Lipid Profile of Process Streams of Palm Oil Mill

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During palm oil extraction, oil loss occurs mainly at three stages of processing, namely sterilization, pressing and clarification. Samples from a semi-commercial palm oil mill were analyzed for their lipid composition (triacylglycerol, diacylglycerol, monoacylglycerol, free fatty acid, phospholipid and glycolipid contents and fatty acid compositions of these lipid classes) and compared with the end product, *viz.*, raw palm oil. The results indicate significant variations between the samples with respect to oil quality and lipid profile. Data relating to the lipid classes showed that sterilizer condensate had the highest levels of free fatty acids (24%), followed by press fiber (12.5%) and sludge effluent (10.9%), as compared to raw oil (1.5%). Diacylglycerol and monoacylglycerol contents were also markedly higher for these streams. Press fiber was characterized by extremely high proportions of phospholipids and glycolipids. Distribution of fatty acids (16:0, 18:1, 18:2 and 18:3) also varied among lipid classes of the process streams, particularly between polar lipids. This paper discusses the compositional aspects of lipids relating to quality of oils of the palm oil mill streams.

KEY WORDS: Condensate, lipid profile, press fiber, process streams, sludge.

Commercially, palm oil is extracted from the mesocarp of the oil palm fruit by following a wet rendering process. The essential steps consist of sterilization, stripping, digestion, extraction, clarification and purification (1,2). During these operations, the fruits and crude palm oil are subjected to varying degrees of thermal and mechanical stresses to obtain maximum yield of oil while preserving the quality of the end product. Nevertheless, 5–10% of the total oil present in the raw material is lost and the quality of the oil also suffers, depending on the process and harvesting conditions (3). In the palm oil mill, oil loss occurs through the sterilizer condensate (sterilization), press fiber (pressing) and sludge effluent (clarification). These are generally known as the waste streams of palm oil processing (4). There is a tendency among millers to recycle the oil from these waste streams, particularly from the sterilizer condensate and sludge, in order to maximize the yield. This could affect overall quality of the end product.

Investigations on the composition and quality of the oil from waste streams and the product during progressive stages of milling are scanty and confined to a few parameters (5–7). Reports are often limited to one particular stage of operation (8). Bek-Nielsen (5) has studied the formation of peroxides at various stages of palm oil milling. To study the feasibility of solvent extraction for oil palm, Chin and Tan (6) have reported the characteristics of oils extracted by solvent from materials taken at different stages of processing. They investigated carotene, tocopherol, free fatty acid, anisidine value, peroxide value, $E^{1\%}_{c233}$, $E^{1\%}_{c269}$ and bleachability of the various oils. Phospholipid levels of various grades of palm oil and its fractions, and from oil recovered from sludge and press fiber was investigated by Goh *et al.* (7). The nature of the oil present in the sludge effluent was reported by Chow *et al.* (8), who examined iron, phosphorus, free fatty acid content and fatty acid composition of the oil. So far, no comprehensive studies regarding lipid composition of the waste streams have been reported. This paper attempts to follow the compositional variations of lipid classes and their constituent fatty acids as well as the quality of the oils of the various process streams as compared to the end product under actual commercial conditions of palm oil extraction.

EXPERIMENTAL PROCEDURES

Collection of samples. Fresh fruits (Tenera variety) were obtained from the Central Plantation Crops Research Institute (C.P.C.R.I., Palode, Trivandrum, India). The different process streams, *viz.*, sterilizer condensate, sludge water, press fiber residue and crude palm oil, were sampled by operating the demonstration plant for palm oil established at C.P.C.R.I., which has a capacity of 1 ton fresh fruit bunches (FFB) per hour. The process and the various process streams are indicated in Figure 1. The process details were reported earlier by Sundaresan *et al.* (1). The plant was operated specifically to collect samples at various stages of operation. Condensate of approximately 300 kg from the sterilizer was collected from an entire batch of 1000 kg FFB. Representative samples were taken from the bulk. The method of extraction of oil was hydraulic pressing, and samples were collected from the press fiber after it was subjected to 75 kg/cm^2 pressure as optimized for the demonstration plant (1). The oil-water mixture (400 kg) from the press with an oil-water ratio of 1:2 (v/v) was clarified. The sludge from the bottom was

