cost is still high and restricts their use in the preparation of processed protein supplements for the supplementary feeding programmes envisaged in the technically developing countries. Much headway has yet to be made in the technology of these products and in organising distribution. Large scale production and consumption of processed protein foods, suitably fortified with vitamins and minerals, will help considerably in making up the many dietary deficiencies and in improving the health of children and other vulnerable sections of the population in several developing countries. It is gratifying to note that several international organizations like FAO, UNICEF and WHO are helping various governments in the production and use of protein-rich foods for the prevention and treatment of protein malnutrition in children.

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Continuous Recovery of Acid Oil

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Abstract

A continuous process for acidulation of all types of caustic soapstocks is described. The soap is diluted, heated, acidulated and centrifuged to yield three products: acid oil, acid water and a sludge phase. Typical performance data on various grades of soapstocks and the recovered products are given.

Introduction

CONTINUOUS PROCESSING has been practiced in the Vegetable Oil Industry for three decades, but is a recent development in the acidulation of soapstock for recovery of acid oil.

Soapstock acidulation by the batch method is widely practiced, but is a marginal operation (1). It is time-consuming, a labor problem, often a hodgepodge of miscellaneous equipment, high in reagent demand, creates disposal problems and too frequently may produce a degraded acidified oil.

Today, however, with technological developments, such as, corrosion-resistant metals, automatic control systems and new types of processing equipment, acidulation of soapstock in a continuous system has become a reality. A fair price for quality acid oil and demand for a nutritive meal additive have given the process economic advantages. Under the impetus of legal regulations for waste disposition, continuous acidulation is becoming a necessity.

For the past four years, The De Laval Separator Company has been developing and extensively testing on a variety of soapstocks from many sources, a process for continuous recovery of acid oil in its pilot plant. A schematic flow sheet of this development appears in Figure 1.

General Process

The caustic soapstock, received directly from the refinery, is blended in a surge tank with a diluent in order to provide a homogeneous mixture of proper viscosity range as feed stream to the system. The di-

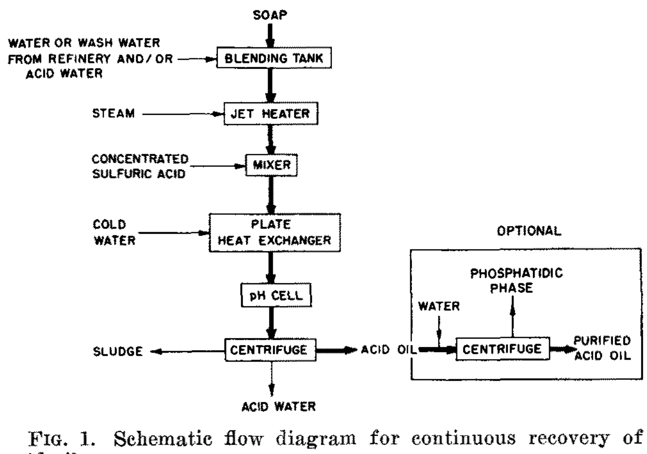

FIG. 1. Schematic flow diagram for continuous recovery of acid oil.

TABLE I

Chemical Analyses of Typical Caustic Soapstock Feed

	Non-degummed cottonseed	Non-degummed soybean	Non-degummed corn	Degummed soybean	Coconut
% Avail. fatty acid [a]	39–53	36–44	36–48	1.8–3.4	27–43
% Moisture	32–51	34–43	41–53	94–96	16–64
% Phosphatides	3–15	6–15	4–7	0.1–0.4	None
% Neutral oil	10–21	8–19	9–13	<0.5	9–21

[a] TFA and OFA.

luted soapstock mixture, generally 20–30% TFA, is heated to 180–200F in a steam jet heater. Then this soap is reacted with concd commercial grade 66°Be′ sulfuric acid in a high shear mixer, passed through a plate heat exchanger and a pH cell. Here, a pH reading of the reaction mixture in the range 3.5–4.0 automatically controls acid pump response.

The acidulated mixture is separated in a PX type self-opening centrifuge into three phases: Acid Oil, Acid Water and Sludge.

Where demands require a premium grade acid oil from such source material as nondegummed soybean oil soapstock, the acid oil phase may be washed with water. In a hermetic centrifuge, this wash mixture is separated into two phases: A purified acid oil of 92% minimum TFA content and a phosphatidic product.

A further refinement to this process may be the addition of vacuum drying equipment to increase the acid oil to 95% + TFA content, with less than 1% moisture.

Each aspect of this continuous acidulation process shall now be described in more detail.

Pretreatment

Table I gives the range of analyses of typical caustic soapstocks that have been treated in this system.

The nondegummed soapstocks are diluted 50 to 100%. The wash water from water wash separators in refinery is frequently used for soap dilution to recover all of the available fatty acids from the refinery section. It is also advantageous to recycle a portion of the acid water waste stream. With half of the required diluent as acid water, sulfuric acid consumption can be reduced by as much as 15%.

