unaffected by reducing the temperature from 26.7°C. (80.0°F.) to 3°C. (37.4°F.) though the amount of moisture transferred through each square centimeter of area was, of course, greatly reduced because of the reduction in vapor pressure. The films of cocoa butter behaved in a similar manner, but an explanation for their behavior is undoubtedly different from that for the highly hydrogenated cottonseed oil. On reducing the temperature of the cocoa butter, the approximately 20% of liquid component solidified, which might be expected to decrease the permeability. However the 20% of liquid component probably solidified in the relatively permeable, low-melting forms. Furthermore shrinkage accompanying the solidification may have created a structure which was porous to some extent.

Theoretically the permeability constant for permanent gases varies exponentially with temperature, a relationship first pointed out by Barrer (1); at ordinary temperatures the permeability constant should approximately double for a rise of 10°C. (18°F.). While many systems involving vapors behave according to this rule, the limited data given in Table II indicate that systems of fats and water vapor do not behave in this manner.

Vapor Pressure. The permeability of the highly hydrogenated cottonseed oil at 26.7°C. (80.0°F.) does not appear to be affected by the changes in vapor pressure shown in Table II though possibly the accuracy of the method employed and the low values found for this material were such that moderate changes would not be detected. The data obtained for cocoa butter at 26.7°C. (80.0°F.) and a film thickness of about 1.6 mm. definitely show that the permeability constant was reduced by reducing the pressure gradient across the film.

The effects of changes in vapor pressure were very large for the chocolate liquor and sweet milk chocolate. When the vapor pressure difference across the films was increased to 26.3 mm. at 26.7°C. (80.0°F.), a difference in relative humidity of 100%, the permeability constant for the chocolate liquor increased to about 540×10^{-12} and that for the sweet milk chocolate to about 1130×10^{-12}. These large permeability constants cannot be attributed to the behavior of the fat component of the films; rather they must be attributed to the nonfat components, the protein, milk solids, sugar, etc. At 100% relative humidity these components absorbed enough moisture to destroy the structure of the film.

Summary

Films of cocoa butter, highly hydrogenated cottonseed oil, mixtures of highly hydrogenated cottonseed oil and cottonseed oil, chocolate liquor, and sweet milk chocolate were prepared; and their permeability to water vapor was determined by the cup method. The permeability constant was calculated in terms of grams of water diffusing through a centimeter cube in one second under a vapor pressure gradient of one millimeter of mercury across the cube.

Under the test conditions employed, the permeability constant for cocoa butter at room temperature was found to vary from 5.8×10^{-12} to 81.6×10^{-12}. The permeability constants for the highly hydrogenated cottonseed oil and the cocoa butter, under comparable conditions at room temperature, was found to be approximately 1.3×10^{-12} and 33×10^{-12}, respectively.

From data obtained with cocoa butter it was concluded that the permeability constant increased with moderate increases in film thickness.

Polymorphism was found to have a large effect on permeability, an approximately 15-fold difference was found between quickly chilled and tempered films of cocoa butter at 3°C. (37.4°F.).

The percentage of liquid component in the fat was found to have a large effect on permeability. The increasing of the percentage of liquid cottonseed oil in highly hydrogenated cottonseed oil from 0 to 40% increased the permeability constant from 1.3×10^{-12} to about 420×10^{-12}.

The permeability of chocolate liquor and sweet milk chocolate at room temperature was increased greatly when the relative humidity on the wet side of the films was increased to 100%. The nonfat components absorbed enough moisture to impair the structure of the film.

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A New Development in Vegetable Oil Refining Equipment

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A NEW DEVELOPMENT in vegetable oil refining equipment has made possible similar advancements in process technology. This device is a rotating contactor, and its application for refining all types of vegetable, fish, and animal oils by any of the processes in common use will be described in this paper. Data obtained from pilot and commercial plant operations on a number of oils show obvious advantages in simplifying the process flow sheet and reducing the number of units to a maximum of two for any size of refining plant.

