Influence of Coconut Oil

Detecting ghee adulteration with coconut oil up to the 10% level using the DSC technique is not possible, since the DSC pattern of ghees shows no change with the addition of the vegetable fat.

In presence of both buffalo body fat and coconut oil, the DSC crystallization of ghee exhibits the characteristic peak located at high temperature, provided that the animal body fat concentration is equal or superior to 5%. Buffalo body fat can therefore be detected as from the 5% level, whether the ghee contains vegetable fat or not.

Quantitative determination of buffalo body fat in ghee is, however, not possible in the presence of vegetable fat. For samples containing only 5% coconut oil, the relative area of the additional peak corresponds to the buffalo body fat concentration; adding more coconut oil reduces this area (see Table I).

ACKNOWLEDGMENTS

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Continuous Acidulation of Soapstock and Recovery of Acid Oil[1]

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ABSTRACT

Requirements for water pollution abatement have created a need for much better recovery of fatty material from soapstock acidulation processes. The present methods of recovery lack reliability, or are relatively capital intensive, or both. A new, continuous system consisting of equipment for acidulating the soapstock, decanting the bulk of acid oil from acid water, and treating the acid water in a coalescer for further separation of emulsified acid oil is described. The emphasis is on operating results from a pilot process using a variety of soapstocks. Fat concentrations below 150 ppm in acid water can be achieved reliably. The process is relatively compact, and simple to operate.

INTRODUCTION

In alkali-refining of triglyceride oils, soapstock is produced as a byproduct. It consists of ca. 70-95% water and 5-30% of fatty material, depending on refining practice and the equipment used. Most of the fatty material, 60-70%, is in the form of sodium soaps of fatty acids with the remainder made up of triglycerides, phosphatidic material, and minor amounts of other, oil-derived compounds.

To recover the fatty material (acid oil), the soapstock is acidulated with sulfuric acid to liberate the fatty acids. This acidulation must be carried out to a relatively low pH of 2-3 to ensure that no soaps remain, which would tend to interfere with the separation of the acid oil phase from the acid water phase. Batch as well as continuous acidulation is being practiced.

The problems associated with the acidulation of soapstock are well known. They are, mainly, the corrosive nature of the process, and the fact that the separation of the acid oil phase from the acid water phase is often relatively poor, which leads to high fat losses and waste-water highly contaminated with fatty material.

The difficulties with corrosion of equipment and buildings are of course solved by using corrosion-resistant materials, but it must be admitted that the costs are considerable. It is therefore of interest to have a relatively compact process arrangement which requires less outlay in building space and equipment. This means that the separation of acid oil from acid water after the acidulation should not require a long time or very elaborate equipment.

Doing the acidulation reaction in a continuous process mode is of course not very difficult to accomplish. Achieving adequate phase separation in a relatively short time with a variety of soapstocks can be very difficult. The problem of oil/water separation has assumed even greater importance in recent years because of much more stringent requirements on the fat content of waste-waters. Regulations now specify that only up to 150 ppm of fatty mate-

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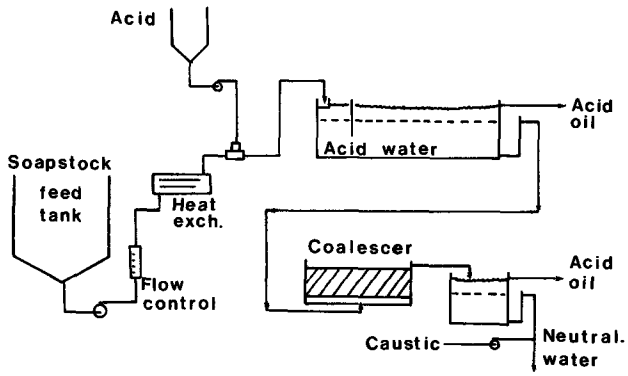

FIG. 1. Continuous acidulation and recovery of acid oil.

rial (Freon TF solubles, [1]) may be contained in wastewaters discharged to municipal sewers. This restriction can be quite difficult to meet.

The separation methods presently in use are either not reliable in achieving this low level of fat concentration, or they are relatively expensive to install and operate. They can be summarized as follows: (a) gravity settling in large vats, usually after batch acidulation; (b) centrifugation, usually after continuous acidulation; and (c) air flotation assisted by polyelectrolyte flocculation, after gravity settling, and operated either in conjunction with batch or continuous acidulation.