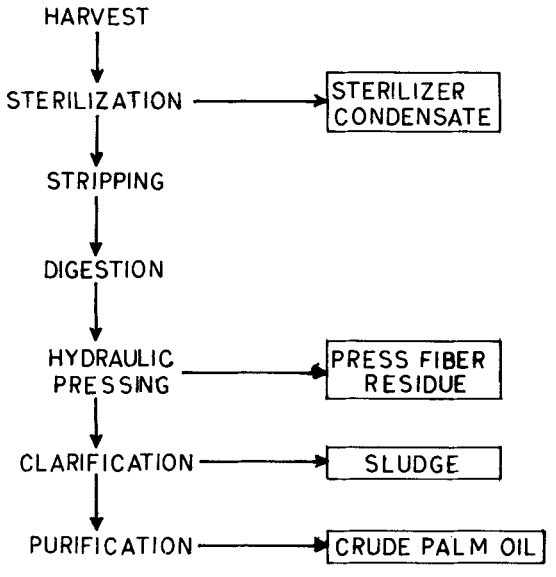

FIG. 1. Flow sheet indicating the various stages of extraction of palm oil and the waste streams from which samples were collected for detailed analysis.

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removed for sampling. Oil from the clarifier was further purified by a high-speed centrifuge for the crude palm oil sample. Two trials were conducted for collection of samples as described, and they were analyzed (in duplicate) separately.

Solvent extraction of mesocarp lipids. Total lipids were extracted with chloroform/methanol (2:1, v/v) solvent mixture from fresh mesocarp as described by Goh *et al.* (7) for oil palm fruits.

Extraction of lipids from process streams. Total lipids of fiber residue was extracted with chloroform/methanol (2:1, v/v), and sludge water and sterilizer condensate lipids were extracted with chloroform (7). The solvents were evaporated under vacuum in a rotary evaporator. The total lipids obtained were dissolved in a minimum quantity of chloroform and stored for further analyses.

Separation of lipid classes. About 20 mg of total lipids were spotted and separated into triacylglycerol, diacylglycerol, monoacylglycerol, free fatty acids and polar lipid classes by thin-layer chromatography on 1-mm thick silica gel G adsorbent with a petroleum ether/diethyl ether/formic acid (60:40:1.6, v/v/v) solvent system (9). Plates were prewashed and equilibrated prior to development, as in standard chromatographic procedures. Lipid bands were detected by exposure to iodine vapor. Triacylglycerol, diacylglycerol, monoacylglycerol and fatty acid fractions were eluted from the gel with chloroform. The polar lipid band was first eluted with acetone to obtain glycolipids, followed by methanol to extract the phospholipids (10). Individual lipid classes were quantitated and fatty acid compositions were determined.

Quantitation of neutral lipid classes. Triacylglycerol, diacylglycerol, monoacylglycerol and free fatty acid classes were quantitated by the oxidative dichromate method of Bragdon (11).

Estimation of phospholipids. Phospholipids were quantitated by elemental determination of phosphorus (12). The phosphorus content was converted to phospholipid by multiplying with the phospholipid factor for palm oil (7).

Estimation of glycolipids. Glycolipids were estimated from the hexose content by using anthrone-thiourea reagent (13). The quantity of glycolipid was calculated as digalactosyldiglyceride from the hexose content.

Determination of fatty acid composition. Methyl esters of the fatty acids were prepared by saponification with alcoholic potassium hydroxide, followed by esterification with alcoholic sulfuric acid reagent according to IUPAC procedure (14). A Hewlett-Packard 5840 A model gas chromatograph equipped with a flame ionization detector (FID) (Hewlett-Packard, Palo Alto, CA) was used for gas liquid chromatography (GLC) analysis of the methyl esters. Methyl esters were analyzed on a 2 m × 2 mm id, 10% EGSS-X on Chromosorb W 100 metal column. Injector and detector temperatures were 250°C and 300°C, respectively. Column temperature was maintained isothermally at 180°C. Carrier gas was nitrogen at a flow rate of 20 mL/min. Methyl esters were identified with reference to standards (Sigma Chemical Co., St. Louis, MO), and the peaks were quantitated by digital integration.