It is not necessary to dilute degummed soybean soapstock or lauric acid soapstocks, such as, coconut and palm kernel oil, from continuous refining systems.

A review of this data shows that there is considerable variation in the range of phosphatides in the non-

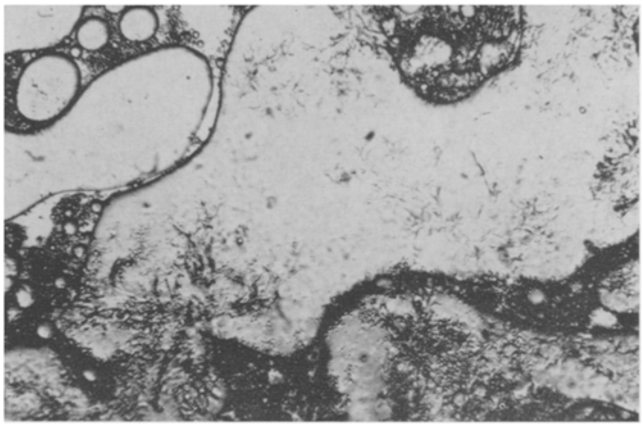

FIG. 3. Cottonseed acidulation mixture from plate cooler.

degummed soapstocks. The % phosphatides in soap varies with the amt of gums in the crude oil feed to refinery, and degree of hydrolyzation in caustic refining operation.

Acidulation

Just prior to entering the mixing area, concd 66°Be′ sulfuric acid is added to the heated soap. In the mixer the soap is chemically split in a few seconds by intimacy of contact with the acid to yield a completely acidulated mixture, as may be illustrated by Figure 2.

This is a photograph of a microscopic examination made of the reaction mixture, as it leaves the mixer. The acid oil appears as white globules (5 to 300μ in size), distributed quite uniformly throughout the dark acid water phase, which has been dyed for contrast.

The reaction is exothermic with 5–20F temp rise.

The heat is used to maintain processing temp of soybean, corn and coconut acidulated foots. The concd acid addition is controlled automatically at a pH range of 3.5–4.0. A study of the titration curves for the various soapstocks has shown the fatty acid fraction is released from the soap at a pH of 4.0 or less. This is also evidenced by a marked drop in viscosity.

If the reaction mixture pH is permitted to fall below 3.0, the acid oil product becomes degraded. There is an increase in oxy fatty acid, mineral acid and ash content and poorer color. At the pH range of 3.0 or less, the reagent usage for acidulation of the soap and neutralization of waste water increases markedly. The physical system, with constant exposure to the higher acidity range, is subject to real corrosion problems.

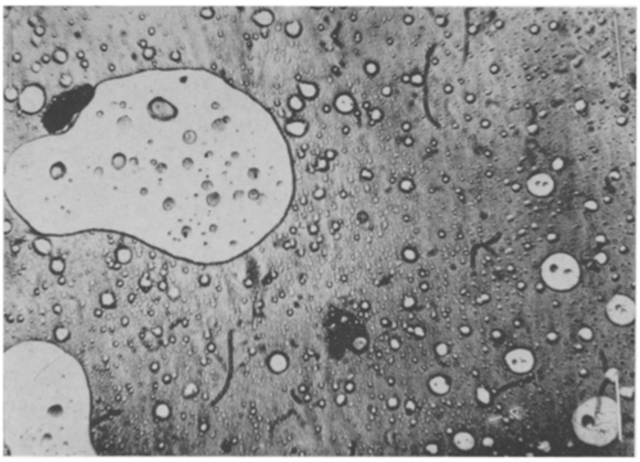

FIG. 2. Acidulated soapstock from intimate mixture.

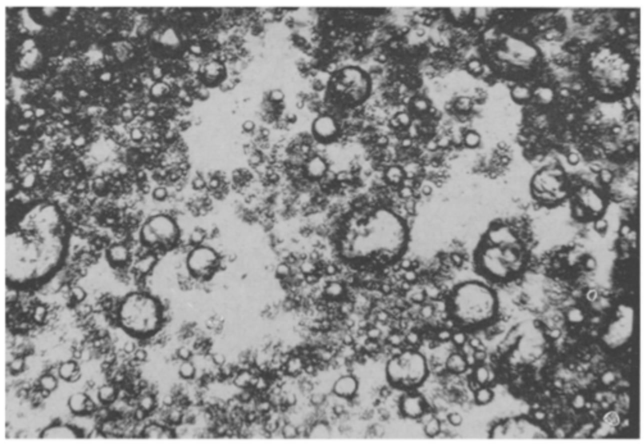

FIG. 4. Oil globules and phosphatidic particles in acid water.

TABLE II

Products from Centrifugation of Continuously Acidulated Nondegummed Soybean Soapstock

	Acid oil[a]	Acid water[b]
% TFA	85–88	<0.06
% OFA	1.0–1.5	
% Water	3.2–6.0	
% Mineral acid	0.01–0.04	0.3–0.5
Iodine value	122–125	

a. There is 99% + recovery of available fatty acids in acid oil.
b. 5-day BOD value for clarified neutralized acid water: 2400–14000.

