Nature of Palm Oil in Centrifuge Sludge Waste Water

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In attempting to improve oil recovery, palm oil retained in the centrifuge sludge waste has been categorized and quantified. It is composed of (i) 30% free oil droplets; (ii) 56% oil released after cellulase treatment followed by detergent washing, and (iii) 14% residual oil which remains diffused and bound to the cell debris. The fatty acid composition indicates that all three oils are palm oil. The separated oil is highly contaminated.

In the clarification section of palm oil mills, suspended solids and water which have not settled out in the static settling tanks are removed from oil. This is done by separators or centrifuges which yield two streams. The first, commonly called the 'recycle,' consists of 69% oil, 2% solids and 29% water. This stream is recycled to the settling tank, while the second stream, a brown-colored viscous liquid consisting of 5–7% solids, 0.5–1% oil and 90–94% 'sludge,' is discharged as effluent. For every ton of palm oil produced, 1.5 tons of sludge are discharged. Proper milling conditions ensure that as little oil as possible is present in the sludge as it constitutes oil loss when discharged. No matter how effective the centrifuges are, the final sludge still contains at least about 12% oil on a dry basis (Bek Nielsen, personal communication, 1982). This represents a loss of more than 1% production oil.

Many laboratory attempts were made to separate the oil from the solids of the sludge, but without success. To quote the Mongana Report, "Cellular debris have been subjected to a large number of treatments with a view of freeing the oil attached to them. It is not possible to describe the hundreds of tests carried out" (1). A study was thus carried out to determine the nature of oil in the sludge, and methods were developed to separate each type of oil present.

EXPERIMENTAL PROCEDURES

Materials. Sludge was collected from a 60-ton/hr mill using nozzle Stork centrifuges. Composite samples of the six centrifuges were used for every analysis. The samples were analyzed on the day following sampling.

Microscopic examination. The sludge was centrifuged at a low centrifugal force of 230 G for 10 min to settle the bigger particles. A drop of the supernatant was transferred to a haemocytometer and observed under the optical microscope. Photos of the free oil droplets (Fig. 1) were taken at 10 × 40 magnification and enlarged to ensure better precision in the diameter measurement using a graduated grate.

The sizes of the plant cells and oil inside the oil bearing cells (Fig. 2) were measured similarly on a diluted sludge sample.

Separation of free oil droplets. A known weight of sludge was heated to 60 C and centrifuged at 7,600 G in a high speed centrifuge Sorvall GSA. A thin scum of oil was observed on the surface of the clear supernatant, and a compact solid separated to the bottom of the tube. The solids were dried and the oil content determined. The supernatant without the film of oil was decanted, dried and Soxhlet extracted but did not contain any extractables. All the free oil droplets had been spun to the surface. The amount of free oil was calculated by subtracting the amount of oil retained in the solids from the total oil of the sludge which was determined by drying a known weight of sample and Soxhlet extracting the oil.

Soxhlet extraction was carried out on the dried sample for at least six hr using 100 ml hexane.

Separation of oil from solids. 100 g of sludge was treated with 1 g cellulase (NOVO) and incubated at 30 C

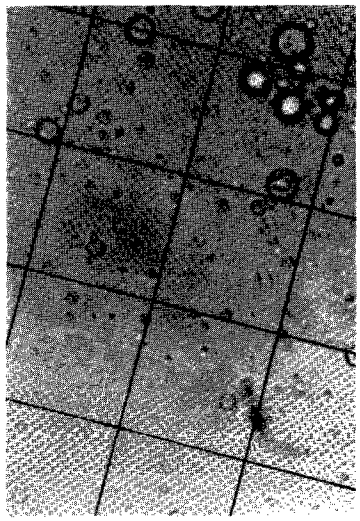

FIG. 1. Free oil droplets from sludge mag 400×.

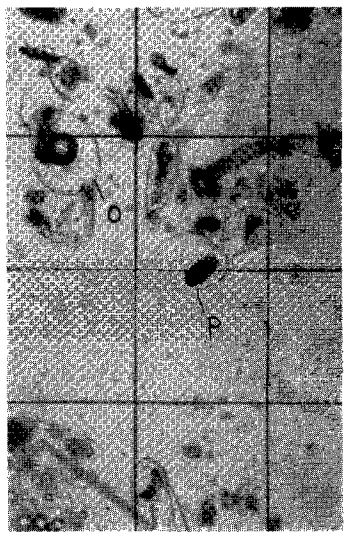

FIG. 2. Plant cell (P) and oil cells (O) from sludge, mag 100×.

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overnight in a shaker water-bath. The sample observed under the microscope indicated that the cell walls were broken (Fig. 3). The sample was then heated to 60 C for two hr and centrifuged. No significant amount of oil was separated. The supernatant was decanted and the solids redispersed with 100 ml of 0.01 mol dm^{-3} sodium dodecyl sulphate and heated to 60 C before recentrifuging. A thin layer of oil was separated. The residual solids were observed under the microscope. All the oil droplets were separated (Fig. 4). The residual solids were dried and Soxhlet extracted to determine their oil content.

