

# Quality of Some Fatty Acids Produced in Malaysia: An Update

Noorazah Zolkarnain\* and Mohtar Yusof\*

## INTRODUCTION

Today's market is becoming more and more demanding of fatty acids with high quality. The fatty acid industry is one of those that are experiencing rapid growth in the Malaysian oil palm industry. It has expanded significantly since the first fatty acid plant was established in 1979. Nowadays, many new fatty acid plants have been built in the Southeast Asian region, using palm oil and coconut oil as the major sources of raw materials for the production of caproic to oleic acids. The export of Malaysian fatty acids has increased by five times in 10 years, from 190 178 t in 1997 to 913 283 t in 2006 (Figure 1). The value of export has also increased by six times in the same period. The export in 2006 was increased by 133 218 t or 17.1% compared to 2005. Fatty acids are the main oleochemical produced in Malaysia, comprising 42.3% of the total oleochemicals exported in 2006 (MPOB, 1998-2007). Figure 1 also shows that the trend of fatty acid export has increased year by year since 1999.

Availability of raw materials and good infrastructure has turned Southeast Asia into a manufacturing hub for the fatty acid industry. Fatty acid producers in Malaysia and Indonesia are also enhancing their manufacturing capacities in response to the increasing demand.

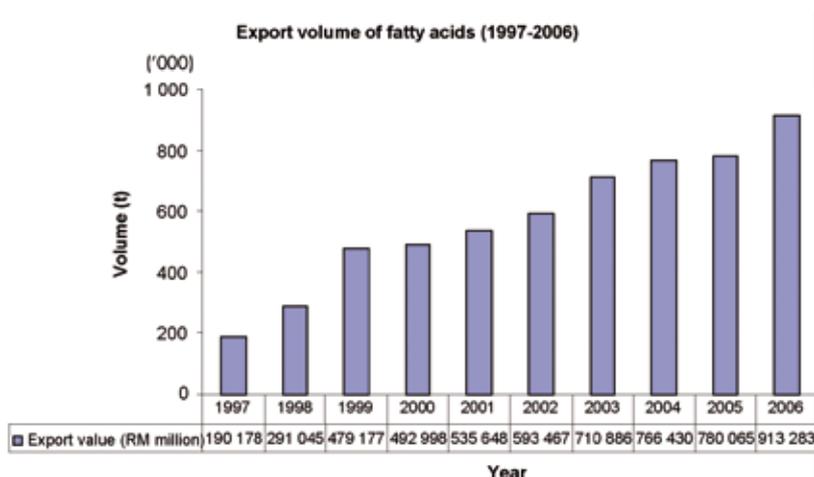
## FATTY ACIDS

Fatty acids are known as carboxylic acids with hydrocarbon chains that are obtained from the hydrolysis of fat or oil. They can be classified into three types, namely, saturated, monounsaturated and polyunsaturated fatty acids. Saturated fatty acids have no double bonds in the alkyl chain, whereas monounsaturated fatty acids have one double bond while polyunsaturated fatty acids have more than one double bond in the alkyl chain. In nature, almost all fatty acids have an even

number of carbons. This is because the fatty acids are synthesized stepwise from acetyl building blocks. With proper selection, fatty acids

can be used as starting materials for the production of valuable oleochemical products. These fatty acids can be used as feedstock in the production of soaps, medium-chain triglycerides, polyol esters, detergents, emulsifiers, plastics, textiles, cosmetics, lubricants and other products (Fereidoon, 2005).

In Malaysia, there are 11 manufacturers of fatty acids. A common method employed for the fatty acid production is by fat splitting, carried out at high temperature and high pressure. Various types of fatty acids have been produced in Malaysia, i.e. crude or refined, and hardened or unhardened, which can be obtained from palm oil or palm kernel oil or their products. Generally, the fatty acids produced can be classified into three categories: high purity, mixed and blended. Solid fatty acids are



Source: MPOB (1998-2007).

Figure 1. Exports of fatty acids from 1997 to 2006.

