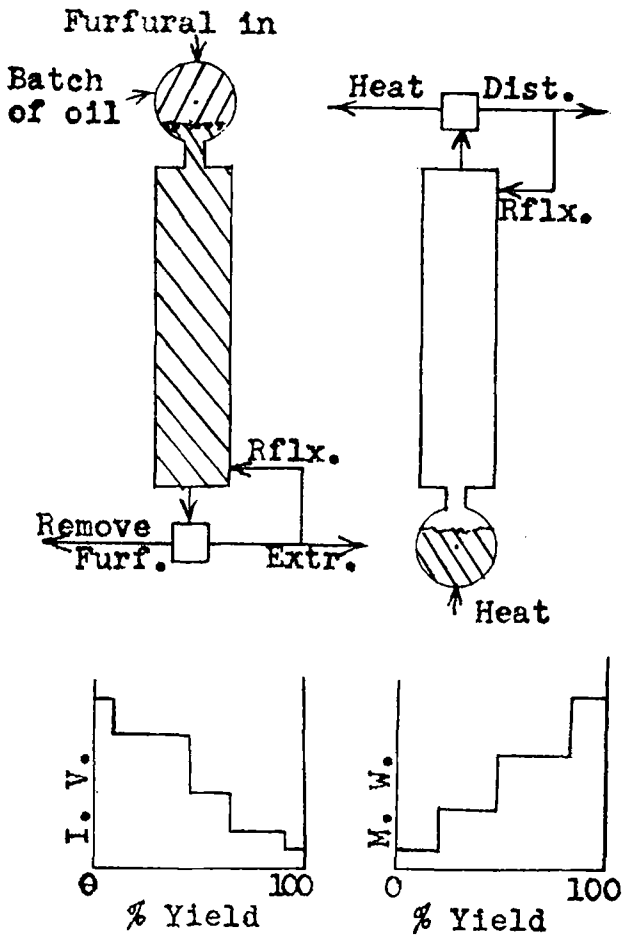


FIG. 4. Analogy between exhaustive batch extraction and exhaustive rectification, with plots of typical yields.

designed for the exhaustive batch distillation or extraction of a definite quantity of material to be fractionated. The right-hand side of the drawing is a sketch of a laboratory distillation apparatus, consisting of a boiling flask containing the test material, a fractionating column having a large number of theoretical plates, and an overhead condenser equipped for returning part or all of the condensate as reflux. Such apparatus is commonly used for separating complex mixtures of hydrocarbons. The batch to be fractionated is placed in the boiling flask, and heat is applied. This causes some of the hydrocarbons to evaporate, and the vapors rise through a fractionating column, eventually reaching the condenser. Here the heat is removed, and the resulting liquid is allowed to run back into the top of the column.

The apparatus is operated initially at total reflux, that is, all the condensate is returned, and this type of operation is continued until a steady state has been reached. At this time the temperature of the vapors leaving the top of the column will have become constant and will be equal to the boiling point of the most volatile component of the mixture being separated. A small stream of the condensate then is withdrawn continuously, but it is only a minor fraction of that actually being condensed. This withdrawal may be continued until all the most volatile constituents have been distilled, and at that time the distillation comes to a halt or at least becomes very much slower. Then it becomes necessary to apply heat at a faster rate and to return the apparatus to total, or nearly total, reflux until the temperature of the vapor at the top of the column again becomes steady at the boiling point of the next most volatile component, which then can likewise be removed by withdrawing a small stream of product.

If the operations outlined above are continued until essentially all the hydrocarbons have been distilled, the results can be plotted in the manner shown beneath the diagram of the distillation apparatus. Some property, such as molecular weight, can be plotted as ordinates against the percentage yield of each fraction, and the result usually is a step-wise curve such as that shown although in many cases the breaks between steps are not as sharp. Each step represents the yield of one particular compound resulting from the separation of the mixture into its components.

In the left-hand side of Figure 4 is shown the exact analogy to exhaustive batch distillation when liquid-liquid extraction is used for fractionating a mixture. In this instance too the liquid-liquid extraction apparatus is upside down as compared to the distillation equipment because the solvent chosen for the illustration is heavier than oil.

If it were not for complications due to the presence of some C_{16} acid, it should be possible with this apparatus to separate soybean oil into rather pure fractions differing from each other in the number of double bonds in each molecule, and such separations actually have been made with limited success (6). In such operation the charge of oil, being lighter than furfural, is allowed to float on the surface of the solvent in the flask or other vessel shown surmounting the extraction column, which latter is filled with solvent up to the level of the oil. Instead of heat being applied at the bottom, as in distillation, furfural is introduced at the top as shown in the diagram. It passes downward through the oil, dissolving a certain quantity, and eventually passes out the bottom of the column where the furfural is removed from the dissolved oil. The resulting extract is returned as total reflux for a considerable time, that is, until its iodine value becomes constant. If the fractionating column has a sufficient number of stages, the iodine value of such recirculated glycerides then will be that of the most unsaturated component of the mixture, and it will be possible to withdraw a small stream of this product exactly as is done in distillation.

