IDENTIFICATION OF VOLATILE COMPOUNDS

THAT CONTRIBUTE TO THE AROMA OF FRESH PALM OIL AND OXIDIZED OIL

Keywords: Volatile; Palm oil; Aroma; Flavour

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Crude and oxidized palm oil were steam-distilled in vacuo to obtain volatile aroma compounds. The steam distillate was then extracted continuously using dichloromethane and the extract was concentrated. The concentrate was analysed using gas chromatography; identification of compounds was by mass spectrometry. The steam distillate from crude palm oil contained compounds such as 2,2,6-trimethylcyclohexanone, 3,3,5-trimethylcyclohex-2-enone, nonanone, nonanal, ethyl benzoate, linalol, trans-allo-ocimene, β-cyclocitral and ionol which were found to be associated with the aroma of fresh palm oil in the aromagram. 3,3,5-Trimethylcyclohex-2-enone was found to have a distinctive palmy, nutty aroma. C_{4-10} alkanals, $C_{5,9,10}$ 2-alkanones, $C_{5,9}$ alkanols, C_{6-9} 2-alkenals, C_{4-5} 2-alkylfurans, $C_{6,10}$ 2,4-alkadienals, 2,2,6-trimethylcyclohexanone and γ-heptalactone were detected in oxidized palm oil.

INTRODUCTION

By contrast with the case of soya bean oil, little information is available on the volatiles of crude, refined or oxidized palm oil. Using paper chromatography and derivatization with 2,4- dinitrophenylhydrazine, Gaddis *et al.* (1961) identified $C_{2,3,6,8,9}$ alkanals, C_{5-11} alk-2-enals, and $C_{7,9,10}$ alka-2,4-dienals in

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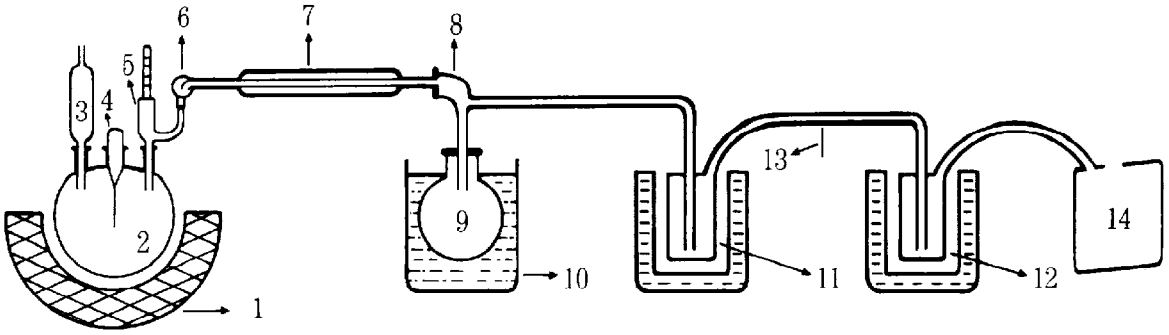

1. Oil bath; 2. Three-necked round-bottomed flask; 3. Separating funnel to store warm water; 4. Capillary; 5.Claisen-head; 6. Steam-trap; 7. Double-surface condenser; 8. Adapter; 9. Flask for distillate; 10. Cooler-methanol and ice water; 11, 12. Gas-traps immersed in liquid air; 13. Capillary; 14 .Manometer and Pump.

Figure 1.
Apparatus for vacuum steam distillation

unheated palm oil. From heated palm oil, he isolated $C_{7,8,9,11}$ alkanals, C_{7-12} alk-2-enals, and $C_{7,9,10,11}$ alka-2,4-dienals. Using the same method Badings *et al.* (1960) identified 2-undecanone in palm oil. Hoffmann and Keppler (1960) determined the configuration of the 2,4-decadienals in palm oil and groundnut oil as that of *trans*-2, *cis*-4-decadienal and *trans, trans*-2,4 decadienal. In bleached palm oil, γ-and δ-lactones were present at concentrations of less than 1 ppm (Van der Ven, *et al.*, 1970).