\* Malaysian Palm Oil Board,  
P. O. Box 10620,  
50720 Kuala Lumpur,  
Malaysia.  
E-mail: azah@mpob.gov.my

normally marketed in the form of flakes or beads.

Fatty acids and their derivatives have a wide range of applications such as in the production of surfactants, cosmetics, personal care products, pharmaceuticals and other industrial specialty performance chemicals. Due to the increased growth in application, the demand for quality fatty acids is growing worldwide. To protect the interest of the consumers, fatty acids used in the production of these products must conform to the highest standards.

### CHARACTERISTICS OF FATTY ACIDS

The physical properties of fatty acids such as their melting point, water solubility, specific heat, viscosity and refractive index are dependent on the chain lengths of the fatty acids and the degree of unsaturation of the hydrocarbon chains. Melting points of fatty acids increase with carbon number, while melting points of unsaturated fatty acids are lower than those of saturated fatty acids of the same carbon chain length. An increase in the chain length and degree of unsaturation will decrease the water solubility of fatty acids, but will increase their refractive index. For specific heat, an increased degree of unsaturation of fatty acids will increase the specific heat value. Unlike the other properties, the viscosities of these fatty acids will increase with chain length, but decrease with an increasing degree of unsaturation (Mohammad *et al.*, 2005).

### SURVEYS ON THE CHARACTERISTICS OF FATTY ACIDS

A survey was carried out in 2003 to update the earlier findings on the characteristics of fatty acids that were reported in 1998 (Mohtar *et al.*, 1998). A random check was conducted in 2006 to evaluate the quality parameters that had been obtained in the 2003 survey. Fatty acid samples were obtained from seven manufacturers in Malaysia. Eight fatty acid samples of different categories, *i.e.* distilled topped palm kernel fatty acid, caprylic-capric acid (C8-C10), lauric acid (C12), myristic acid (C14), palmitic acid (C16), stearic acid (C18), stearic acid 35% and stearic acid 52%, were analysed to characterize their quality parameters. Distilled topped palm kernel fatty acid, caprylic-capric acid, lauric acid and myristic acid are products from palm kernel oil, while palmitic acid, stearic acid and their blends are products from palm oil.

The quality parameters monitored were acid value, saponification value, iodine value, titre value, moisture content and fatty acid composition. Analyses were done according to the following AOCS or Malaysian Standard test methods (*Table 1*).

The chemical and physical characteristics of fatty acids produced in Malaysia are shown in *Tables 2* and *3*. For comparison, the characteristics of fatty acids carried out in the previous survey are presented in *Tables 4* and *5*.

#### Acid Value (AV)

This parameter is also known as the acid number. It is defined

as the number of milligrams of potassium hydroxide required to neutralize organic acids present in 1 g of sample. It is one of the quality parameters adopted to indicate the quality of fatty acids. The sample must first be dissolved in a suitable solvent (which is neutralized ethanol) before titrating it with a standard alkali (standardized sodium hydroxide) in the presence of phenolphthalein as an indicator. To prepare neutralized ethanol, about 50 ml ethanol is placed in a flask and the solution brought to boil over a hot plate. Then, about 0.5 ml of phenolphthalein is added into the solution and neutralized by adding 0.1 N sodium hydroxide drop by drop until a permanent faint pink colour is obtained.

The mean molecular weight (MMW) of the pure monocarboxylic fatty acid or its mixture can be calculated as  $MMW (g\ mol^{-1}) = 56100/AV$ . The molecular weight will be smaller if the acid value is higher. The acid values of fatty acids decrease with an increasing number of carbon atoms in their molecules.

Fatty acid producers in Malaysia have consistently produced high quality fatty acids from 1998 to 2006. This is indicated by the mean of acid values of the fatty acids obtained from the surveys in 2003 and in 2006, which were found to be within the reported values as published in 2001 (Mohtar *et al.*, 2001).

