Soap and Related Products: Palm and Lauric Oil

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ABSTRACT

There are three main methods for producing soap: direct saponification of fats and oils, neutralization of fatty acids and saponification of fatty acid methyl esters. Our unique process of soapmaking, based on the methyl ester saponification method, is described here. By this process, high-quality toilet soaps can be produced from palm stearin and palm kernel oil as well as tallow and coconut oil.

A new sulfonation process was developed to produce high-quality α-SFMe (α-sulfo fatty acid methyl ester) from palm stearin as the starting material. Quality and performance of α-SFMe bear comparison with those of LAS, AES, AS or AOS. Thus α-SFMe is a promising surfactant for detergents and will contribute to expanding the use of palm oil in the near future.

INTRODUCTION

Fatty acid methyl esters have been used mainly as intermediates for fatty alcohols. From the viewpoints of physical and chemical properties, fatty acid methyl esters have the following advantages as compared with fatty acids: easy to handle because of lower melting points, more stable in storage, noncorrosive in the equipment used, and easy to distill because of lower boiling points.

Two routes are available for manufacturing fatty acid methyl ester: esterification of fatty acid obtained by fat-splitting, and direct interesterification of fats and oils with methanol (methanolysis process). According to the latter route, methyl esters with the above-mentioned advantages can be produced at relatively low costs. Thus the esters have been reevaluated as intermediates for various fatty acid derivatives. Among the raw materials for fats and oils, palm oil has been gaining attention as a material for soaps and detergents since the recent increase in its production in Malaysia.

The present paper reports on a unique process of soapmaking via fatty acid methyl ester and the development of α-sulfo fatty acid methyl ester (α-SFMe) derived from palm oil, which is highly promising as a surfactant for detergents.

METHYL ESTER SAPONIFICATION PROCESS

Soapmaking Process

There are three methods for manufacturing neat soap (65-70% anhydrous soap): direct saponification of fats and oil, neutralization of fatty acids and saponification of fatty acid methyl esters (Fig. 1). The first two methods are commonly used in soap industry.

Direct saponification. This is a traditionally used method in which fats and oils are saponified with alkali solution to yield fatty acid alkali salt (soap) and glycerol. This method requires complex procedures of salting out and washing to recover the glycerol formed by saponification and to remove impurities from the soap. In large-scale production, continuous methods are used, i.e., the Sharples process, DeLaval process and Monsavon process are typical (1).

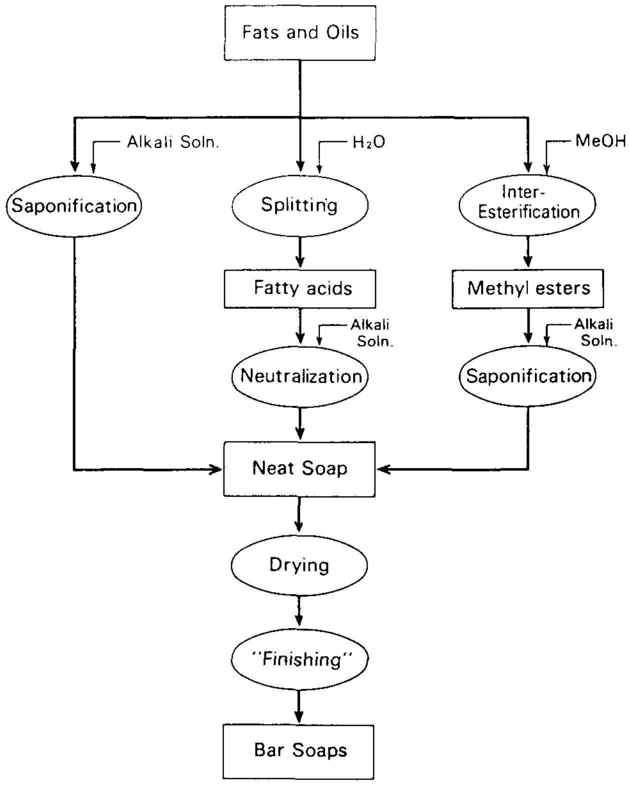


FIG. 1. Manufacturing processes of neat soap from fats and oils.

