Refining and Fractionating Soybean Oil With Furfural"

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~-]-~l IE p r " oductmn of fully refined soya oil fractions from crude degummed oil by means of liquidliquid fractionation has been accomplished using furfural as the selective polar solvent. It has been known for some time $(1, 2)$ that glyceride oils may be fractionated on the basis of unsaturation within the glyeeride molecule by means of partially miscible, selective, polar solvents. More recently a process has been developed employing these principles for not only fractionating soya oil into a drying oil but also for preparing a fully refined raffinate for food oil purposes.

Fraetionating and refining of soya oil by means of liquid-liquid techniques with furfural is dependent upon the fact that the oil is not completely miscible with the solvent at normal temperatures. Therefore, when crude or degummed soya oil is contacted with furfura] below the temperature of miscibility two fractions are obtained. The raffinate or oil predominant phase has concentrated in it the more saturated glycerides and the break constituents with the more unsaturated glycerides, free fatty acids, chlorophyll, other pigments, and unsaponifiable constituents concentrating in the furfural predominant extract phase. Although it is impossible to obtain effective separations in a single batch extraction, very remarkable fractionations have been obtained by employing continuous countercurrent extraction with the use of reflux.

In order to clarify the operation of refining and fractionating in continuous countercurrent columns, a simplified drawing is shown in Figure 1.

Furfural in a ratio of three to five parts per part of feed oil is fed into the top of the primary column. I)egummed soya oil is introduced at an intermediate point between the furfural feed and the reflux posi-

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tion and reflux is introduced near the bottom portion of the column. The reflux medium may be extract product oil, naphtha or a combination of naphtha and extract product oil.

The raffinate solution or food oil fraction passes out the top of the primary column to evaporators and strippers opcrating under vacuum for the eomplete removal of solvent. This raffinate or food oil fraction has removed from it the free fatty acids, chlorophyll, and other natural pigments. The break constituents present in the feed oil are concentrated in the raffinate and are fully removed from it by a special inexpensive method, the details of which cannot be disclosed at this time. This rafflnate is a fully refned oil and may be hydrogenated directly without any further refining.

The more unsaturated glycerides, free fatty acids, chlorophyll, carotene and other natural pigments, unsaponifiable constituents, and traces of break material are concentrated in the furfural extract fraction obtained in the primary eolunm. This extraet solution may be distilled if desired for the removal of solvent, however, the resulting extract oil will then be quite dark and have concentrated in it the free fatty acids present in the original oil.

It has been found that the major portion of the free fatty acids, chlorophyll and other natural pigments, unsaponifiable matter, and traces of furfural soluble break constituents can be removed from the more unsaturated glycerides by eountercurrently extracting the extract solution from the primary column with naphtha in a secondary column. The naphtha generally used for this secondary extraction, as well as for a reflux medium in the primary column, is a high flash V . M . and P . naphtha with a boiling range of 145° C. to 185° C. The solvent is removed from this naphtha extract fraction, leaving a break free, high iodine value paint oil fraction of good color and low free fatty acid content. This prodnet is a varnish grade oil and may be used directly in the varnish kettle withont further refining.

The furfural solution obtained from the bottom of the secondary column yields on distillation a blaek by-product amounting to 0.5 to 1.0% of the feed oil. This by-produet is a concentration of the free fatty aeids, coloring pigments, and unsaponifiable matter.

Experimental Data

Fractionation of the Oil. In any solvent refining process one of the major costs of operation is that of steam and water required for solvent removal and recovery. The quantity of steam required per pound of feed oil is in direct proportion to the solvent ratio employed and likewise the quantity of condenser water required is in direct proportion to the solvent ratio. A large reduction in solvent ratio will therefore result in considerably reduced cost of operation.