Dirinck *et al.*(1977) identified C_{5-9} alkanals, $C_{7,9,11}$, alkenals, $C_{7,9,10}$ alka-2,4-dienals, $C_{7,9}$ alka-2-ones, α-and β–ionone, and γ-heptalactone in the steam distillate of palm oil. Dirinck's aromagrams showed the following odours: green odours (n-hexanal); oily fatty odours (n-heptanal); odours of oxidized burnt fat, frying odour (2,4-decadienal isomers); musty odour (2-methylheptan-2-one); pleasant, fruity odour (butyl acetate) and floral odour (β-ionone). Miuro *et al.*(1980) fractionated palm oil by vacuum distillation and followed this with saponification. They found that the carbonyl-free fractions had a distinct palm oil-like flavour and from heated β-carotene they found eight fractions which had a palm oil-like taste.

Sensorial analysis (Dirinck *et al.*, 1983 and Dirinck *et al.*, 1984) indicated that crude palm oil had a nutty like aroma. The present work was carried out to identify the compounds responsible for this nutty aroma; it also included a study of oxidized crude palm oil.

EXPERIMENTAL

Vacuum steam distillation was carried out on:

(a) Crude palm oil

1.5 l of crude palm oil was placed in a three-necked flask, and the whole apparatus was assembled as in *Figure 1.* The flask was

heated in an oil bath at 60°C and a vacuum of 20mm Hg was achieved by means of a water pump. The steam distillate collected amounted to three litres.

(b) Oxidized palm oil

The procedure in (a) was repeated with 200 g of oxidized oil in place of crude palm oil; 2 litres of distillate were collected at the same temperature and pressure.

The volatiles from the steam distillates were then continuously extracted with dichloromethane. Distillation of the dichloromethane using a Vigreux fractionating column yielded the volatile concentrates from the oxidized and fresh oils. 0.3 µl of each concentrate was injected into the gas chromatograph and analysed qualitatively.

Gas Chromatography-Mass Spectrometry

The instruments used were a Varian Aerograph 2700 gas chromatograph linked to a MAT 112 mass spectrometer. The mass spectrometer was directly coupled to the gas chromatograph by means of a platinum capillary tube (length 50 cm, internal diameter 0.113 mm) heated to 250°C and allowing a constant flow of 2 ml per minute of effluent into the mass spectrometer source. An effluent splitter was installed to send about 50% of the total effluent to a FID-detector which recorded the volatile compounds. The operating conditions of the gas chromatography-mass spectrometry system were: 250 m x 0.6 mm i.d., wide-bore glass column coated with a liquid phase of SE-52; linear programming from 30°C to 220°C at 1°C/min ; carrier gas, helium at 2.8 ml/min, and make-up to 4 ml/min before FID-MS splitter, and to 30 ml/min before the FID-detector; temperature of gas chromatograph injector port 250°C; ion source 250°C; ion source pressure 10^{-5} mm Hg; trap current 300 µA; filament voltage 70V; scan speed 100 masses/second.

Aromagrams

Aromagrams were taken by sniffing the eluting products from the column at the sniffing port. A Varian Aerograph 2700 gas chromatograph with a splitter installed in the detection oven was used. Four parts of the carrier gas went to the sniffing port and one part to the FID-detector. A trained person was involved in running the aromagram. For each peak an aroma description was given. Operating conditions were : 150m x 0.6mm i.d. wide-bore glass column of SE-52; linear programming from 30°C to 220°C at 1 ml/min; carrier gas helium, with make-up to 30 ml/min; splitting ratio of FID to sniffing port, 1:4; temperature of injector port and detector, 250°C.