Fatty acid neutralization method. Fatty acids are neutralized with alkali solution to make soap. Mainly used are distilled fatty acids made by continuous hydrolization of fats and oils at high temperatures (250 C) and under high pressures (50 kg/cm^2) without catalysts. No salting out or washing procedures that are required in direct saponification are needed. Since fatty acids have undesirable properties such as relatively high melting point, thermal change in quality and corrosive action, proper attention should be given to their handling. Typical continuous processes are the Mills process (P & G), the Mazzoni SC process and the Armour process (2).

Methyl ester saponification method. The third method is to interesterify fats and oils using methanol to produce methyl ester which is then saponified with alkali solution to produce neat soap. This method has been vigorously studied in the U.S.A. since 1940 but the method seemed not to come off well. Lion Corporation succeeded in the industrial application of the continuous process of methyl ester saponification in 1960 (named ES-process). Following accumulated improvements, the process now produces good-quality methyl ester to manufacture high-quality toilet soaps in large scale (3).

ES-Process

A schematic flow diagram of the ES-process is shown in Figure 2. The ES-process consists of esterification of free fatty acids, interesterification of fats and oils, saponification of fatty acid methyl ester and recovery of glycerol and methanol. Chemical reactions in each step are shown in Figure 3.

Esterification of free fatty acids. This procedure is a preliminary treatment for the interesterification of fats and oils. Free fatty acids contained in fats and oils, which inhibit the catalytic action of the alkali in the next interesterification procedure, are converted into methyl esters by esterification. Characteristically, in this step a special synthetic resin is used as catalyst. Fats and oils containing free fatty acids are mixed with methanol and converted into methyl ester by continuous passage through the packed column of the catalyst resin. The low reaction temperature of 60 C prevents degradation of the raw oils and the fixed catalyst bed eliminates the need for catalyst filtration and separation.

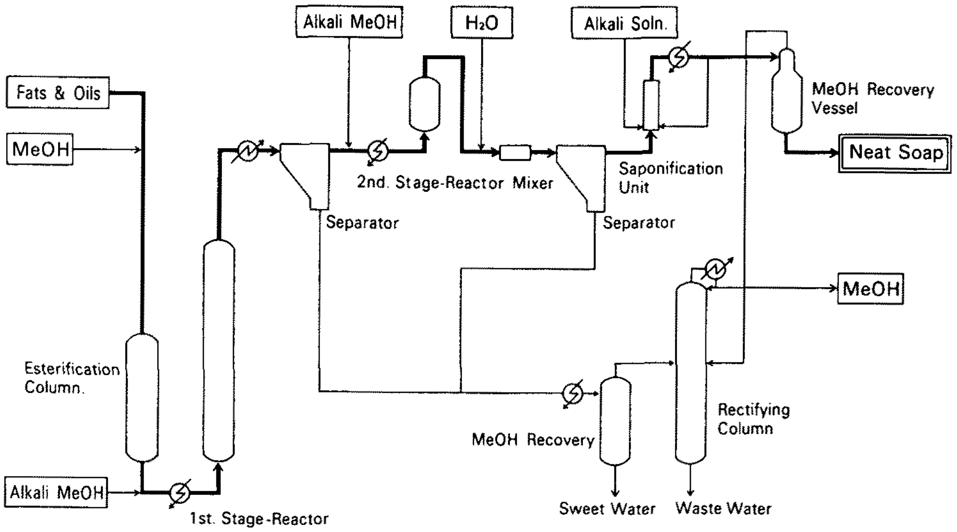
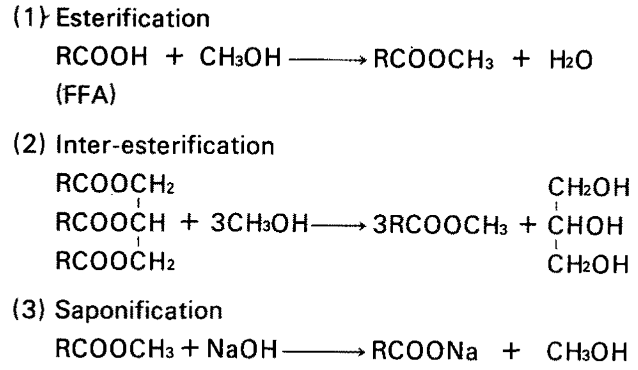