RESULTS AND DISCUSSION

Details of the process and collection of the samples are given in the experimental section. The values presented in Table 1 for the composition of lipid classes were obtained for the various process steps as described. The results show an appreciable variation among the process streams. Sterilizer condensate contained the lowest levels of triacylglycerol (54.5%), whereas oil extracted with solvent from fresh mesocarp had the highest levels (97.0%). Corresponding values for free fatty acids were 24.0% and 0.7%, respectively, for these samples. Partial glycerides also showed significant variations. The distribution of the polar lipids, phospholipids and glycolipids exhibited a much greater variation when compared to the neutral lipid classes. For instance, crude palm oil contained the lowest amounts of phospholipids and glycolipids, whereas press fiber had nearly 20–50 times greater levels of these lipids.

Total lipids from fresh mesocarp of unbruised fruits of correct maturity were extracted with solvent to determine the lipid composition actually present in oil palm fruits without being altered by process conditions. Values reported by other authors for triacylglycerol content of mature oil palm fruit mesocarp show great variation, from 98% (15) to 78% (16). These differences can be attributed to maturity of the fruit and method of extraction of lipids. The high value for triacylglycerol of 97.1% with low values of 2.0% for diacylglycerol, 0.2% for monoacylglycerol and 0.7% for free fatty acids reported here indicate that fruits extracted under proper conditions will have low levels of free fatty acid and partial glycerides with maximum triacylglycerol, as are actually present in the fresh fruit. These values agree with those of Jacobsberg (15). Any

TABLE 1

Lipid Composition of Oils from Various Process Streams of Palm Oil Mill

Lipid class	Sterilizer condensate	Press fiber	Sludge	Crude palm oil	Solvent-extracted oil from fresh mesocarp
Neutral lipid (relative %)					
Triacylglycerol	54.9	65.4	72.8	93.0	97.1
Diacylglycerol	11.5	16.6	10.1	4.5	2.0
Monoacylglycerol	9.6	5.6	6.2	0.9	0.2
Free fatty acid	24.0	12.5	10.9	1.5	0.7
Polar lipid (ppm total lipid)					
Phospholipid	6721	25975	6636	1443	5633
Glycolipid	13925	20311	1139	438	2492

deviation from this composition can be attributed to post-harvest conditions in the field and in the mill.

In a typical palm oil mill, universally practiced process steps are sterilization, stripping, digestion, pressing, clarification and purification. The major oil loss occurs through the sterilizer condensate, press fiber and sludge, with an approximate oil loss of 2%, 6% and 2%, respectively.

During milling operations, the palm fruits are subjected to varying degrees of thermal and mechanical abuse, resulting in chemical and quality alterations of the oil. Sterilization was conducted at steam pressure of 3 kg/cm^2 (equivalent to 130°C) for 1 hr. During this process, about 50% of the total steam requirement for palm oil processing was consumed. The condensate obtained from this step carried about 1–2% of the total oil. Low levels of triacylglycerol (Table 1) could be due to accelerated hydrolysis at elevated temperature, which was further confirmed by the high levels of free fatty acid and partial glyceride, as reported here. High levels of polar lipids in condensate indicate that more structural lipids from the fruit exocarp (outer skin) were extracted. Therefore, the oil present in the condensate may also be derived from the exocarp. Eng *et al.* (3) and Bek-Nielsen (5) have reported that oil from the condensate was heavily contaminated with iron and was in a highly oxidized state. Bek-Nielsen (17) has recommended against the recycling and mixing of this recovered oil with production oil.