RESULTS AND DISCUSSIONS

A gas chromatogram of the steam-distillate of fresh crude palm oil is shown in *Figure 2*, and the corresponding aromagram in *Figure 3*. The lists of identified compounds and odours are presented in *Tables 1* and *2* respectively.

An empirical relationship can be observed between the chromatographic peaks and the peaks of the aromagram. The compounds responsible for imparting the palm aroma are aldehydes, ketones and terpenes such as n-nonanal, 2,2,6-trimethylcyclohexanone, 3,3,5-trimethylhex-2-enone, nonanone, linalol, *trans-allo*-ocimene and cyclocitral. The compound 3,3,5-trimethylhex-2-enone has a distinctive nutty, palm aroma. A few peaks (numbers 10, 13, 14, 15 and 16) are suspected to be monoxygenated terpenes but they could not be positively identified due to a lack of reference mass spectral data. Ionol (2,6-ditertiarybutyl-4-methylphenol) was also detected. In addition to the palm aroma compounds, other compounds such as n-pentanal, n-hexanal, 2-pentylfuran and 2-methyl-2-hepten-6-one were also detected.

As expected, oxidized palm oil showed a totally different chromatographic pattern. The chromatogram is given in *Figure 4* and identified compounds are listed in *Table 3*. The steam distillate contained mostly aldehydes and ketones. The C_{4-10} aliphatic aldehydes and the C_{6-9} unsaturated trans-2-alkenals were also found in the sample. *Trans*-2-nonenal, a compound responsible for the hardening flavour in peanut oil, was also detected together with *trans, cis*-2,4-decadienals which are