FIG. 2. Schematic flow diagram of the ES-process.



(1) Esterification

$$RCOOH + CH_3OH \longrightarrow RCOOCH_3 + H_2O$$

(FFA)

(2) Inter-esterification

$$\begin{array}{l} RCOOCH_2 \\ \quad | \\ RCOOCH \\ \quad | \\ RCOOCH_2 \end{array} + 3CH_3OH \longrightarrow 3RCOOCH_3 + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

(3) Saponification

$$RCOOCH_3 + NaOH \longrightarrow RCOONa + CH_3OH$$

FIG. 3. Chemical reactions in each step of the ES-process.

Interesterification of fats and oils. Processed fats and oils are converted into methyl esters by interesterification with methanol together with a small quantity of NaOH as catalyst at 60 C and under approximately atmospheric pressure. The raw oil conversion rate into methyl ester is at most 96% in the one-stage reaction owing to the chemical equilibrium. To circumvent such chemical equilibrium, a two-stage reaction is used in which the glycerol formed in the initial reaction is continuously removed in a specially designed separator and interesterification is again performed, achieving a high conversion rate of more than 99%. On the other hand, colored matter and impurities are occluded in a small quantity of the soap formed by the action of the alkali catalyst, yielding a dark brown layer separated from the ester layer during the process of separation. This refining action yields light-colored methyl esters at a high conversion rate. Interesterification is the most important procedure in the ES-process.

Saponification of fatty acid methyl esters. Methyl ester and alkali solution are supplied to the saponifier at a constant rate with rapid saponification at 100 C. The methanol secondarily produced in the reaction is recovered in a methanol recovery vessel, yielding neat soap with more than a 99% saponification rate.

Glycerol/methanol recovery. The lower layer discharged from the separator contains methanol, glycerol, soap and water. The methanol contained in the lower layer is recovered in a methanol recovery tower and yields sweet water as its residue. The sweet water is treated with sulfuric acid to yield 70% crude glycerol and a dark oil layer with accumulated impurities. The dark oil is used for lower grade soap. The methanol recovered is rectified and reused.

Advantages of the ES-process.

1. Methyl ester/soap of light color can be obtained in high yield.
2. Soap obtained has a good color and excellent quality stability because the low temperature during the process prevents degradation of the oil and methyl ester, and also because methyl ester is considerably refined in the interesterification step.
3. Glycerol of high concentration (more than 70%) is recovered in good yield.
4. Fatty acid methyl ester can be distilled and refined if necessary, allowing the use of raw oils.
5. No corrosion occurs in the equipment.
6. Methyl ester used as the intermediate is more stable in storage and easier to handle than fatty acids because of low melting point.
7. The low temperature and atmospheric pressure required for the process allow easy plant maintenance.

We are manufacturing quality toilet soaps by this ES-process using tallow and coconut oil as the base materials. Recently palm oil has been gaining attention as a raw material for soap. We have conducted trial production of soap using palm stearin and palm kernel oil by the ES-process and have confirmed its quality is as high as that of soap from tallow and coconut oil.