The fractionation of soya oil at solvent ratios of 6 to 14 parts per part of feed oil has been previously reported (3). This present report is limited to the results obtained in fractionating degummed soya oil with furfural in amounts varying from 3 parts to 5 parts per part of feed oil. At these low solvent ratios and at the relatively low yields of extract or paint oil fraction obtained, it is possible effectively to use naphtha alone as a reflux medium. As such it is used in the range of .2 to .3 parts per part of feed oil wheu low solvent ratio fractionations are employed. The results obtained at 3 to 1, 4 to 1, and 5 to 1 solvent ratios, when fractionating soya oil in a commercial plant, arc shown in Table I. In this plant the primary extraction column was 22 inches in diameter and 87 feet high, the packing being onehalf inch Berl saddles.

It will be observed in Table I that although the iodine values of the three extract fractions are maintained relatively constant at all three solvent ratios, the iodine value of the raffinate decreases with an increase in extract yield.

The above fractionations at 3 to 1, 4 to 1, and 5 to 1 solvent ratio were conducted on solvent extracted degummed soya oil. These runs were made on a series of tank cars from one producer and all cars had relatively the same physical constants. The physical constants of the feed oils used are given in Table II.

TABLE II Solvent Extracted Degummed Feed Oil **Used**

	3 to 1		5 to 1
		4 to 1	
	135.7	135.1	135.1
	0.49	0.43	0.43
% Unsaponifiable Matter	162	1.37	1.37
	70	70	70
	13.5	13.6	13.6
	0.00020	0.00018	0.00018
	0.0052	0.0051	0.0051

Since the above feed oils have essentially the same constants the products produced at the varying solvent ratios may be compared to determine the effect of solvent ratio on the product.

Extract. The iodine value of the extracts produced at all three solvent ratios was essentially the same. The composition of these extracts as determined by the alkali isomerization procedurc (4, 5) is shown in Table III. The method used was the tentative procedure sent out to collaborators by the 1948 Spectroscopy Committee of the American Oil Chemists' Society.

~The per cent saturated acids determined by the alkali isomerization procedure includes the unsaponifiable matter.

An examination of the results listed in Table III show that the compositions of extracts of similar iodine value are essentially similar even though produced at different yields.

A comparison of the composition of a feed oil with that of the extract is given in Table IV.

¹The per cent saturated acids determined by the alkali isomerization procedure includes the unsaponiflable matter.

From Table IV it is noted that the extract fraction contains approximately 11% more drying acids than the feed oil and has had removed from it a similar amount of non-drying oleic and saturated acids.

Bodying Rate of Extract. The time required for each of the soya extracts produced at 3 to 1, 4 to 1, and 5 to 1 solvent ratios to reach a Gardner-Holt $Z₁$ body was determined under very carefully controlled conditions. The cqnipment used was a 13-gallon closed stainless steel kettle, equipped with agitator, an inert gas feed, and a 2-inch vent connected to a suction venting fan. IIeat was applied to the kettle by means of electric strip heaters which were controlled by a Variac transformer. The temperature was continuously recorded on an automatic recording instrument so that at the end of the run a time-temperature record was permanently available. This permanent record gave assurance that the bodying was carried out at a constant temperature throughout the run. The bubbling of inert gas in the oil during bodying and venting the kettle to a suction fan made possible the production of bodied oils having acid values and bodying losses comparable to larger scale commercial operations. In all runs a bodying temperature of 575° W. was used and 0.2 cu. ft./min. of inert gas was bubbled through the sixty-pound charge.

The properties and the time required to prepare each of these bodied extract oils is given in Table V.

Uncatalyzed soya extract required about 3 to $3\frac{1}{2}$ hours more time to reach a Z_4 body than a refined and bleached linseed oil. Although more time is required for the cooking, the color of the final bodied oil in the case of extracts produced at 4 to 1 and 5 to 1 solvent ratios is equivalent to alkali refined and bleached linseed oil. The color of the extract produced at 3 to 1 solvent ratio is somewhat darker, probably due to a greater concentration of natural pigments in the original extract. The acid value of the bodied uncatalyzed extract is somewhat higher than that of the linseed due to the longer cooking time required. The bodying rates of the extracts of similar iodine value are shown to be essentially the same even though these extracts are produced at different yields.