After all of this component has been exhausted, it will be found that little or no oil is dissolved in the furfural leaving the bottom of the extraction column, and it will be necessary to increase the rate of introducing furfural, just as it became necessary to increase the rate of heating in distillation. If the liquid-liquid extraction column continues to operate at this higher furfural rate, with all extract again being returned as reflux, equilibrium will be reached again, with the iodine value of the reflux equalling that of the next most unsaturated component of the mixture. This component then can be removed by withdrawing a small stream of extract while maintaining a high reflux ratio.

Continuing this process until all the oil shown in the container at the top has been selectively extracted will yield results which can be plotted in the form shown beneath the diagram of the extraction apparatus. The iodine value of each fraction can be plotted

against the percentage in which that portion exists in the complete mixture. A step-wise curve should be obtained, much the same as when distillation is used to separate materials having different molecular weights over different boiling points.

The preceding method for conducting an exhaustive batch fractionation by means of liquid-liquid extraction has been applied occasionally in various laboratories to separate mixtures of hydrocarbons and of other materials which are not readily separable by means of distillation. The field of fats and oils is an excellent example of one in which a fractionating tool such as this should find wide application for it offers the possibility of separating materials which cannot be fractionated by any other method without extreme difficulty.

Crystallization

It is of further interest to reflect briefly on some of the insufficiently exploited possibilities of crystallization as a tool for making exact separations of various fatty materials. Nearly all crystallization procedures described in the literature on fats and oils utilize only one stage of separation, that is, the actual separation is made between a solid and a liquid in equilibrium with each other. This is quite analogous to a single batch distillation, in which the vapor evolved is in equilibrium with the liquid remaining behind. In the case of distillation, as was pointed out earlier, the driving force, or the difference in composition between the liquid and vapor, can be amplified many times by conducting the process in such a manner that the two phases flow countercurrently past each other with reflux, interchanging their respective latent heats while various components of the mixture pass from one phase into the other. The same should be possible in crystallization, but the mechanical details necessary in order to carry out such a process appear to have received little, if any, study.

In the case of liquid-liquid extraction it was noted that the maximum separation between extract and raffinate in equilibrium with each other when furfural is the selective solvent amounts to only 14 units in iodine value. Under analogous conditions, if crystallization is used as a separating means, the difference in iodine value at equilibrium may amount to as much as 50 or 60, or even 80, units. If such tremendous driving forces could be amplified many-fold, as is done in numerous applications of extraction and distillation, it can be seen clearly that separations between closely similar materials could be accomplished far more efficiently than with any of the procedures now available.

Conclusion

The preceding example of a little-explored portion of the fractionation field is simply one of many that could be cited to illustrate both the possibilities for developing fractionation processes in the vegetable oil industry and the future that awaits some of the now undeveloped processes for effecting segregation. Because of the extremely mixed nature of triglycerides as they occur in nature, it is necessary to make separations of many types, both in the laboratory and in commercial operation, and it behooves specialists in the oil field to study the science of fractionation and enhance its usefulness toward accomplishing their needs.

REFERENCES

1. Anonymous, "Prescription for Glycerides," The M. W. Kellogg Company, New York (1946).

2. Demmerle, Richard L., "Emersol Process," Ind. Eng. Chem. *39*, 126-131 (1947).

3. Freeman, Stephen E., U. S. 2,200-390-1 (1940).

4. Gloyer, S. W., "Furans in Vegetable Oil Refining," Ind. Eng. Chem. *40*, 228-236 (1948).

5. Kenyon, Richard L., Gloyer, S. W., and Georgian, C. C., "Selective Extraction of Vegetable Oils with Furfural," Ind. Eng. Chem. *40*, 1162-1170 (1948).

6. Unpublished experiments conducted at the Northern Regional Research Laboratory, Bureau of Agricultural and Industrial Chemistry, United States Department of Agriculture, Peoria, Illinois.

The Nutritive Value of the Residues from Oil Extractions

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WHILE this short course is primarily concerned with the production, processing, and refining of edible oils, I don't think it's inappropriate that we inject a brief discussion on the values of the residues that may be left on the removal of the oils and fats from either the fat-rich plant materials, or animal materials. I suppose most of you think of the oils and fats as your prime product of the industry, and I suppose that's correct. If the price of fats continue to come down, I'm not so sure but what some of these so-called by-products might not become the product of your industry, and oils might become the by-product. At least your processing procedures do affect, or may affect, the value of these protein rich residues which are left. Now this evening we shall confine our discussion almost entirely to the nutritive value of some of these protein rich by-products.