#### Saponification Value (SV)

This is defined as the milligrams of potassium hydroxide required to hydrolyze 1 g of sample. It is used to characterize fatty acids or esters, and to measure the average

TABLE 1. METHODS USED IN THE FATTY ACID ANALYSES

Item No.	Quality parameter	Method of analysis
1.	Acid value (mg KOH g <sup>-1</sup> )	AOCS Da 14-48 (1997)
2.	Saponification value (mg KOH g <sup>-1</sup> )	AOCS Tl 1a-64 (1997)
3.	Iodine value (g I <sub>2</sub> /100 g)	MS 817: Part 3: 1997
4.	Titre value (°C)	AOCS Tr 1a-64 (1997)
5.	Moisture content (%)	MS 252: Part 7: 1992 MS 817: Part 4: 1998
6.	Fatty acid composition (%)	MS 252: Part 22: 1994

molecular weight of all the fatty acids present. SV is determined by heating a fatty acid sample under reflux with an ethanolic potassium hydroxide solution and then, back titrating the excess hydroxide with a standardized hydrochloric acid solution until a faint pink end-point is obtained. Like AV, phenolphthalein is also used as the indicator. The titration should be carried out immediately after the

heating stage, otherwise a lower SV is obtained because the saponified solution will absorb carbon dioxide from the atmosphere, and this will affect the titration result.

A higher SV indicates that the fatty acid in the sample has a low average molecular weight. It was also observed that the SV decreased with an increasing carbon chain length of the fatty acids. This parameter is important for

soap producers in determining the quantity of caustic soda required to completely saponify fat or fatty acids.

Most of the SV of the fatty acids surveyed in 2003 and 2006 were similar to those published in 2001.

#### Iodine Value (IV)

This value measures the unsaturation moiety of fatty acids expressed as the number of grams of iodine absorbed by a 100-g sample. Samples with higher IV commonly have poor colour and poor oxidative stability properties. The most common method used for determining IV is the Wijs test, which is applicable to fatty acids and their derivatives containing isolated (methylene-interrupted) double bonds. The accuracy of this test depends on the quality of the Wijs solution which is sensitive

TABLE 2. CHARACTERISTICS OF SOME FATTY ACIDS PRODUCED IN MALAYSIA ANALYSED IN THE 2003 AND 2006 SURVEYS

Product	Acid value (mg KOH g <sup>-1</sup> )		Saponification value (mg KOH g <sup>-1</sup> )		Iodine value (g I <sub>2</sub> /100 g)		Titre (°C)		Moisture content (%)	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Distilled topped palm kernel fatty acid	248.5-251.6	250.3	249.2-252.3	250.6	16.7-19.6	18.5	26.1-27.4	26.7	0.04-0.24	0.12
Caprylic-capric acid	354.2-363.7	358.2	354.6-364.3	358.8	0.1-0.4	0.3	0.6-6.1	4.3	0.04-0.50	0.18
Lauric acid 98%	278.7-281.1	279.5	279.5-282.4	280.5	0.04-0.20	0.06	43.3-44.0	43.6	0.03-0.09	0.05
Myristic acid 99%	244.8-245.8	245.5	245.7-247.4	246.4	0.10-0.20	0.10	53.7-54.2	54.0	0.02-0.12	0.05
Palmitic acid 95%	217.4-219.5	218.5	218.3-220.9	219.7	0.1-0.2	0.1	60.6-62.6	61.8	0.05-0.17	0.13
Stearic acid 35%	208.0-211.6	209.9	209.0-212.4	210.8	0.04-0.30	0.13	54.8-56.1	55.4	0.01-0.34	0.14
Stearic acid 52%	205.1-207.5	206.7	206.4-209.1	207.7	0.2-0.4	0.2	55.6-56.3	56.1	0.02-0.24	0.11
Stearic acid 90%	195.5-198.8	197.0	196.2-200.6	198.0	0.3-0.9	0.6	67.5-68.4	67.9	0.05-0.33	0.14