DEVELOPMENT OF α-SFMe

Background

As shown in Figure 4, one of the derivatives developed from fatty acid methyl ester is α-sulfo fatty methyl ester (α-SFMe), an anionic surfactant formed by sulfonation of fatty acid methyl ester. At present, linear alkylbenzene sulfonate (LAS), alcohol ethoxy sulfate (AES), alcohol sulfate (AS) and α-olefin sulfonate (AOS) are mainly used as anionic surfactants for detergents. Most of these materials have been synthesized starting from petroleum. Since the oil crisis in 1973, however, natural fats and oils have been reevaluated and α-SFMe synthesized from fats and oils has been gaining attention as a raw material. α-SFMe, though its synthesis had been long known and studied, posed problems to be solved in terms of its quality such as unsatisfactory color and byproduct of di-sodium α-sulfo fatty acid (α-SFNa2) of low performance.

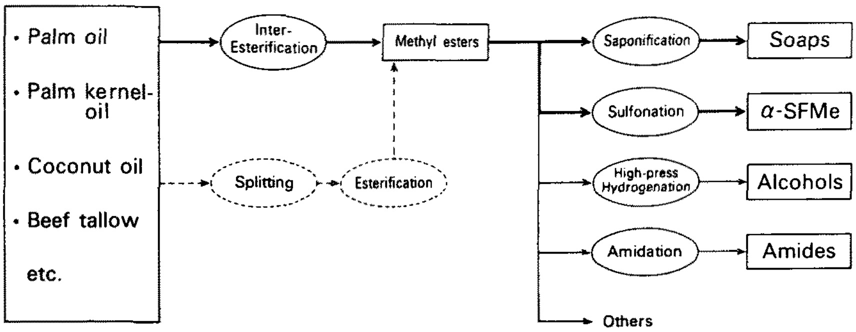


FIG. 4. Derivatives from fatty acid methyl esters.

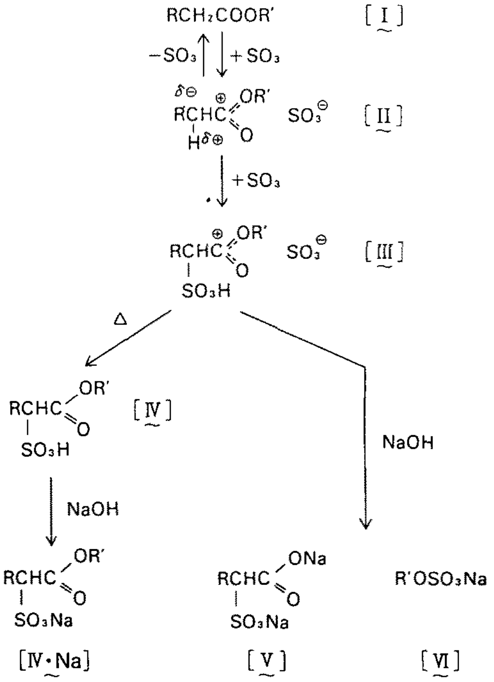


FIG. 5. Mechanism of sulfonation of fatty acid esters (6).

New α-SFMe Process

Palm stearin or beef tallow is used as the starting material. Hardened palm stearin methyl ester is sulfonated by gaseous sulfur trioxide to give α-SFMe. Several studies (4-7) have been reported on the mechanism of this reaction, which has not yet been fully clarified. One of the previously reported mechanisms is shown in Figure 5 (6). Most of the reports commonly suggest that the reaction occurs via an intermediate with 2 moles of SO_3 and neutralization without elimination of the SO_3 added to the methyl ester group forms a byproduct α-SFNa2 (di-salt). This suggestion reasonably explains the phenomenon, though the structural formula of the intermediate is not fully clarified.