It has been pointed out previously (1) that separation of gum and soapstock from oils did not depend solely on high centrifugal force as obtained in centrifuges; rather coalescing surface and residence time play equally important roles. Moreover a combination of these factors and relatively lower separating force in the contactor accomplishes the same and, in most instances, superior results.

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Low operating speeds minimize wear, noise, frequency of cleaning, and power consumption. Results are especially improved when reagent strength, percentage of treat, mixing, holding time, temperature, and associated factors are carefully determined and automatically controlled to produce a practically neutral oil and a liquid soapstock low in neutral oil.

The rotating contactor consists of a 36-in. diameter rotor spinning in a horizontal plane on two anti-friction bearings. At each end of the shaft are hydraulically balanced mechanical seals for feeding and withdrawing liquids continuously. The rotor is driven by a fluid drive and motor, permitting changing of r.p.m. as desired and acceleration to operating speed without excessive torque.

Two operations, re-refining and water washing, are carried out simultaneously in a single machine (Fig. 1). Specially designed sections are provided for each operation. The clarifying section (A) is capable of producing clear, clean oil with less than .2% of moisture while the separating section (C) produces a liquid soapstock practically oil-free.

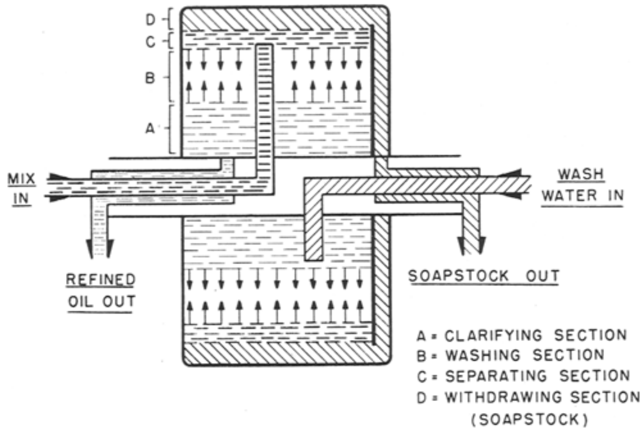

FIG. 1. Flow of liquids through rotating contactor.

Effective mixing and water washing takes place in section (B) while the oil which is separated from the soapstock passes fresh incoming wash-water before it leaves the rotor at the center. The soap withdrawal section (D) is equipped with hot-water nozzles for handling viscous soapstocks. These are rarely needed however for re-refining operations. The wash water joins the relatively small percentage of soapstock, diluting it and producing soapstock—wash water solution which leaves the machine as a clear liquid, free of oil.

MANY SOAPSTOCKS, such as those from coconut, palm, and palm kernel oils, do not require high separating force but cannot stand over-mixing because of emulsion tendencies. Conversely hard-to-wash oils and those containing large amounts of gums such as cottonseed, soy, and corn, can stand more vigorous mixing, which requires greater separating force. The wide range of controllable mixing energy within the rotor, coupled with adjustable separating power, combine to make the rotating contactor an unique and versatile process tool for vegetable oil and fat industries.

All types of oil and refining processes have been handled in commercial or pilot operations. The "mixin" position and wash-water nozzles may be varied to suit the specific process application. The position of the separating zone within the rotor and its magnitude can be controlled remotely by means of a back pressure-valve from the operating panel. Operating pressures are relatively low (40-70 p.s.i.), depending upon the strength of caustic used and rotor speed. The differential between feed pressure and back pressure on the refined oil is a guide to separating zone position and is maintained at about 2 to 5 lbs. This feature is automatic as are others described in a previous paper (2).