Of these three methods, gravity settling in large vats after batch acidulation is the most commonly used. It can produce acid water below 150 ppm of fatty material, but this is, first of all, not reliable and, secondly, it requires at least 8-12 hr of settling time in many cases to achieve even reasonably low values. The investment in vats and building space is high and the cost of maintenance is high.

Centrifugation does not produce sufficiently low fat concentrations according to the literature. Values in the range of 300-7,400 ppm of fatty material in the acid water are reported by Todd and Morren (2), and by Crauer (3). Centrifuges are, of course, very expensive and present obvious difficulties in a corrosive environment.

Air flotation assisted by polyelectrolytes, after gravity settling, also does not reliably reduce fat concentrations. It is often coupled with lime neutralization of the acid water and dewatering of the resulting sludge using filters or decanter centrifuges. With this combination, the fat concentrations achieved are sufficiently low, but the installation and operating costs are relatively high.

Another method to achieve better removal of fatty material is suggested from practice in petroleum oil/water separation technology. There, use is often made of coalescers. These are devices which encourage very small droplets, micron and submicron size, to form larger drops in the one hundred micron range (5). These separate quickly from the continuous phase by gravity.

Coalescers are usually used to separate oil from water in ships' bilges, oil-well emulsions, storage tank bottoms, and similar cases in which gravity separation does not work sufficiently well or sufficiently quickly (4). Coalescers are usually not recommended in cases where emulsifying agents are present. This would seem to make their use on acid water not promising. Despite this apparent limitation, coalescence devices were tested on acid water, and a coalescer was developed which was capable of achieving the very low fat concentrations required by regulations.

EXPERIMENTAL DETAILS, RESULTS AND DISCUSSION

Based on preliminary tests, a relatively simple and compact continuous acidulation process consisting of an acidulation stage, a gravity separation stage and a coalescence stage was developed on a pilot scale.

Figure 1 is a flowsheet of the process with the main

TABLE I

Continuous Acidulation of Soapstock and Acid Oil Recovery

Soapstock		Acid water		Time coalescer was on stream	
		Fat content			
Type	Fat content (%)	From gravity sep. tank (ppm)	From coalescer (ppm)	Continuous (hr)	Cumulative (hr)
Gravity separation tank: ca. 0.5 hr avg residence time Coalescer depth: 10 cm					
SB/RS	6.1-4.1	1,000-1,100	10-23	6	6
RS	5	900-1,600	10	6+6	18
RS	4.3	1,300-8,000	1,140-10	5+5	28
RS/SB	3.8-7.4	3,000-63	28-10	5+5	38
RS/Corn	4.9-16.9	2,000-5,500	10-99	4+7	49
RS/SB	3.3-6.0	2,700-60	10-26	5+5+5	64
RS	6.3	6,700	60-237	1	65
Regen.	0.4/pH 8	–	–	1	–
	0.4/pH 2	–	–		–
RS	6.1	5,800-1,800	10-30	2.5	2.5
Gravity separation tank: ca. 1 hr residence time Coalescer depth: 30 cm					
SB	2.3-2.7	90	20	12	
Coco	14.6-9.0	1,770-3,100	17-23	20	
RS/SB	2.4-3.1	640-52	11-54	32	

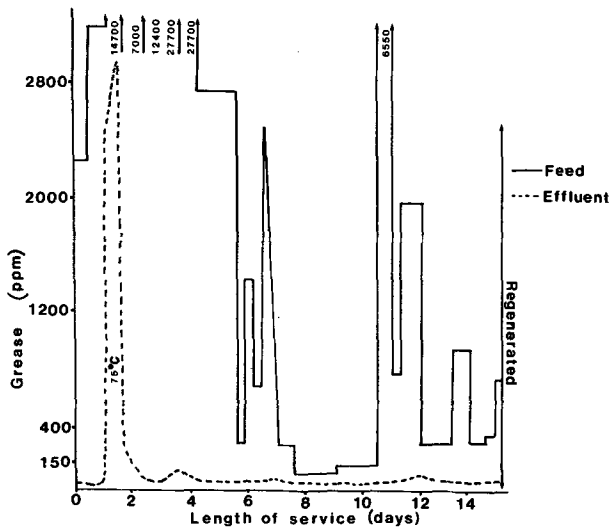

FIG. 2. Semi-pilot plant tests: long-term coalescer performance; new bed.