TABLE 3. FATTY ACID COMPOSITION OF THE FATTY ACIDS IN THE 2003 AND 2006 SURVEYS

Product	Fatty acid composition (%)											
	C6:0	C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C20:0	Others
Distilled topped palm kernel fatty acid	-	-	0.36	53.8	17.6	9.60	0.03	2.30	14.4	1.60	0.07	0.17
Caprylic-capric acid	0.59	53.7	44.2	1.20	-	-	-	-	-	-	-	0.27
Lauric acid 98%	-	-	0.20	99.5	0.20	0.02	-	-	-	-	-	0.10
Myristic acid 99%	-	-	-	0.31	99.5	0.11	-	0.01	-	-	-	0.09
Palmitic acid 95%	-	-	-	0.03	0.82	97.7	-	1.06	-	-	-	0.11
Stearic acid 35%	-	-	-	0.07	0.64	60.0	-	38.7	0.01	-	0.36	0.03
Stearic acid 52%	-	-	-	0.07	0.47	53.1	-	60.0	-	-	0.54	0.03
Stearic acid 90%	-	-	-	-	0.01	3.51	-	94.7	-	-	0.77	0.13

TABLE 4. CHARACTERISTICS OF FATTY ACIDS PRODUCED IN MALAYSIA FROM AN EARLIER STUDY

Product	Acid value (mg KOH g <sup>-1</sup> )		Saponification value (mg KOH g <sup>-1</sup> )		Iodine value (g I <sub>2</sub> /100 g)		Titre (°C)	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Distilled topped palm kernel fatty acid	245.7-255.7	250.3	246.5-256.1	251.6	16.6-18.5	17.6	25.5-27.0	26.5
Caprylic-capric acid	353.1-361.7	358.2	356.3-365.5	359.0	0.12-0.70	0.45	4.7-6.8	5.8
Lauric acid 98%	276.2-281.5	279.3	277.0-285.0	280.9	0.04-0.57	0.19	43.2-44.0	43.7
Myristic acid 99%	244.4-249.0	246.3	247.0-252.0	247.9	0.10-0.50	0.29	53.2-54.5	53.9
Palmitic acid 95%	215.4-220.8	218.8	218.0-221.3	219.8	0.08-0.57	0.34	61.0-62.8	62.1
Stearic acid 35%	210.8-212.6	211.6	213.6-217.0	214.9	0.21-0.29	0.24	55.0-55.5	55.1
Stearic acid 90%	196.1-199.2	197.1	200.9-202.0	201.4	0.55-0.90	0.72	67.0-68.5	67.7

Source: Mohtar *et al.* (2001).

TABLE 5. FATTY ACID COMPOSITION OF FATTY ACIDS PRODUCED IN MALAYSIA FROM AN EARLIER STUDY

Product	Fatty acid composition (%)											
	C6:0	C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C20:0	Others
Distilled topped palm kernel fatty acid	0.05	0.02	0.28	52.1	16.9	11.1	-	2.8	15.0	1.6	0.02	-
Caprylic-capric acid	0.17	53.3	44.6	0.48	0.06	0.02	-	-	-	-	-	0.77
Lauric acid 98%	-	-	0.27	99.1	-	-	-	-	-	-	-	-
Myristic acid 99%	-	-	-	0.70	99.0	0.20	-	0.10	-	-	-	0.06
Palmitic acid 95%	-	-	-	0.02	0.82	97.9	-	1.10	-	-	-	0.2
Stearic acid 35%	-	-	-	-	0.40	63.3	0.13	35.8	-	-	0.30	-
Stearic acid 90%	-	-	-	-	-	4.70	0.06	94.2	0.03	-	0.80	0.05

Source: Mohtar *et al.* (2001).

to light and has limited storage stability. Instead of carrying out the wet analysis, the theoretical IV of fatty acids can also be determined from the fatty acid composition analysed using gas chromatography, by calculating the weighted average of the IV of the individual unsaturated fatty acids as given in AOCS Recommended Practice Cd 1c-85 (AOCS, 2007). The IV of the common pure unsaturated acids are as follows: palmitoleic acid, 99.76; oleic acid, 89.86; linoleic acid, 181.0; linolenic acid, 273.5, gadoleic acid, 81.75 and erucic acid, 74.97 (Frank and Richard, 2001).