Figure 6 shows the schematic flow diagram of the newly developed α-SFMe. The sulfonating agent, SO_3 gas, is manufactured by the sulfur burning process. Palm stearin methyl ester is supplied to the sulfonator where it is sulfonated by the SO_3 gas. The sulfonator is a film-type reactor originally developed by Lion for sulfonation of such surfactants as AOS and AES [named T.O.-Reactor (8)]. It allows mild sulfonation by controlling the reaction temperature. The sulfonated substance separated from exhaust gas in the gas-liquid separator is transferred to the specially designed acid-treatment unit, where the sulfonated substance is sufficiently mixed with methanol and a small quantity of hydrogen peroxide. Remarkable bleaching effect is obtained in this step. The bleached substance is neutralized by vigorous mixing with NaOH solution in the neutralizer. Lastly, the methanol contained in the neutralized slurry is recovered in the methanol recovery unit giving a high concentration (50-60% A.M. content) of α-SFMe slurry without α-SFNa2. Typical qualities resulting from this process (9) are shown in Table I. Its advantages are:

- The manufacture of α-SFMe containing substantially no α-SFNa2, previously considered impossible, is made possible.
- The process allows the manufacture of α-SFMe of good color, comparable to that of petroleum-derived surfactants such as LAS.
- Slurry obtained has 60% active matter, compared with the former maximum content of 35%.
- A continuous sulfonation plant that is used for LAS,

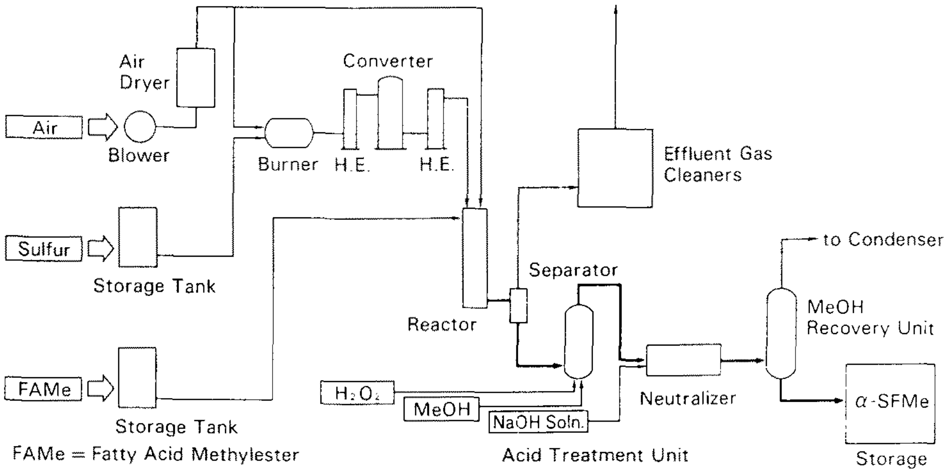


FIG. 6. Schematic flow diagram of the newly developed process for α-SFMe.

TABLE I

Typical Qualities of α-SFMe

		New process	Previous process
Active matter	(%)	55	35
α-SFMe	(%)	55	26
α-SFNa₂	(%)	trace	9
$\frac{\alpha\text{-SFMe}}{\alpha\text{-SFMe} + \alpha\text{-SFNa}_2} \times 100$	(%)	ca. 100	74
Color (5% Klett)[a]		50	200
Un-reacted oil	(%)[b]	1.6	3.0

Raw material: Palm stearin methyl ester (hardened, distilled).

[a] 5% A.M. soln., 40 mm cell, No. 42 Blue filter.

[b] % based on A.M.

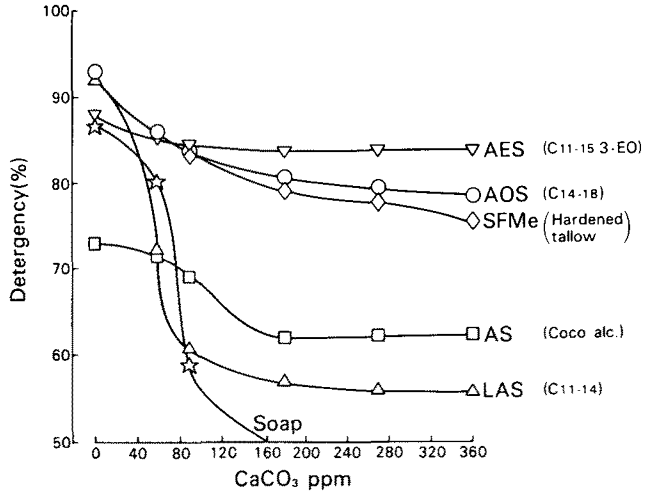


FIG. 7. Water hardness vs. detergency of surfactants in phosphate-free formulation (10).