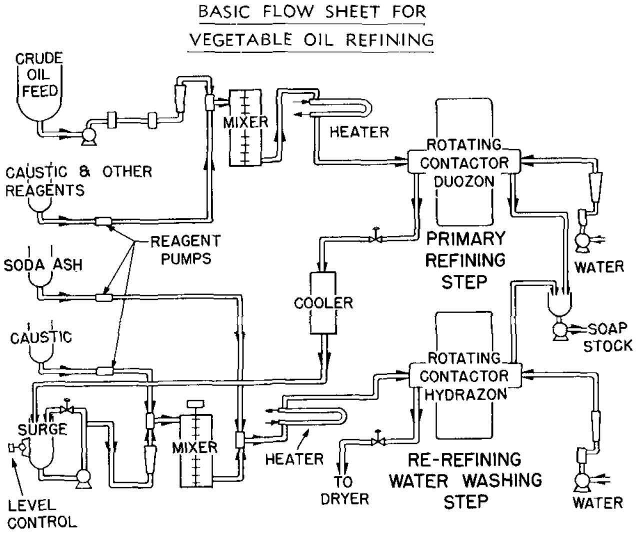

FIG. 2

The most widely accepted refining processes in use today are miscella refining, caustic refining, soda ash refining, C.S.A. (caustic-soda ash) refining, ammonium hydroxide refining, plus re-refining and water washing, and degumming followed by re-refining and water washing. These processes and their various combinations are used to produce finished products of certain specifications. Development of the rotating contactor was stimulated by the need for a contacting and separation unit with sufficient flexibility to meet the requirements of the most common plant designs.

Over the past two years an intensive development program has produced a contactor which can greatly simplify and improve refinery operations. Changes in raw material and product specifications which are governed primarily by market demands are easily accommodated because of the versatile characteristics of the Podbielniak Contactor.

An example of this versatility is the ammonia degumming process, which produces gums containing free fatty acids and other compounds of nutritional value. The nutritional value of these materials is normally destroyed in the caustic refining process. Their use as a cattle feed supplement greatly increases the desirability of this process in many market areas.

A BASIC FLOW SHEET for the standard processes is shown in Figure 2. By unique equipment design a three-step process by former standards can be reduced to a two-step operation. Reagent tanks and chemical feeder pumps are arranged to supply the proper reagent into the main oil flow. These are controlled from an oil flow meter equipped with either an

TABLE I

Re-Refining and Water Washing Data on Water Degummed Soy Bean Oil

Contactor operations							Oil effluent			Soapstock	
Speed r.p.m.	P.S.I.		Temp. °F.		H_2O % C-C	Caustic % 20° Bé.	H_2O %	% P p.p.m.	Soap p.p.m.	Free oil %	T.F.A. %
	In	Out	In	Out							
2100	59	57.5	159	132	14	1.8	0.22	12.2	120	.03	6.03
2100	59	57.5	159	132	15.4	1.8	0.28	13.5	104	Nil	4.22
2100	58.5	57.5	159	133	14.1	1.7	0.29	14.9	100	Nil	4.86
2100	59.5	57.0	160	133	17.2	1.5	0.27	14.9	86	Nil	5.79

% Counter-current wash water determined from sodium balance (mixture in and soapstock).
Soap in effluent oil reported as sodium oleate.

electrical transmitter to a pneumatic activating system or an electronic amplifier. All reagent pumps operate from this main control, and the output of each is positively proportioned to the oil flow at all times. Pipe zone mixers, residence time mixers, heaters, and coolers complete the flow sheet.

In the primary step either gums or soapstock are separated from the oil by a Duozon rotating contactor. The oil then flows to a small surge chamber. Positive level control in the surge chamber assures continuous operation with the re-refining and water-washing operations carried out in the second rotating contactor known as the Hydrazon. Soapstock discharging from Duozon joins that from the Hydrazon, diluting it sufficiently to permit pumping by a simple gear pump.

The oil from the Hydrazon is processed further by vacuum-drying, bleaching, and deodorizing.