The loose fruits obtained after stripping of the sterilized bunches were converted into a mash in a digester maintained at 95°C with live steam (1). This digested mash was then subjected to hot pressing to extract the crude oil-water mixture. Highest oil loss (6.0%) occurred at this stage because oil is entrained in the press fiber residue. The press fiber contained cellulosic fiber, fruit exocarp (skin) and calyx, along with the seed. The oil content of the press fiber and the lipid composition of this oil showed exceptionally high levels of polar lipids and partial glycerides (Table 1). A previous report from this laboratory (18) on the distribution of lipids within the fruit, *viz.*, exocarp and mesocarp, confirmed that exocarp contained markedly higher levels of polar lipids. These lipids are structural components of membranes and are not easily extractable by the method adopted here; thus, they are retained in the press fiber residue oil. Goh *et al.* (7) have reported high values for phospholipids from press fiber waste. According to Bek-Nielsen (17), solvent extraction of residual oil from the fiber would extract a low-quality oil, containing phosphatides and other nonglyceride impurities. High levels of partial glycerides in the press fiber (Table 1) could be attributed to an adsorptive property of the fibrous residues.

The oil-water mixture from the press was subjected to clarification at 95°C to separate the crude palm oil from the watery sludge (Fig. 1). Oil recovered from the sludge had high contents of phospholipids (6636 ppm) and glycolipids (1139 ppm). Goh *et al.* (7) have shown that oil from sludge water has appreciable levels of these lipids because substantial amounts of hydratable polar lipids are removed along with the water phase during milling. The higher levels of partial glycerides obtained here could be due to their greater water solubility as compared to triacylglycerol.

In this experiment, about 90% of the oil present in the fresh fruit was obtained as crude palm oil, the final product stream. Composition of the different lipid classes of commercial palm oil has been reported by several authors in studies related to crystallization (19–21). The values obtained here (Table 1) fall within that range. However, when compared to the oil extracted with solvent from fresh mesocarp, the lower content of triacylglycerol is likely due to the hydrolysis of triacylglycerol, resulting in relatively higher diacylglycerol, monoacylglycerol and free fatty acid fractions during milling. Solvent extraction removes the entire polar lipids present in the fruit, which explains the higher content of these lipids. Commercial crude palm oil is obtained by a wet extraction process during which the structural lipids are not extracted, thus explaining their lower levels in crude oil.

Fatty acid compositions of the total lipids of the various streams of the palm oil mill are given in Table 2. Except for sterilizer condensate, other streams did not show appreciable variations in their fatty acid profiles. Greater proportion of saturated fatty acids and correspondingly lower unsaturated acids in sterilizer condensate could be due to thermal oxidation of unsaturated fatty acids during sterilization. With respect to fatty acid composition of other streams, the values reported in this study are compatible with commercial crude palm oil (8,15,22,23).

Table 3 shows the fatty acid compositions of phospholipid and glycolipid classes of various streams of the palm oil mill. It is interesting to note the association of 18:2 and 18:3 with the polar lipids. While 18:2 was mainly associated with phospholipids, 18:3 was primarily found to be in the glycolipid fractions. Furthermore, it can be stated that most of the 18:3 present in the fresh mesocarp lipids was concentrated in the glycolipid fraction, as the concentration of this acid is negligible in the total lipids. This association of 18:2 with phospholipids and of 18:3 with glycolipids has been observed by Goh *et al.* (7) for crude palm oil samples and by Oo *et al.* (16) and Bafor and Osagie (24) in the developing oil palm fruit. Except for sterilizer condensate, other streams had more or less similar fatty acid profiles for polar lipids. In case of sterilizer condensate, unsaturated fatty acids were appreciably lower for reasons already stated.

The fatty acid composition of various neutral lipid classes are presented in Table 4. Perusal of this Table shows no marked deviation in fatty acid distribution among the neutral lipid classes from the various process streams. This suggests that although there was significant difference in the distribution of neutral lipid classes (Table 1), the relative percentage of the component fatty acids were not subjected to great variations due to selective hydrolysis or to process conditions. However, there was a slight reduction in the total unsaturation in the end product (crude palm oil). Earlier reports for fatty acid composition of neutral lipid classes extracted from mature fruits with respect to development studies agree with those reported in Table 4 (16,24).