A sample of the soya extract and an alkali refined and bleached whole soya oil were catalyzed with 0.25% beta methyl anthraquinone (6) and their bodying rates to Z_4 viscosity compared with alkali refined linseed oil as well as alkali refined and bleached linseed oil. These rates arc shown in Table VI.

¹Alkali refined.
²Alkali refined and bleached.

An examination of Table VI shows that soya extract catalyzed wilh 0.25% beta methyl anthraquinone bodies to Z, viscosity from 2 to 3 hours faster than uncatalyzed linseed oil and approximately $3\frac{1}{2}$ hours faster than whole soya oil catalyzed with an equivalent amount of beta methyl anthraquinone.

Drying of Extract Oil. The comparison of drying rates of various oils when testing clear films with added drier gave results which were not reproducible due to difficulty in obtaining uniform film thickness with clear oils. In order to obtain results which would show the true drying characteristic of the oil in question, a test was devised whereby the oil was ground with a single pigment, rutile titanium dioxide, and thinned with solvent and drier. The drying results obtained by this simple grind showed differences in oils not perceptible in the clear oil films and also the drying rates obtained were in better correlation with complete paint formulations.

This one pigment paint was ground on a laboratory stone mill, using the following proportions:

The above proportions of pigment, oil, and thinner were mixed together and then ground to give a stock paste. To 40 grams of the ground stock paste there was added 1.75 grams of a drier in naphtha solvent consisting of 3.15% lead and 0.6% manganese as naphthenatcs. The final stock after the addition of drier had the following specifications:

> 0.42% lead on basis of oil, 0.08% manganese on basis of oil, 27.0 % *pigment* volume *concentration,* 4.0 lb. oil per gallon.

It is emphasized again that the above mixture is not to be considered a complete paint formulation but merely a means of checking the drying characteristics of oils.

Soya extracts produced at 3 to 1, 4 to 1, and 5 to 1 solvent ratios, crude and alkali refined linseed oil as well as crude and alkali refined soya oil were ground into a single pigment paint as described above. These paints were all ground on the same mill under identical grinding conditions.

In order to obtain comparative drying results the drier was added to all paints at the same time and they were then applied on glass panels with a Bird Applicator to a film thickness of .0015 inch. The paints were allowed to dry under room temperature conditions of approximately 80 to 85° F. The time required for these one-pigment paints to set to touch was then noted and in this manner it was possible to obtain comparative drying rate of soya extract with linseed oil as well as with whole soya oil. The results of these drying tests are given in Table VII and it will be noted that the soya extract and crude linseed oil set to touch in essentially the same time.

In addition to the above drying tests the soya extract has been formulated into complete paints and found to be equivalent to linseed oil in drying and durability. Exposure panels as well as test houses formulated into outside white honse paints show the paint prepared from 100% soya extract to be equivalent in respect to durability, dirt collecting, and color retention to that prepared from linseed oil. After a two-year period test honses located in industrial areas show the dirt collection of linseed oil paint and soya extract paint to be about equal.

Conclusions Regarding Extract. From the evidence presented above it has been concluded that degummed soya oil may be inexpensively refined at relatively low furfural to oil ratios so as to yield an extract fraction which is a varnish grade, break free oil and which is equivalent to linseed oil in drying.

Raffinate. The sova raffinate or food oil fraction drawn off the top of the primary fraetionation column is lower in iodine value and free fatty acid content than the feed oil. In addition to the removal of free fatty acids, there has also been the removal of objectional natural pigments from the oil. The break constituents which have been concentrated in the raffinate are removed by a simple inexpensive method, the details of which cannot be disclosed at this time.

A comparison of the properties of rafflnates produced at 3 to 1, 4 to 1, and 5 to 1 solvent ratios with their corresponding feed stock is given in Table VIII.