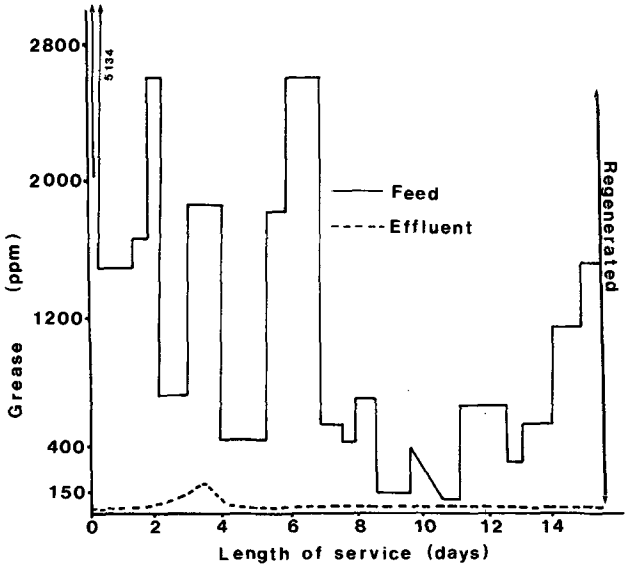

FIG. 3. Semi-pilot plant tests: long-term performance; regenerated bed.

components of each stage as follows: (a) continuous acidulation with flow-control, heat exchange, acid metering, and the acidulation zone; (b) gravity separation and decanting of the bulk of the acid oil phase from the acid water phase in a continuous-flow gravity separator tank; and (c) separation by coalescence of "emulsified" acid oil from acid water in a bed of fiberglass, gravity separation of the two phases in a small decanter tank and neutralization of the acid water.

The capacity of the test arrangement was 80 L/hr (200 lb/hr).

The performance of this process during the early stages of its development is shown in the upper portion of Table I. Soapstocks with a fatty material content in the range of 2.3-16.9% were used. The acidulation was done to a pH of ca. 2 and at a temperature of 105 C. The gravity separator tank was sized to give an average residence time of 0.5 hr. The lower 75% of tank volume was occupied by the acid water layer, and the upper 25% by the acid oil layer and skimmed-up emulsion. The coalescer bed depth was 10 cm.

The data show that the fat concentration in the acid water discharging from the predecanter tank varied widely from 63 ppm with soybean oil soapstock to 8,000 ppm with rapeseed oil soapstock. After treatment in the coalescer, the fat concentration in the acid water was reduced to 10-99 ppm, except for a period of low-temperature operation during start-up which produced 1,140 ppm. No deterioration in coalescer performance was indicated over twelve operating periods of 4-7 hr duration each, for a total of 64 hr. After 65 hr of operating time had accumulated, the fat concentration rose to 237 ppm when acid water at 6,700 ppm of fatty material was processed. The process was then stopped for regeneration of the coalescer.

After the regeneration procedure, which required about 1 hr, acid water containing as much as 5,800 ppm of fatty material was reduced to 10-30 ppm in a test-run of 2.5 hr.

These tests show that the process arrangement was capable of achieving the objective set for it, but that to be practical, some improvement, particularly in the length of time the coalescer would function adequately, was desirable. To achieve this, the coalescer bed depth was increased from 10 cm to 30 cm, and the size of the gravity separation tank was doubled to reduce the fat-load in the acid water entering the coalescer. Increasing the size of the gravity separator also had the advantage of reducing the possibility of discharge of skimmed-up emulsion together with acid oil. The lower portion of Table I gives typical results achieved after these two changes. Also, unlike the previous tests, the process was now operated in a truly continuous fashion rather than in 4-7 hr operating intervals.

The data show that the effect of the longer residence time in the gravity separator was to achieve significantly lower concentrations of fat in the acid water than was the case previously. Acid water from rapeseed and soybean soapstocks, for example, were at 52-640 ppm, whereas concentrations of several thousand parts per million occurred with these in the previous tests. (Episodes of emulsion discharge together with acid oil were also reduced, as expected.) Coconut oil soapstock still produced acid water at a high fat concentration.

With the coalescer at 30 cm depth, and the somewhat lower fat concentration in the acid water feed, fat concentrations well below 100 ppm during 32 hr of continuous operation were achieved without deterioration in performance. This indicated that, perhaps, several days of continuous operation are possible without regeneration of the coalescer.