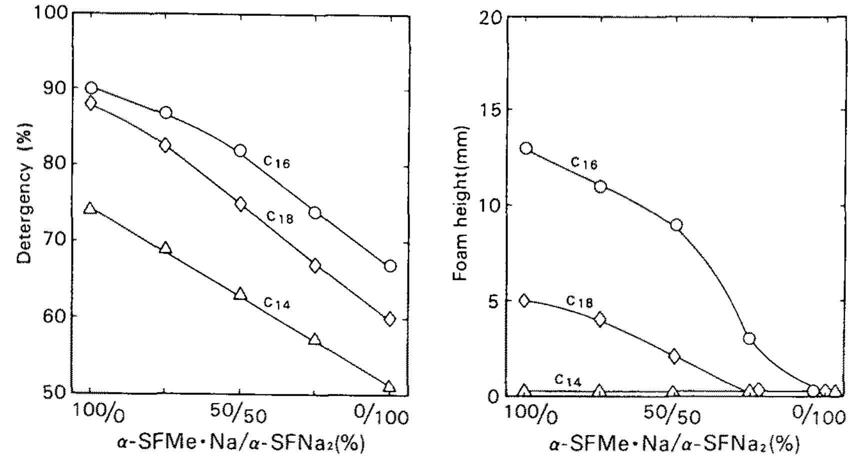


FIG. 8. Effect of binary system α-SFMe/α-SFNa2 on detergency and foaming properties in phosphate-free formulation (6). (Water hardness 54 ppm)

AES, etc., can be used for the production of α-SFMe with some additional equipments.

- α-SFNa2 content can be controlled in the range of 0-50%, if necessary, by changing conditions.
- α-SFMe with good odor is obtained.

The quality disadvantages of α-SFMe, i.e., byproduct to be controlled and color improvement, have been solved by the development of this process.

Adaptability of α-SFMe to Detergents

α-SFMe is available as a surfactant for detergents with the following advantages:

- It has high detergency and hard water resistance (Fig. 7).
- As the order of excellence is C16 α-SFMe > C18 α-SFMe > C14 α-SFMe in terms of detergency and foaming, beef tallow and palm stearin composed of C16 and C18 carbon chain are best as the raw oils. Note that an increase in α-SFNa2 leads to a sudden lowering of performance, so that the substance should be carefully handled during the detergent manufacturing process (Fig. 8).
- It has good biodegradability (Fig. 9). We have already established the techniques of manufacturing detergents compounded with α-SFMe synthesized from palm stearin.

FUTURE TRENDS

The development of a process which allows the manufacture of high-quality α-SFMe has opened the way for a new way of application of palm stearin to detergent, although the application of palm stearin to soap is not a novel idea. At present surfactants for detergents such as LAS, AES, AS and AOS, are mostly dependent on petroleum-derived materials, while a part of fatty alcohol is manufactured from coconut oil. Since the oil crisis, however, natural fats and oils have been expected to gain more and more significance as industrial raw materials because they are renewable as compared with petroleum-derived materials that are expected to be exhausted, and also because their production is expected to be substantially increased by biotechnology and agricultural technology. As α-SFMe is a surfactant equal or superior to LAS, AES, AS or AOS, we believe that

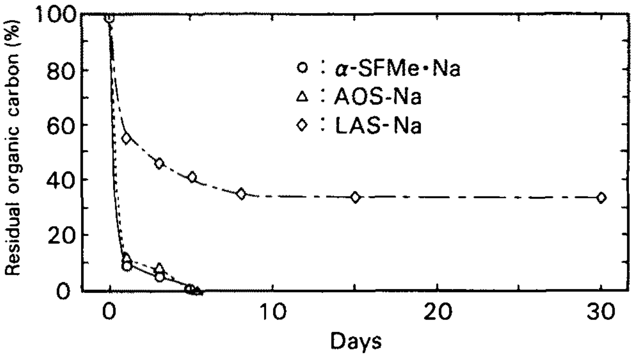


FIG. 9. Biodegradability of α-SFMe, AOS and LAS by residual organic carbon method (6).

palm oil will compete well with petroleum-derived materials and rank as one of the significant materials for detergents in the near future.