Centrifugation

To aid separation, the cottonseed acidulated mixture is cooled in a plate heat exchanger to the range of 110–130F. On cooling, the phosphatides form a fluffy suspension in the reaction mixture. The viscosity of the cooled mixture is one-fifth the value, noted directly out of mixing chamber.

Microscopic examination of a cooled sample of cottonseed acidulated foots (Figure 3) illustrates how the oil globules have agglomerated and develop into large masses of free oil in the water suspension. In this photograph, the oil phase appears as the white globules with dark boundries.

If the area between the large oil masses is examined at higher magnification (Figure 4), numerous small oil globules are observed.

In the water media, there is seen the fine phosphatidic particles in suspension. They are 1 to 3μ in size.

Following the plate heat exchanger and pH cell, the acidulated mixture enters the PX self-opening type centrifuge for separation into three phases. The zone in the separator bowl is controlled to meet the product requirements of the particular plant. For example: An acidulated nondegummed soybean reaction mixture can produce an acid oil-phosphatidic phase, a clear acid water phase and heavy solids which accumulate as a third phase at the periphery of the centrifuge bowl. Or the separation may be controlled in the centrifuge to give a relatively clear acid oil phase. The phosphatides are then discharged as a suspension in acid water phase.

In each case, the heavy impurities, such as meal, accumulated in the bowl wall area are discharged from the centrifuge as a sludge phase and are acceptable as a meal additive. This slurry discharge is made with controlled opening of the centrifuge for a few seconds at specifically timed intervals, without any interruption of plant flow.

When the plant requirements specify a clear acid water for neutralization and disposal, the quality of products obtained from the PX centrifuge may be as given in Table II.

These data are for centrifuged acidulated nondegummed soybean foots.

The variation in BOD figures (2400–14,000 mg/liter) is attributable to the amt and type of impurities present in the original crude oil, as well as plant processing conditions. For example, carbohydrates in soapstock, and use of acid water recycle, will increase BOD values.

TABLE III

Data on Purified Acid Oil (2 Stage System)

	Soybean	Corn
% TFA	91.5–93.2	93–94
% OFA	0.8–0.9	2.3–2.6
% Water	1.7–3.5	0.9–1.6
Iodine value	129–135	112–114
% Mineral acid	Trace	Trace
pH of Ash	6.5–7.0	6.5–7.0

TABLE IV

Typical Acid Oil Analyses—Single Stage Continuous Acidulation of Various Soapstocks

	Nondegummed Cottonseed	Degummed Soybean	Coconut
% TFA	88–93	95.3	92–96
% OFA	1.0–4.0	3.2	1.4–1.5
% Water	1.0–3.0	1.4	1.0–1.5
Iodine value	102	132	

Optional Purification

Certain plants, for marketing purposes, require soybean and corn acid oil of at least 92% TFA content, while sewering a clear neutralized acid water. Such a quality acid oil may be obtained by washing with limited amt of water the acid oil phase from initial or primary separation. The fine phosphatidic suspension is washed from the acid oil and, on centrifugation in a hermetic vegetable oil separator, yields a purified acid oil and a phosphatidic phase. Typical anlyses of this purified product is given in Table III.

Washing increases the TFA content from range of 85–88% in feed to 91–94% in purified acid oil product, with correspondingly higher iodine values. The water washing operation removes mineral acid and insolubles. Thus, the purified oil has a low ash and a pH of 6.5–7.0.

This centrifuged purified soybean acid oil, recovered from washing stage, shall contain at least 85% of the available fatty acids in original soap feed. The purified corn acid oil may contain 90–95% of the available fatty acids.

If such a purified acid oil is vacuum dried, the finished product may analyze 95% + TFA, 1.6% OFA, with less than 1% moisture.

Discussion

Data on the acid oil product from other types of soapstock, acidulated in the single stage system, is given in Table IV.

In the degummed soybean and coconut soapstock acidulations, there is 99.9% recovery of the available fatty acids in the acid oil phase. However, the recovery from nondegummed cottonseed foots acidulation is dependent upon the zone control in the centrifuge, and specific needs of the plant. Fatty acid recovery in the acid oil phase may be 85–99.9% of the available fatty acids in soapstock feed.

The acid water phase from centrifugation of degummed soybean and coconut acidulation mixture has a 5-day BOD in range of 2000.

A review of the total fatty acid content of acid oils has shown that the amt may vary in the oil on a dry basis: in soybean acid oil 91–96%; in cottonseed acid oil 91–96.5%. This difference is influenced by the neutral oil content of the soap. The lower the neutral oil content of the soap, the higher the TFA content of the acid oil. Therefore, high TFA Acid Oil may indicate good refinery operation, if and when the continuous acidulation process immediately follows continuous refining operation.

The analytical procedures used in appraisal of the soapstock and acid oil are the Official AOCS Methods. The BOD determination on the acid water are by the Winkler Method (3), the standard method for examination of industrial wastes.

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