T. S. Hamilton

You know, most industries do depend, or at least much of the profits of many industries do depend, to a large extent, on the value of these so called by-products, so anything in the way of processing which might affect the value of these by-products should be at least considered. Most of these residues from the removal of the oil from the oil-bearing seeds, or the removal of the fats from the fat rich animal tissues are rich in protein, usually quite low in carbohydrates, low in fiber, and many of them, also, quite low in ash. So we can think of them, then, primarily as protein supplements, or protein rich products. They find their greatest use, of course, in supplementing the protein-low feeds that are ordinarily grown on the farm.

If we think for a moment that for a rapidly growing animal, or for high-producing cows or chickens, the protein content of those rations should be somewhere in the neighborhood of eighteen or twenty per cent in order that they may produce as rapidly, or grow as rapidly as we would like. Now, farm grown feeds do not contain twenty per cent protein. Number 2 corn today contains on an average of about 8½ per cent protein. Some of our other small cereal grains may go as high as 12, still, that's far from 20. Our young, rapidly growing pasture on a dry basis may go as high as 20 or 25 or 30 per cent; but under natural conditions, of course, those are diluted to such an extent, that, on a fresh basis, these are of pretty low protein content. Only the ruminants can consume enough pasturage to obtain all of their protein from such diluted material. The straws and hays contain about 12 per cent, on down to 4 or 5 or 6, depending on the quality and the kind. So, farm grown ingredients for our rations, must be supplemented if we are to have a ration containing 18 or 20 per cent protein.

So we depend, to a very large extent, upon these protein supplements from your industry. We never have had enough protein supplements to balance our farm grown feeds, that is, to bring them up to the 18 or 20 per cent which we think are desirable for rapidly growing and high producing animals. Last year, we came more nearly balancing our protein low, farm grown feeds with protein from the protein supplements sources, than any year previously. I think we're still shy about 7 per cent or something like that, but, nevertheless, we almost balanced our rations with the protein supplements which were available from all sources.

We know, of course, that these residues vary in their total protein content. The protein supplements from plant sources vary perhaps from, we'll say, 34 per cent in some linseed oil meals, to as high as 55 per cent for a completely extracted sunflower seed meal. In the case of protein supplements of animal origin, they may be as low as 50 or 55 per cent for meat and bone scraps to 80 per cent for blood meal, and special preparations may go to 90 or even 95 per cent protein. So they differ, in the first place, quantitively, that is, in their total protein, and when I say protein, I usually think of total nitrogen multiplied by six and a quarter.

From the nutritive point of view, that's a perfectly satisfactory way of figuring out the protein of supplements, for the protein supplements that are manufactured in the body average about 16 per cent protein. In other words, we're thinking of nitrogen rather than any particular form of protein. So, from that point of view, the factor which best relates the nitrogen to the total protein of the body, is perhaps the best factor to use when thinking in terms of nutrition. Now, of course, if you want to characterize a protein chemically and physically, then you should use the factor which best relates its nitrogen content to its total protein value. But in nutrition we simply say crude protein, or total protein, or most of the time we simply say protein, and in doing so, we are thinking of total nitrogen multiplied by a conventional factor of six and a quarter.

But these supplements differ not only with respect to their total protein value, which may vary from 34 to 90 to 95 per cent, but they also differ in quality or biological value. When we say quality, or when we say biological value, we think of the extent to which the protein furnishes the amino acids which the body needs, in the proper proportions. The more nearly the protein source furnishes the amino acids which the body needs, the more completely will it be utilized. That is what we mean by a high quality or a high biological value protein.

Proteins, of course, are made up of amino acids. Most of the proteins that we know of contain anywhere from 14 or 15 up to 21 or 22 different amino acids. If we analyze proteins found in the animal bodies, we will find that most of those proteins contain 21 or 22 amino acids. In other words, they contain most all of the amino acids, yet these proteins may contain amino acids in different proportions. In the plant kingdom, we have exactly the same thing. We have the possibility of making innumerable proteins simply because we have anywhere from 2 to as many as 22 different amino acids combined in any mathematical proportion that you might conceive. If you're mathematically inclined, you might set down some time and see how many different proteins would be possible. That is the reason why we have so many, many different kinds of protein.