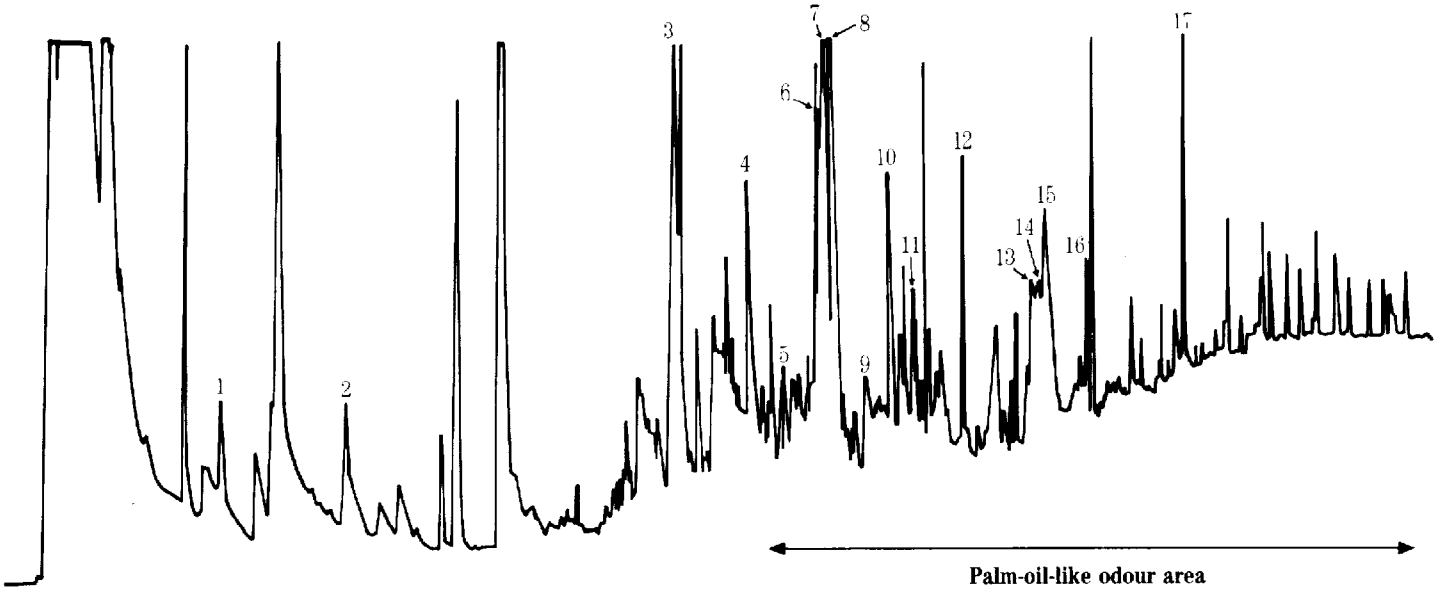

Figure 2.
Volatiles from Steam Distillation of Fresh Crude Palm Oil

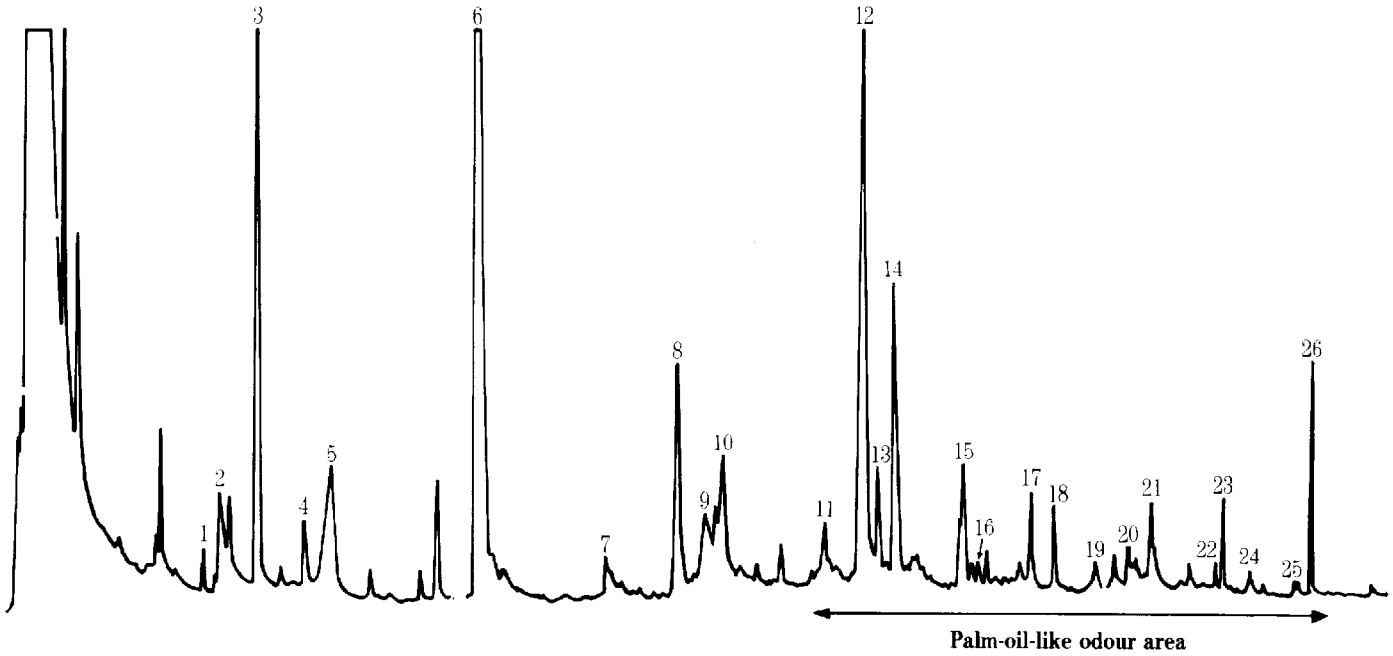

Figure 3.
Aromagram of Volatiles from Steam Distillation of Fresh Crude Palm Oil

TABLE 1.
VOLATILES FROM STEAM DISTILLATE OF FRESH CRUDE PALM OIL
(Refer to Chromatogram in *Figure 2*)