TABLE VIII Properties of Feed Oil and Roffinates

	3 to 1		4 to 1		5 to 1	
	Feed	Raffinate		Feed Raffinate	Feed	. Ra¶inate
Iodine Value % Free Fatty	135.7	132.3	135.1	1128.5	135.1	125.0
$Acid$	0.49	0.061	0.43	0.037	0.43	0.044
Lovibond Red	13.5	1.8	13.6	1.7	13.6	1.7
Lovibond Yellow	70	18	70	20	70	17
Gardner Break Positive Negative Positive Negative Positive Negative						

An approximation of the carotenoid pigments was made from a spectrophotometric curve of the oil in cyclohexane solution. The oil showed an absorption maximum at 4,480 to 4,500 Angstrom units. The carotenoid pigments are expressed as per cent betacarotene. It was felt that such a method was suffieiently accurate to compare the relative quantities of earotenoid pigments in the raffinate and feed stocks.

In order to determine the approximate amount of chlorophyll present in the feed stock and the raffinate oil a spectrophotometric curve of the oils undiluted by solvent was determined. Maximum absorption was obtained in the range of 6,500 to 6,800 Λ ngstrom units. When maximum absorption was obtained at 6,700 Angstroms, calculations were made on the basis of chlorophyll-a, and when maximum absorption was obtained at 6,525 Angstroms the calculations were made on the basis of chlorophyll-b (7). The amount of chlorophyll shown in Table IX is the total calculated chlorophyll present in the sample. This analysis showed that 95.5% of the chlorophyll was removed by the solvent process at 3 to 1 ratio, 97.2% at 4 to 1 ratio, and 98.4% at 5 to 1 ratio. The amount of chlorophyll present in the feed oil and the raffinate is shown in Table IX.

TABLE 1X Chlorophyll Content of Feed Oils and Raffinates

Feed	Raffinate		
.0002	.000009		
	95.5 .00001		
	99.8		
4 to 1			
Feed	Raffinate		
.00018	.000005		
	97.2 .00003		
	99.4		
5 to 1			
Feed	Raffinate		
.00018	.000003		
	98.4		
	.00003 99.4		
	.0052 .0051 .0051		

The sova raffinate or refined food oil fraction is somewhat similar to alkali refined and bleached soya oil in its properties. These properties are compared in Table X to those of a commercially available refined and bleached soya oil as well as to a sample of solvent extracted degummed oil which was refined and bleached in the laboratory.

¹The original oil used was the same as used in preparing the 4 to 1 solvent ratio raffinate.

The solvent refined oil is comparable to alkali refined in respect to free fatty acid content as well as chlorophyll and carotene content. Pigments other than chlorophyll or carotene are likewise removed by the Molecular Selection process as evidenced by the lower Lovibond red color obtained. This lower Lovibond red color is probably obtained due to solubility of some red or brown pigment in the furfural predominant fraction.

The three refined oils listed in Table X were given a laboratory hydrogenation and deodorization to determine the processing characteristics and final color of a melted shortening. Hydrogenation was at 30 lb. pressure, 300° F., in the presence of 0.11% active nickel (used as Raney nickel catalyst). Hydrogenation rates were comparable for a 1-liter batch charge of oil. Deodorization was accomplished in all-glass equipment at 200°C. and 1 mm. absolute pressure. The results obtained by hydrogenating and deodorizing these samples are given in Table XI. The properties of two well-known commercially available shortenings are likewise listed in this table for the purpose of comparison.

From Table XI it can be observed that the rate of hydrogenation of the solvent refined oil is comparable to that of the alkali refined. The color of the final hydrogenated and deodorized oil is considerably better than the alkali refined oil or the commercial shortenings. The reason for this improved color of final hydrogenated and deodorized product is undoubtedly due to the removal of pigments in solvent refining of the oil which are not removed by alkali refining.

The composition of the raffinates produced at 3 to 1, 4 to 1, and 5 to 1 solvent ratios is given in Table XII. These compositions were determined by the method of alkali isomerization using the Beckman Spectrophotometer.

procedure includes the unsaponifiable matter.

The above three raffinates do not differ too greatly in composition despite the fact that there is some slight change in iodine value. The best comparison to show the trend in change of composition is between the raffinate produced at 3 to 1 ratio having an iodine value of 132.6 and that produced at 5 to 1 ratio having an iodine value of 125.6. The raffinate of 125.6 iodine value has a lower linolenic and linoleic acid content and a higher oleic and saturated acid content than the 132.6 iodine value fraction as is to be expected.