Mass balance of oil. Total oil in sludge = Free oil droplets + oil removed by enzyme and detergent treatment + oil extracted from residual solids.

Characterization of the oil. The free oil and oil separated after detergent washing were highly emulsified. This oil-in-water emulsion was liquid-liquid extracted by shaking it in a separating funnel with hexane. The solvent was evaporated and the oil analyzed.

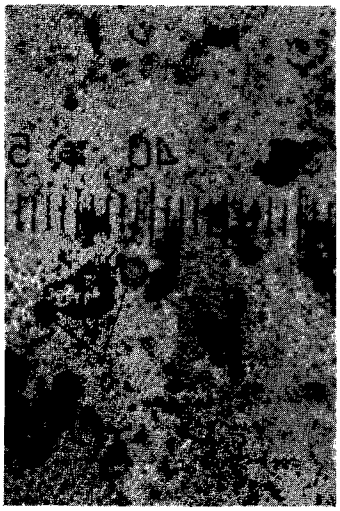

FIG. 3. Sludge after cellulase treatment mag 100×.

FIG. 4. Sludge after cellulase and detergent washing mag 100×.

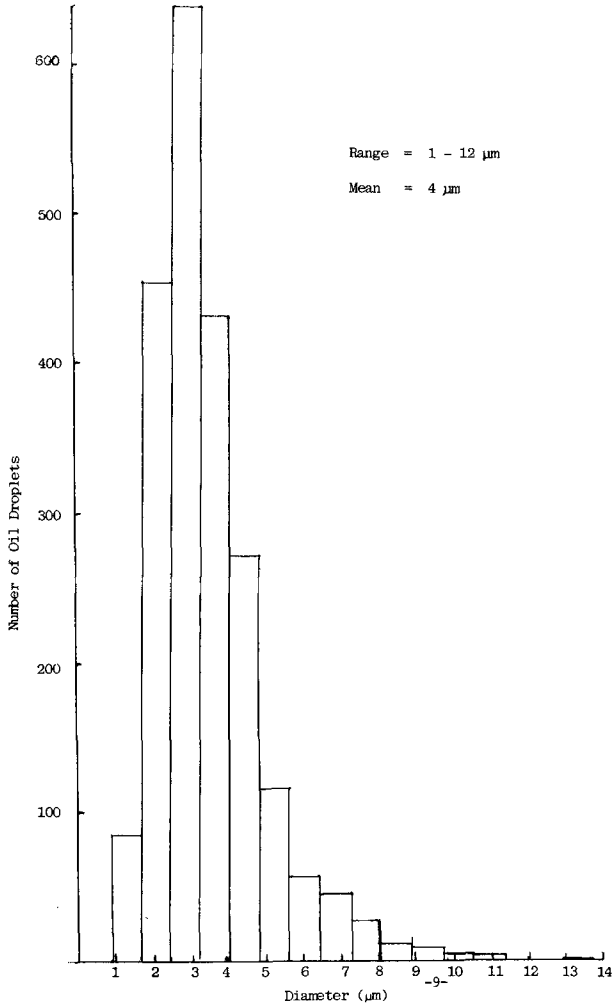

FIG. 5. Size distribution of free oil droplets.

The free fatty acid was determined using the VOTC method and free fatty acid calculated as palmitic acid using the formula:

$$\% \text{ FFA} = \frac{25.6 \times t \times M}{w}$$

where t = volume of sodium hydroxide solution (ml)
M = molarity of sodium hydroxide solution
w = weight of oil used (g)

Iron was measured using a Perkin Elmer 373 Flame Atomic Absorption Spectrophotometer. A 10% solution of oil in methyl isobutyl ketone was aspirated directly into the flame. Phosphorus determination was carried out using a Perkin Elmer 5000 Atomic Absorption Spectrophotometer using a graphite furnace. A 1% solution of oil in 1.57% of lanthanum 2,4-pentadionate in chloroform was injected into the furnace. Standard calibration graphs were made prior to analyzing the samples.

Methylation was done according to the International Standard Method (2) using boron trifluoride. Fatty acid methyl ester compositions were analyzed by Perkin Elmer Sigma 115 Capillary Chromatograph using a 60-m long,

0.25-mm diameter fused silica capillary column. The injection and detector temperature were 290 C, oven at 180 C with helium carrier gas.

RESULTS AND DISCUSSION

The microscopic examination showed that the sludge contains free oil droplets (Fig. 1) besides cell debris and whole cells (Fig. 2) with and without trapped oil droplets.

The free oil droplets have an assymmetric size distribution skewing toward the larger diameter (Fig. 5). These oil droplets can be completely separated by high speed centrifugation of at least 7,600 G, but the normal mill centrifuges of about 1,500 G are unable to separate these. This oil is labelled Type I and represents 30% of the total oil retained in sludge.