Now, in the body, we have proteins, many different kinds of protein, yet they contain most of the different amino acids, 20, 21, 22. Yet the animal body cannot synthesize all of these amino acids. It must depend upon some outside source. Fortunately, the plant cells and fortunately too, many microorganisms can synthesize from simple nitrogen sources, and with some source of carbohydrate or energy, all 22 of them. Plant cells, and many micro-organisms, can do that. The animal body needs all 22, and yet the higher forms of animal cells cannot synthesize but about nine or 10 of them. They synthesize those nine or 10, of course, from the others which are supplied to them.

Now, the amino acids which the body cannot synthesize are referred to as essential amino acids. The other 9 or 10 or 11 the body can synthesize, apparently at very rapid rates, so that if the essential amino acids are supplied the animal, the animal can take care of his needs by synthesizing the others. Those amino acids which the body can synthesize are referred to as non-essential. So, we depend upon the plant kingdom very largely, occasionally upon the micro-organisms, for the synthesis of the essential amino acids.

We find then, that proteins may differ in two respects: they may differ quantatively in the total percentage of protein which they furnish, and qualitatively, that is, depending on their biological value. Protein supplements, therefore, may have exactly the same total protein concentration and yet may differ markedly in their quality. Therefore, so far as satisfying the animals needs, the total protein is of very little value. It is the quality of the protein as well as the total protein which counts.

Referring again to the proteins which the animal deposits in its tissues, while we find a rather complex mixture of 21 or 22 different amino acids, protein supplements of animal origin are often deficient in one or more amino acids. The amino acids which usually limit the usefulness of animal proteins for feeding purposes are methionine and cystine. In the plant kingdom, it is not methionine and cystine that ordinarily limit the usefulness of its protein supplements, but some other amino acids, usually it's lysine. Now, there's usually plenty of lysine or at least an adequate amount in animal products, but there is a deficiency of the sulphur-bearing amino acids, methionine and cystine. So, when we mix animal proteins with plant proteins, the deficiency of the sulphur-bearing amino acids in the animal proteins will be made up by the slight excess which occurs in the plant proteins, and the deficiency of lysine, which ordinarily occurs in the plant proteins, is made up for by a slight excess of lysine in the animal proteins.

I don't think it's any coincidence that man, who for the most part has had the choice of the foods which he eats, has become accustomed to eat such combinations as an egg and a bread sandwich, animal protein and a plant protein. They supplement each other very well. Bread and milk, steak and potatoes, fried chicken and french fries, corned beef and cabbage, or even ham on rye with a bottle of beer. I don't think it's mere coincidence that we enjoy these combinations. The supplementing effect of these proteins have been found to be good for us.

Unfortunately, our animals today don't have the choice that man has in selecting their feed. He doesn't have the chance to combine the animal proteins with the plant proteins such as we are accustomed to do, so it's up to us to supply the proper combination to our animals if we expect them to do well.

I think the best way of illustrating the supplementing effect of different supplements would be to show you by means of slides, the extent to which some of these common protein supplements supplement corn. Now, corn is our basic carbohydrate for this locality, and we will use as much corn as possible. So fifty or sixty parts of the ration will be made up of corn. Now, that's not going to furnish over five per cent; the rest of the 20 per cent protein then must come from our protein supplements. Now, while we would not recommend a mixture of just corn and one protein supplement, they will serve as illustrations. I have used 60 per cent corn, and then, sufficient amount of various protein supplements to bring the total protein in the ration up to 20. That's not a good ration, but, nevertheless, I think it will illustrate the extent to which these various proteins, as we know them today, may supplement corn.

On the left-hand side of the slides are figures which indicate per cent. A hundred would indicate when these ten different essential amino acids satisfied the requirement of a growing chick. We know pretty well how much, on a percentage basis, of each these ten amino acids, is needed in a ration to completely satisfy, without excess, the amino acid requirements of a growing chicken. The abbreviations at the bottom indicate arginine, histidine, isoleucine, leucine, lysine, threonine, tryptophane, valine, methionine, plus cystine are combined, because the animal body can convert methionine into cystine, and phenylalanine plus tyrosine, since the body can convert plenylalanine into tyrosine.

The shaded portion of the graph indicate the extent to which 60 per cent corn in a ration would meet the requirements for these essential amino acids. Now, notice in the case of arginine that the corn would supply only 35 per cent of the arginine required by the chicken; would supply 65 per cent of the histidine, 13 per cent of the lysine needed and so on across. The corn is quite deficient in lysine and tryptophane. Now, I've added to this ration a sufficient amount of various protein supplements to bring the total protein in the ration up to 20 per cent. No more than that. It's just about as bad to have certain excesses as it is to have deficiencies, and to meet some of the requirements of our animals today, part of our problem is to minimize the excess.