Peaks	Retention Time (Min)	Compounds	Molecular Weight	Aroma Description
1	36.3	n-pentanal	86	sharp, fishy
2	52.9	n-hexanal	100	green, grassy
3	98.3	mixture: 2-pentylfuran	138	sweet, fruity
		2-methyl-2-hepten-6-one	126	mushroom, musty
4	110.7	2,2,6-trimethylcyclo-hexanone	140	
5	114.8	3,5,5-trimethylcyclohex-2-enone	138	
6	119.8	2-nonanone	142	Characteristic unpleasant aroma
7	121.4	n-nonanal	142	tallowy
8	122.3	linalol	152	floral
9	126.4	*trans*-allo-ocimene	136	
10	129.7	unidentified	154	
11	133.0	ethyl benzoate	150	fruity
12	139.6	β-cyclocitral	152	lemon-like
13	149.5	unidentified	156	
14	150.3	unidentified	152	
15	151.6	unidentified	152	
16	156.9	unidentified	152	
17	170.2	ionol	196	green

responsible for the frying, green and oily aroma (Schmidt, 1959). The two isomers, *trans,trans*-2,4-hexadienal and *trans,cis*-2,4-hexadienal, were also detected.

The ketones found to be present were $C_{5,9,10}$ 2-alkanones, 2,2,6-trimethylcyclohexanone, oct-3-en-2-one and γ-heptalactone, which has a characteristic sweet, nutty, caramel aroma. In addition to the aldehydes and ketones mentioned, n-pentanol, n-nonanal, 2-butylfuran and 2-pentylfuran were also identified in this sample. Since most of these compounds were the volatiles common in oxidized oils in general, an aromagram was not carried out.

CONCLUSION

Analysis of the vacuum steam distillate of crude palm oil indicated that the typical palm oil odour fell in the highly dense terpene area of the chromatogram. The identified terpenes were: linalol, *trans-allo*-ocimene and β-cyclocitral. The steam distillate from oxidized palm oil showed the presence of the aldehydes and ketones which were responsible for the normal off-flavours. Compounds such as hexadienal, nonenal and decadienals were detected in the present work by contrast with earlier studies using the headspace technique (Dirinck *et al.*, 1983 and Dirinck *et al.*, 1984).

TABLE 2.
AROMA DESCRIPTION OF COMPOUNDS IN FRESH CRUDE PALM OIL
(Refer to Aromagram in *Figure 3*)

Peak	Retention (Min)	Aroma Description	Compounds
1	41.3	sweet, floral	
2	43.7	perfume	
3	47.9	aldehyde	
4	54.5	green, grassy	n-hexanal
5	57.0	caramel	
6	76.8	aldehyde`	n-heptanal
7	93.3	green, aldehyde	benzaldehyde
8	102.4	sweet, fruity, mushroom	2-pentylfuran and 2-methyl-2-hepten-6-on
104.9	green, aldehyde	n-octanal	
10	108.2	metallic	2,2,6-trimethylcyclo-hexanone
11	120.6	palm oil, nutty	3,5,5-trimethylcyclo-hexanone
12	126.4	benzaldehyde (musty)	
13	128.0	aldehyde, green	n-nonanal
14	129.7	leather, heptanal, fishy	
15	138.8	palm oil, nutty	
16	139.61	painty	
17	147.0	nutty, green, lemon-like	β-cyclocitral
18	150.7	palm oil, nutty	
19	156.1	terpene	
20	160.3	pears, tomatoes	peak 13
21	163.6	palm oil	peak 15
22	171.0	painty	
23	172.7	palm oil	
24	175.9	oily	
25	181.7	floral	
26	184.2	green	ionol

TABLE 3.
VOLATILE COMPOUNDS FROM STEAM DESTILLATE OF OXIDIZED PALM OIL
(Refer to Chromatogram in *Figure 4*)