The above findings demonstrate the drastic differences in oils from the various process streams in terms of lipid composition and quality. There is a tendency among the palm oil processors to recycle waste stream oils to obtain higher oil yield. The high levels of partial glycerides, free fatty acids and polar lipids in the oils from sludge and sterilizer condensate, when mixed with the end product,

TABLE 2

Fatty Acid Composition of Total Lipids from Various Process Streams of Palm Oil Extraction

Fatty acid (wt. %)	Sterilizer condensate	Press fiber	Sludge	Crude palm oil	Solvent-extracted oil from fresh mesocarp
12:0	0.1	0.1	0.1	0.1	0.1
14:0	1.8	1.2	1.3	1.4	1.3
16:0	49.2	42.6	43.3	44.5	40.2
18:0	4.6	4.5	4.6	4.7	4.9
18:1	36.7	38.9	39.5	38.9	40.6
18:2	7.3	11.6	10.8	10.0	12.3
18:3	0.3	1.1	0.4	0.4	0.6

TABLE 3

Fatty Acid Composition of Phospholipids and Glycolipids of Palm Oil Process Streams

		Fatty acid (wt. %)						
Process stream	Lipid class	12:0	14:0	16:0	18:0	18:1	18:2	18:3
Sterilizer condensate	Phospholipid	0.4	2.3	45.4	5.0	37.8	8.9	2.2
	Glycolipid	0.8	1.5	53.6	5.0	31.9	5.0	0.2
Press fiber	Phospholipid	0.1	0.4	31.1	1.5	40.6	24.2	2.1
	Glycolipid	0.2	0.6	23.8	2.6	30.8	17.7	24.3
Sludge	Phospholipid	0.5	0.7	37.5	3.1	39.2	16.3	2.7
	Glycolipid	0.6	1.4	35.9	3.6	30.3	11.7	16.5
Crude palm oil	Phospholipid	—	2.1	38.4	4.6	42.6	11.7	0.6
	Glycolipid	0.2	1.2	40.2	4.8	36.0	11.4	6.2
Solvent-extracted oil	Phospholipid	—	2.0	35.1	2.6	35.1	24.6	0.6
	Glycolipid	2.0	3.6	30.5	5.4	32.7	14.9	10.9

TABLE 4

Fatty Acid Composition of Triacylglycerol, Diacylglycerol, Monoacylglycerol and Fatty Acid Fractions of Process Streams of Palm Oil Extraction

		Fatty acid (wt. %)						
Lipid class	Process stream	12:0	14:0	16:0	18:0	18:1	18:2	18:3
Triacylglycerol	Sterilizer condensate	0.1	1.4	44.9	5.2	37.9	9.6	0.9
	Press fiber	0.7	2.2	47.6	3.6	36.5	9.2	0.2
	Sludge	0.1	1.4	43.7	4.2	40.5	10.0	0.1
	Crude palm oil	0.1	1.3	45.0	4.8	38.5	9.8	0.5
	Solvent-extracted oil	—	1.4	41.2	4.9	41.0	11.2	0.3
Diacylglycerol	Sterilizer condensate	0.2	1.4	45.2	5.3	37.3	9.7	0.9
	Press fiber	0.5	1.4	37.0	4.0	45.1	11.2	0.8
	Sludge	0.2	1.2	36.5	2.8	43.9	15.2	0.2
	Crude palm oil	0.5	1.3	35.3	3.4	45.7	12.4	1.4
	Solvent-extracted oil	1.2	1.4	30.7	3.6	45.4	16.9	0.8
Monoacylglycerol	Sterilizer condensate	1.0	2.3	46.3	8.0	36.4	5.7	0.3
	Press fiber	4.7	3.2	39.5	5.9	36.5	9.1	1.1
	Sludge	3.2	2.6	44.5	7.4	34.1	8.2	—
	Crude palm oil	6.3	3.8	38.9	5.8	35.7	9.2	0.3
	Solvent-extracted oil	1.4	7.0	38.0	6.3	35.5	10.8	0.9
Free fatty acid	Sterilizer condensate	0.2	1.8	54.0	4.9	33.3	5.6	0.2
	Press fiber	0.4	1.4	44.9	4.5	39.7	8.2	0.9
	Sludge	0.2	1.5	45.8	4.8	37.5	9.4	0.8
	Crude palm oil	1.3	2.1	46.8	4.2	37.4	7.9	0.3
	Solvent-extracted oil	6.8	4.2	37.5	6.2	34.5	10.3	0.4

would impair oil quality for storage and subsequent refining processes (23,25,26).

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