Based on this experience, further tests were done on a semi-pilot plant scale to try and determine more accurately how long a 30-cm deep coalescer bed could be expected to function before regeneration would be required. The results of these tests, which were done using acid water from a variety of soapstocks and at various concentrations of fatty material, including some very high concentrations, are shown in Figures 2 and 3. The coalescer was operated continuously, with shutdowns only over weekends.

It can be seen in Figure 2 that in spite of large variations in the fat concentrations of the acid water feed, the coalescer reduced the fat levels to less than 100 ppm without much change in its effectiveness over 15 days of operation. There was one episode of poor performance after the first

day of operation in which the coalescer was overloaded for about one day due to low operating temperature coincident with very high fat concentrations in the acid water feed.

After the 15 days of continuous operation, the coalescer was subjected to a regeneration cycle. This was done in part because of very gradually increased fat levels in the acid water effluent (but not yet exceeding 100 ppm), and in part to gain more experience with the regeneration procedure and possible effects on pressure drop and structural integrity of the coalescer after a long operating cycle.

In Figure 3, the fat concentrations achieved after regeneration in a further 15 days of operation are shown. The concentrations achieved were generally below 50 ppm, except for a period of relatively poor performance at 150-200 ppm between the third and the fourth day after regeneration. At the end of the 15-day period, another regeneration procedure was done to test bed-integrity. The run was then terminated.

These tests show that continuous operation of at least two weeks, and possibly even of one month, can be expected. Also, it is possible that a fiberglass coalescer as used in these tests can be regenerated repeatedly without adverse effects on pressure drop or structural integrity.

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Quantitation of Estolide Triglycerides in Sapium Seeds by High Performance Liquid Chromatography with Infrared Detection

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ABSTRACT

The kernel oil of Chinese tallow (*Sapium sebiferum*) seed contains tetraester triglycerides composed of *trans*-2,*cis*-4-decadienoic acid joined in an estolide linkage to 8-hydroxy-5,6-octadienoic acid. A rapid (< 10 min) method of separation and quantitation of the triglyceride and estolide triglyceride fractions of the oil has been developed using high performance liquid chromatography with infrared detection.

The Chinese tallow tree, *Sapium sebiferum*, a rapidly growing 30-40 ft deciduous tree that grows well in the southern coastal United States, is being examined as a potential crop for marginal land (1). It has virtually no natural enemies, is tolerant of wetlands and salt marshes, and annually produces large quantities of white seeds approximately the size of a pea (1). The seeds are covered with a vegetable tallow (12-35 wt % per seed) composed of triglycerides containing saturated and monounsaturated fatty acids. The seed kernel contains a liquid oil (13-32 wt % per kernel), Stillingia oil, which is unusual in that it contains tetraester triglycerides composed of an allenic hydroxy acid (8-hydroxy-5,6-octadienoic acid) joined in an estolide linkage to *trans*-2, *cis*-4-decadienoic acid (2, 3). To facilitate measurement of the intact estolide triglycerides for plant breeding and further study, we have developed a rapid method of separation and quantitation of triglycerides and estolide triglycerides by high performance liquid chromatography (HPLC) with infrared (IR) detection.

MATERIALS AND METHODS

Seeds of *S. sebiferum* were provided by Simco of Texas, Inc. (Houston, TX). Whole seeds were refluxed for 6 hr with hexane to remove the vegetable tallow from the outer seed coat. The seeds were then ground and extracted with petroleum ether using a Butt apparatus to obtain the kernel oil.

The kernel oil was analyzed on a high performance liquid chromatographic system consisting of an M-6000A pump (Waters Assoc., Milford, MA), a column (25 cm x 4.6 mm) of Partisil PXS 10/25 PAC (Whatman, Clifton, NJ) and an IR detector for liquid chromatography (Du Pont, Wilmington, DE) set at 1750 cm^{-1} and 0.1 A full scale. Samples were eluted within 10 min with 10% tetrahydrofuran in hexane at a rate of 2 mL/min. A typical injection contained 2-3 mg of oil in 10 μL of eluting solvent. A laboratory-wide computer system (4, 5) was used to determine peak areas.

To obtain purified estolide for standards, 1 g of kernel oil was placed on a dry column (1 cm [id] x 21 cm) of 60/200 mesh Hi-Flosil column support (Anspec. Co., Inc., Ann Arbor, MI) and eluted successively with 250 mL each of 3%, 10% and 20% diethyl ether in hexane at ~5 mL/min. During the chromatography, 50-mL fractions were collected and progress was monitored by HPLC. The oil was separated into two components by column chromatography