Peak	Retention Time (Min)	Compounds	Molecular Weight	Aroma Description
1	28.9	n-butanal	72	green
2	40.5	2-pentanone	86	wine-acetone-like
3	44.6	n-pentanal	86	green, grassy
4	62.8	2-methylpentanal	100	
5	66.1	n-hexanal	100	green, grassy
6	72.7	1-pentanol	86	
7	83.4	trans-2-haxenal	98	green, grassy, leafy
8	88.4	2-butylfuran	124	
9	90.9	*trans,trans*-2,4-hexadienal	96	
10	95.0	n-heptanal	114	oily, putty
		trans,cis-2, 4-hexadienal	96	
11	101.6	benzaldehyde	106	bitter almond
12	111.5	*trans*-2-heptenal	112	putty, fatty
13	117.7	2-pentylfuran	138	liquorice
14	123.1	n-octanal	128	fatty, sharp
15	129.7	2,2,6-trimethylcyclo-hexanone	140	
16	133.0	oct-3-en-2-one	126	
17	136.7	*trans*-2-octenal	126	woodbugs, fatty
18	142.5	2-nonanone	142	unpleasant aroma
19	147.9	n-nonanal	142	tallowy, fatty
20	161.5	trans-2-nonenal	140	tallowy, cucumber
21	166.5	n-nonanol	142	rose-orange aroma
22	167.7	2-decanone	156	
23	171.0	n-decanal	156	orange peel, fatty
24	183.8	*trans,cis*-2, 4-decadienal	152	frying, burnt, green
25	191.7	γ-heptalactone	128	sweet, nutty, caramel