The sludge also contains a large amount of individual plant cells which are irregular but mainly ellipsoidal in shape. Some contain oil vacuoles (Fig. 2) in a broad range of sizes (Fig. 6). The oil droplets have smaller diameters than the average encountered in whole cells prior to clarification, where sizes range from 23–74 μm. Large oil vacuoles decrease the density of the cell to below 1, and these cells are separated into the recycle stream by the mill centrifuge. Adequate sterilization, digestion and pressing would decrease the presence of cells with oil vacuoles in the sludge or recycle stream. The oil droplets in the sludge adhere to the protoplasmic contents of the plant cell, as after the cell wall is broken no significant amount of oil could be separated out (Fig. 3). A subsequent washing with sodium dodecyl sulphate detaches the oil droplets from the solid debris; 56% of oil could be separated by these treatments. This oil is labelled Type II. No more oil droplets were observed in the residual cell debris after combined enzyme and detergent treatment (Fig. 4). However, after drying the treated solids and subsequent Soxhlet-extraction a small amount of residual oil (14%) was recovered. This is labelled Type III. This oil is diffused and strongly bound to the protoplasmic residues.

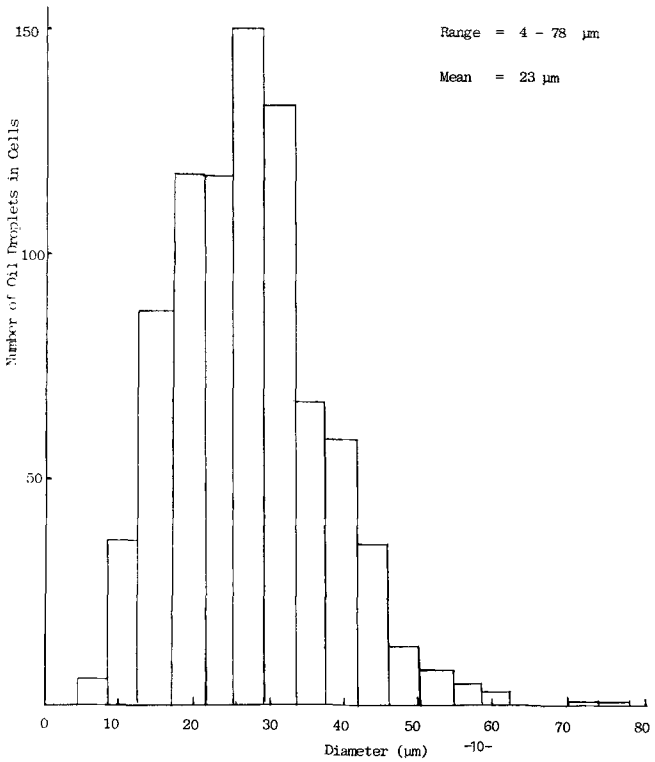

FIG. 6. Size distribution of oil droplets in oil cells.

TABLE 1

Quality of the Various Types of Oil Separated

Oil	Iron (ppm)	Phosphorus (ppm)	Free fatty acid (% as palmitic acid)
Production oil	6-16	13-24	2-4
Type I	30	9	9
Type II	8	2	6
Type III	17	3	6

TABLE 2

Fatty Acid Composition of the Various Types of Oil Separated

	Fatty acid composition							
	C_{12}	C_{14}	C_{16}	C_{18}	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	C_{20}
Production oil	0.3	1.2	44.5	4.6	39.7	8.5	0.2	0.2
Type I	0.5	1.1	44.5	3.8	39.1	9.6	0.9	0.3
Type II	0.5	1.4	45.2	4.4	38.6	9.0	0.5	0.3
Type III	0.9	1.6	46.8	3.8	38.8	7.2	0.4	0.3

Oil Types I and II exist as stable oil-in-water emulsions. These may be due to some emulsifying agents which form an adsorbed film around the dispersed droplets, thus preventing coalescence (3).

Possible emulsifying agents present in sludge are free fatty acids, monoglycerides, proteins or phospholipids. Finely divided solids around the droplets may prevent coalescence, too. Liquid-liquid extraction is necessary to break the emulsion so that the oil separates into the organic layer. Liquid-liquid extraction also separates some of the contaminants into the organic phase, thereby contaminating the oil. The high free fatty acid and iron content may not be an indication of the intrinsic quality of the oil. The low phosphorus content could be the result of the liquid-liquid purification process during the extraction. The quality of the three types of oil extracted is poor (Table 1) when compared to production oil. However, the fatty acid compositions of the three types of oil extracted do not differ significantly from the normal composition of palm oil (Table 2).

The cellulase-treated sludge is very much lower in viscosity and suspended solids, and this would be beneficial to the clarification stage of the milling process in that a shorter separation time of oil from sludge may be achieved. This may even reduce the amount of treatment required for the effluent. However, to recover the oil solely by using the enzyme and detergent treatment is economically unjustified.

ACKNOWLEDGMENT

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REFERENCES

1. Mongana Report, *Report on Production and Storage of Palm Oil, Book I, Congopalm,* Co-Operative Society Registered in Congo, 1952–1955, pp. 140.
2. *Animal and Vegetable Fats and Oils,* Preparation of methyl esters of fatty acids, Ref. No. ISO 5509, 1st Edn., International Organisation of Standardisation, Switzerland, 1978.
3. Shaw, D.J., in *Introduction to Colloid and Surface Chemistry,* 2nd Edn., Butterworth Group, London, 1970, p. 207.

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