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Other Oleochemical Uses: Palm Oil Products

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ABSTRACT

Production and consumption of palm oil and its products are discussed as they relate to industrial products. The large volumes of palm oil being produced and projected for future production should increase the use of its byproducts in oleochemicals. Tallow is the most competitive fat to palm oil in these applications, but its market share (at least in Japan) seems to be declining. An enzymatic process for hydrolyzing fats and oils by a solid phase process is described.

INTRODUCTION

In the near future, palm oil is expected to be one of the largest fat and oil resources along with soybean oil. The main use of palm oil is in food products. Technologies such as fractionation, hydrogenation, and interesterification have made it possible to use more palm oil for these edible purposes. Industrial uses of palm oil could be learned based on those of tallow, whose fatty acid composition is similar to that of palm oil. This presentation discusses mainly what kinds of palm oil products should be considered as the raw materials for industrial uses; what kinds of technological improvements will be expected for the development of industrial applications, and what are potential new uses.

OUTLOOK FOR PALM OIL

The high potential for palm oil is described in relation to: world fat and oil production; palm oil production in Malaysia; vegetable oil production and fatty acid composition.

World Fat and Oil Production

World fat and oil production has reached 56.6 million tons with an increase of 16.7 million tons in the last ten years (Table I). In particular, the growth of vegetable oils for food was very remarkable, i.e., palm oil production was tripled, and soybean and rapeseed oils were doubled. Animal fat production showed less than 20% growth, but tallow and butter production did increase. It is remarkable that the proportion of vegetable oils for edible uses in world fat and oil production increased from 61% to 69%. The growth of world fat and oil production in the past 10 years was due to the large harvests of palm, soybean and rapeseed oils. It is assumed that this tendency will continue in the future.

TABLE I

World Oil and Fat Production in 1970 and 1980

	1970	1980	Decade growth (%)
	(10,000 metric tons)		
Edible vegetable oils			
Soybean	608	1,222	201
Palm	172	506	294
Sunflower	380	478	126
Rapeseed	188	387	206
Coconut	214	326	152
Cottonseed	262	321	123
Peanut	327	280	86
Olive	125	193	154
Others	161	220	137
Subtotal	2,437	3,933	161
Industrial vegetable oils			
Linseed	111	64	
Others	64	63	
Subtotal	175	127	73
Marine animal oils			
Fish	104	117	
Others	21	7	
Subtotal	125	124	99
Animal fats			
Tallow and grease	435	604	139
Lard	413	383	93
Others	411	493	120
Subtotal	1,259	1,480	118
Total	3,996	5,664	142

Source: U.S. Department of Agriculture.

Palm Oil Production in Malaysia

Palm oil production, which showed the largest growth compared with other fat and oil resources, has reached 13% of world vegetable oil consumption for food in 1980, up from 7% in 1970. Palm oil production in Malaysia, having reached 3.5 million tons (60% of world production) in 1982, is expected to rise to 4 million tons in 1985, and to 6 million tons in 1990s (Table II). The big increase of palm oil in Malaysia is mainly dependent upon cultivation of idle land by FELDA, new hybrid seeds yielding bigger harvest and oil and pollination by the weevil.

Malaysia exported 3 million tons of palm oil and products in 1982, 93% of which was palm oil products (Table III). This figure was equivalent to 85% of total production. Taking these into account, the development of industrial applications of palm oil and products is getting more and more important.