Table I shows data on re-refining and water washing of degummed soybean oil. The hot water from washing was controlled by a globe valve and rotameter. However a more precise measurement was obtained from a sodium balance. This was achieved by analyzing the mix entering and the soap wash-water leaving the machine. It is interesting to note the extremely low moisture content of the oil. The absence of free oil in the soap wash-water is also significant because it contributes to a refining loss near theoretical.

A rotary contactor capable of performing the functions of both steps of the process has been tested in pilot-plant operations on a number of different vegetable oils (4).

Table II presents data on refining of crude palm kernel oil. Data on the refining of crude corn oil have been provided previously (4). The low operating pressures of the rotary contactor should be noted particularly. The condition of the refined oil and the effluent soap-water solution is worthy of notice because of the unusual clarity of each. The low moisture-content (0.22%) in the oil throws less burden on vacuum driers. Acidulation of a liquid soapstock solution is simplified.

The ammonia refining process produces a gum which has considerable fatty acid content and is much more easily discharged at relatively low operating pressures.

Periodic cleaning of the contactor is not required at the low operating speeds. Any meal or fines which come through from the expellers is held by the gum or soapstock and discharges with it continuously. Cleaning of the machine is achieved by displacing the gum or soap hold-up with hot oil. In re-refining and water-washing operations the machine is cleaned simply by flushing with hot water.

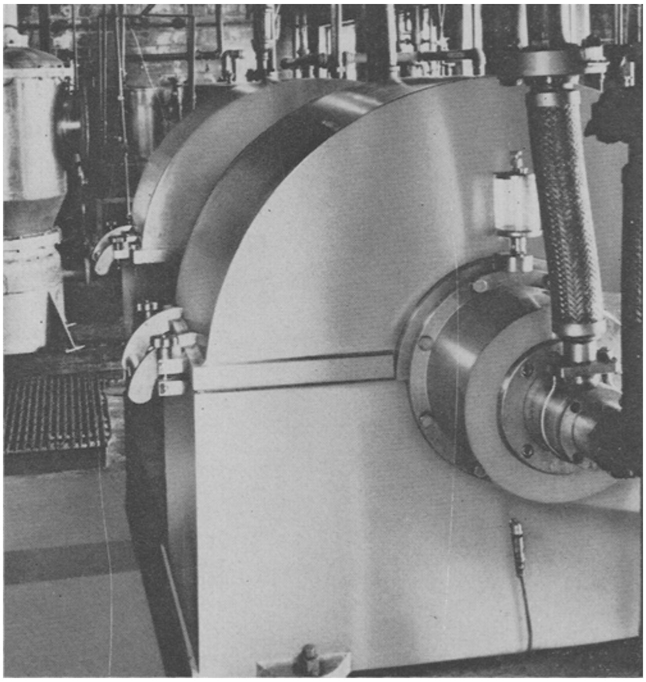

FIG. 3.

The effectiveness of washing miscella-refined cottonseed oil has been shown (3) in a machine designed for pressure operation, which makes it especially suit-

TABLE II

Refining Performance Rotary Contactor
(Crude Palm Kernel Oil—6.1% F.F.A.)

Preheat temp. °F.	Speed r.p.m.	Press. p.s.i.g.		Flow rate lbs./min.	Temp. °F.		Refined oil	Soapstock
		In	Out		In	Out		
190	2100	58	61	8	184	180	Clear	Fluid
190	2100	56	61	8	184	181	Clear	Fluid
190	2050	52	56	7.8	188	185	Clear	Fluid

Note: 10° Bé caustic soda of 0.05 excess used.

Analyses	Refined oil:	Soapstock: (as is basis)
	F.F.A. = 0.05% Soap = 300 p.p.m.	Moisture = 62.6% Free oil = 1.9% T.F.A. = 34.5%

able for this as well as the ammonium hydroxide process by eliminating leakage of hazardous vapors.

A typical plant installation is shown in Figure 3, showing the compactness and neat housekeeping possible with the rotating contactor. These plants range in size from 4 to 10 tank cars per-day capacity.