A comparison of the composition of the raffinate produced at 5 to 1 solvent ratio with that of the feed oil from which it was produced is given in Table XIII.

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A raffinate having an iodine value approximately 10 units lower than that of the feed oil shows appreciable reduction in the linolenic and linoleic acid content over that of the feed oil. The relatively high drying acid content still remaining in this raffinate helps to explain why it is possible through more efficient methods to fractionate sova oil into 70% extract of 153 iodine value and 30% raffinate of 95 iodine value (3). In order to operate in this manner higher solvent ratios are required and the cost of operation per pound of oil processed is increased somewhat due to increased steam and water consumption.

¹The per cent saturated acids determined by the alkali isomerization procedure includes the unsaponifiable matter.

Conclusions Regarding Raffinate. It has been found possible to fully refine crude degummed soya oil at relatively low solvent ratios to produce fractions which hydrogenate as rapidly as alkali refined oil and which on deodorization yields a product of improved color. Operations at low solvent ratio enable the process to produce a drying oil fraction and at the same time be competitive with alkali refining in respect to cost of operation.

Soya By-Product. The by-product produced at three solvent ratios was uniform in yield and in composition. This composition is given in Table XIV.

From the composition given in Table XIV it can be seen that the by-product is a concentration of free fatty acids, coloring matter, and unsaponifiable constituents. This fraction therefore, is an excellent raw material for the production of high jodine value fatty acids, soya sterols, and tocopherol. The by-product after saponification and subsequent acidification and vacuum distillation yielded distilled fatty acids with an iodine value of 160.

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The Semicontinuous Deodorization of Fats'

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YOMMON batch deodorization of edible fats and oils, which has changed little in its essentials during the past 30 to 40 years, is in several respects a somewhat unsatisfactory process. For one thing, it requires a great deal more steam than would appear reasonable for a straightforward stripping operation. On the average, about 25 pounds of stripping steam are used for each 100 pounds of oil deodorized (4). To this amount must be added 75 to 100 pounds for the maintenance of vacuum, hence in many refineries the steam chargeable to the deodorization department approaches 50% of the total amount consumed in the plant. In recent years steam requirements have been reduced by the general adoption of Dowtherm heating to produce high operating temperatures, but the benefits of high temperature deodorization are limited by the fact that carbon steel and many other common metals and alloys used for deodorizer construction have a pro-oxidant effect on the oil which becomes serious as the temperature rises to high levels. Nickel and aluminum are not injurious to the stability of the oil at elevated temperatures (8), but the latter metal is lacking in structural strength and also presents cleaning problems, whereas nickel, even when used in clad construction, is so eostly that it has not found wide use.

The upper shell and vapor outlet of a batch deodorizer are invariably much cooler than the oil charge

and form an effective condensing surface for easily condensible materials carried by the stripping steam. It is generally recognized that reflux from the upper portions of the deodorizer is a factor contributing greatly to the difficulty of stripping the last traces of volatiles from the oil. The expedient of jacketing and heating the upper shell has been proposed (6), but not generally adopted. Decreasing the headspace above the oil or constricting the upper portion of the vessel to increase the steam velocity will minimize reflux but will at the same time tend to increase loss of oil from the deodorizer by entrainment.

Part of the relative inefficiency of steam utilization in deodorization as presently practiced is inherent in batch operation. Owing to the lack of flexibility of steam ejectors, the consumption of steam for maintaining vacuum on batch vessels cannot be reduced during heating or cooling periods when little stripping occurs, and actually the injection of steam is required only to agitate the oil mass and promote heat exchange with heating or cooling coils. In large plants reasonably good smoothing of steam, water, and Dowtherm vapor loads is attained by staggering the operating cycles of a number of deodorizers, but small batch deodorizer installations are characterized by intermittent heavy demands for these various utilities, interspersed with periods when demands are low or non-existent.

Continuous deodorizing systems overcome the disadvantage of batch deodorization with respect to

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