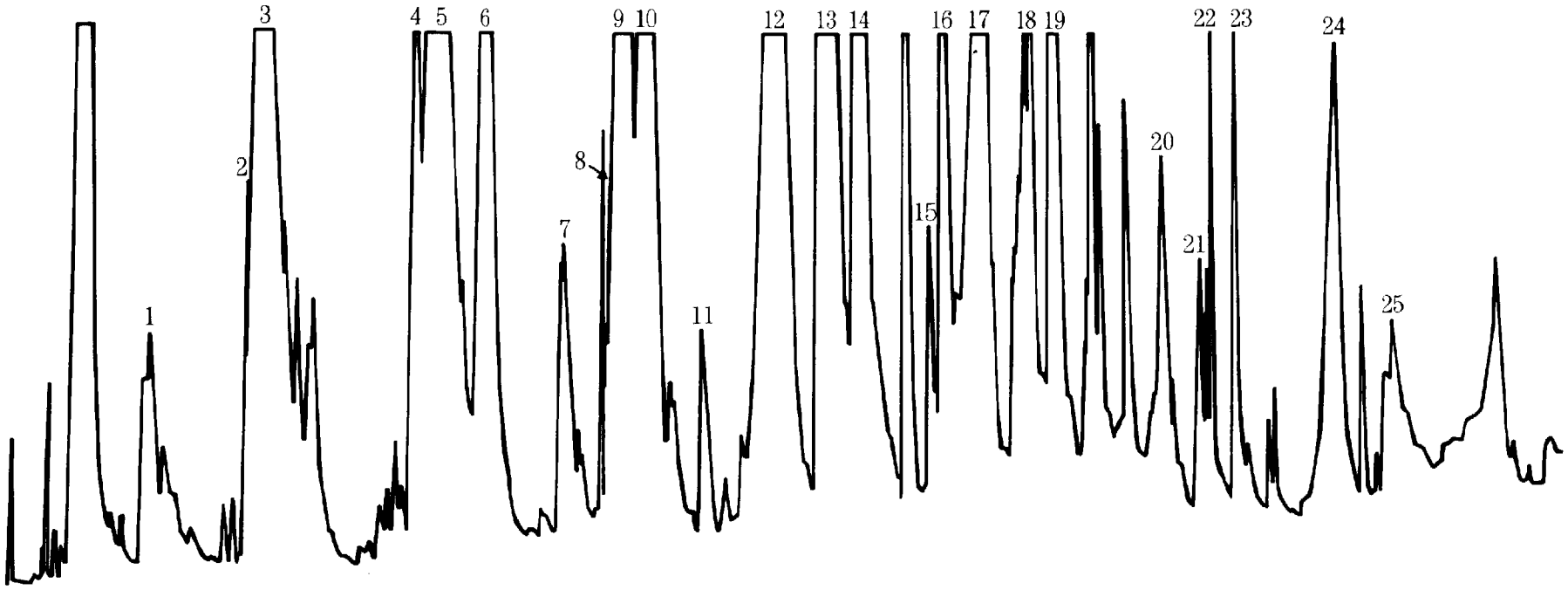

Figure 4.
Volatile Compounds from Steam Distillation of Oxidized Palm Oil

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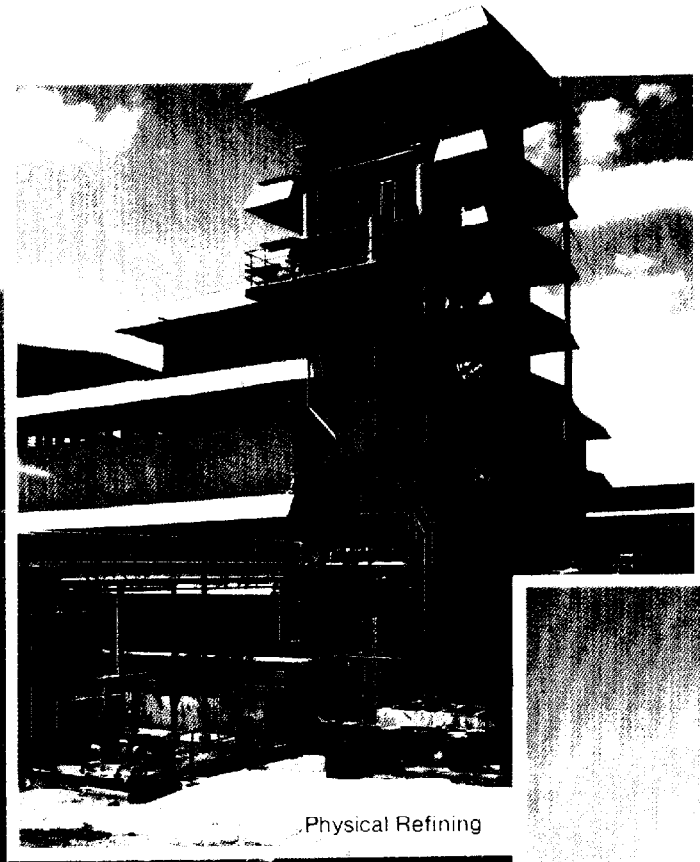

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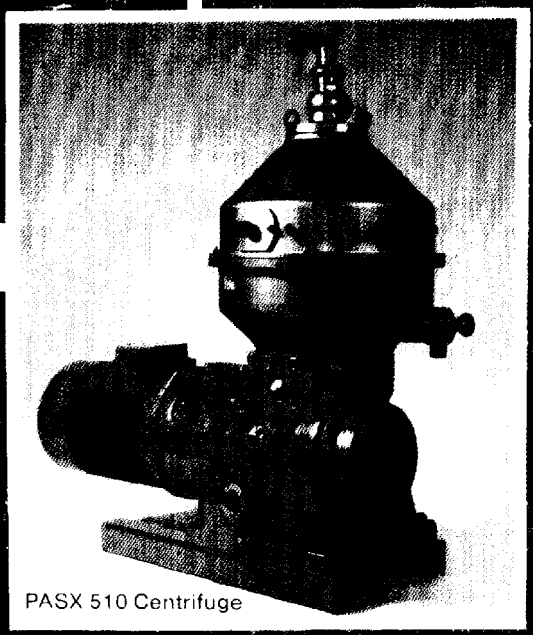

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