Summary

New developments, using the rotating contactor, in the vegetable oil processing industry have been described and illustrated. Results from various refining operations on a number of oils have been presented. Economies from reduction of capital expenditures and operating costs are expected to accrue to the user. He can also choose the process to give those products best suited to the market. The improved rotating contactor offers to the vegetable oil processor a most versatile plant.

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Application of Gas-Liquid Partition Chromatography to the Quantitative Estimation of Monoglycerides[1,2]

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THE ISOLATION and fatty acid analysis of monoglycerides have recently received particular attention in regard to studies of the positional arrangement of fatty acids in natural triglycerides. Such studies have been made possible by the discovery that the hydrolysis of triglyceride by pancreatic lipase is a series of directed stepwise reactions from triglyceride to αβ-diglyceride to β-monoglyceride (8, 14). Thus the nature of the fatty acids present in the β-position of the original triglyceride is readily determined by isolation of the β-monoglycerides from the hydrolysate and analysis of their component fatty acids (9, 15).

Monoglycerides have been separated from mixtures of mono-, di-, and triglycerides by countercurrent distribution (4), silicic acid chromatography (3), reversed-phase chromatography on siliconized kieselguhr (13), or silica gel adsorption chromatography (12, 11). To obtain the β-monoglycerides free from the α-isomer, Borgström (3) proposed treating the isolated monoglycerides with periodic acid and then separating the β-monoglycerides from the products of oxidation of the α-isomers (glycoaldehyde esters) by silicic acid chromatography. Because of the ease of $\alpha \rightleftharpoons \beta$ isomerization of monoglycerides, Savary and Desnuelle (15) recently modified the procedure by treating the total glyceride mixture with periodic acid and then separating the resulting glycolaldehyde esters from the unreacted β-monoglycerides on a siliconized kieselguhr column; the di- and triglycerides remained on the column with the solvent system used.

The present investigation was aimed at developing a method for determining the fatty acid composition of monoglycerides in a mixture of glycerides, without first having to isolate the monoglycerides. The approach used was to convert only the monoglycerides to volatile derivatives, which could then be separated by gas-liquid partition chromatography (GLPC). Conversion of α-monoglycerides to their isopropylidene derivatives (1) appeared to be a promising method. However it was found that, although the isopropylidene α-monoglycerides containing C_2 to C_{18} fatty acids were readily separable by GLPC, the higher members of the series (C_{16}–C_{18}) had excessively high retention-times. Furthermore this method would be applicable only to the α-monoglycerides since the β-isomers do not form isopropylidene derivatives under the conditions used.

A more feasible method proved to be the conversion of both α- and β-isomers to allyl esters of the corresponding fatty acids, *via* the dimesyl derivatives, as outlined in Figure 1. Both α- and β-monoglycerides were found to be converted quantitatively to allyl esters, and the allyl esters of C_8 to C_{18} fatty acids proved to be readily separable by GLPC. Furthermore β-monoglycerides could be determined separately by the same method after removal of the α-isomers by periodate oxidation. Finally the analysis of monoglycerides could be carried out equally well

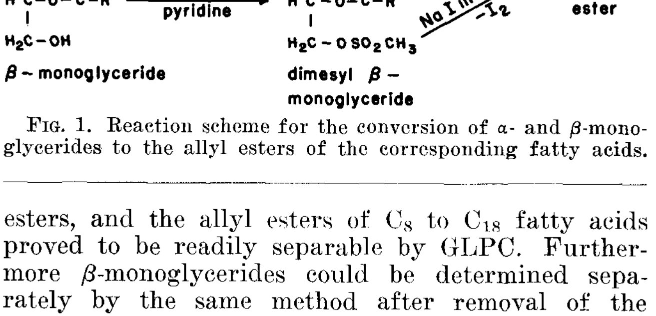

FIG. 1. Reaction scheme for the conversion of α- and β-monoglycerides to the allyl esters of the corresponding fatty acids.

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[3] National Research Council Postdoctorate Fellow, 1956–1958.