Most of the saturated fatty acids have low IV, normally below 0.1 g I<sub>2</sub>/100 g. However, for the unhydrogenated fatty acids such as distilled topped palm kernel fatty acid, the IV ranges from 16.7

to 19.6 g I<sub>2</sub>/100 g with a mean of 19.9 g I<sub>2</sub>/100 g.

The IV of fatty acids surveyed in 2003 and 2006 were similar to those published in 2001.

#### Titre Value

This parameter is used to determine the solidification point of fatty acids. It is defined as the temperature at which a sample of melted fatty acid solidifies under specific cooling conditions. The determination can be carried out using two different approaches. For any fatty acid sample that has a titre value above 35°C, the medium used for the titre test is water. Meanwhile, for samples with titre values below 35°C, the test is carried out in a water-ethylene glycol mixture. This test is very useful if there is a need to predict

the purity of the acid or types of fatty acids present in a sample.

Theoretically, the titre value of fatty acids will increase with an increasing number of carbon atoms in their molecules. However, the survey showed that titre values of blended fatty acids, *i.e.* stearic acid 35% and stearic acid 52%, were lower than that of stearic acid 90% or palmitic acid. Stearic acid can form a eutectic mixture with the palmitic acid present, which is a typical behaviour for a mixture of two saturated acids having two-carbon atoms in their chain length. However, the stearic acid with purity of 90% has a higher titre value compared to palmitic acid. The same observation was found in the caprylic-capric acid mixture.

The titre values of fatty acids surveyed in 2003 and 2006 were similar to those published in 2001.

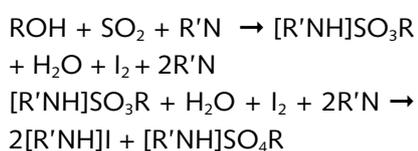
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### Moisture Content

The moisture content is measured by the loss in mass after heating a sample at  $103 \pm 2^\circ\text{C}$  in an oven at atmospheric pressure until practically constant mass is reached. The loss in mass could be due to moisture and volatile matter that are present in the sample. In these surveys, two different methods were used to determine the moisture content in the sample: the Karl Fischer coulometric method (Malaysian Standard, 1998) or the hot plate method (Malaysian Standard, 1992). The Karl Fischer method is used to determine moisture only. As fatty acids with C14 and below contain high volatile matter, the hot plate method is not suitable for measuring the water and volatile matter contents in these samples; instead the Karl Fischer method was used.

The Karl Fischer reagent reacts specifically with water and can detect the presence of water at as low a content as 0.1% or less. This method based is on the Bunsen reaction, which is the reaction between iodine and sulphur dioxide in an aqueous medium. In the Karl Fischer coulometric method, first, iodine is produced by electrolysis of the reagent containing iodide ions, and then, the water content in a sample is determined by measuring the quantity of electricity which is required for the electrolysis (*i.e.* for the production of iodine), based on the quantitative reaction of the generated iodine with water:



As may be seen from the reaction equations above, the alcohol reacts with sulphur dioxide ( $\text{SO}_2$ ) and base to form an intermediate alkylsulphide salt, which is then oxidized by iodine to an alkylsulphate salt. This oxidation reaction consumes water. The reactive alcohol is typically methanol or 2-(2-ethoxyethoxy)ethanol, also known as diethylene glycol monoethyl ether (DEGEE), or any other suitable alcohol. The classic Karl Fischer reagent contains pyridine, a noxious carcinogen, as the base. The reagents most frequently used today are pyridine-free and contain imidazole or primary amines instead. For accurate results, the Karl Fischer coulometer is periodically calibrated by using a commercially available liquid standard of known moisture content.

The hot plate method is used to measure both the contents of moisture and volatile matter in C16 and C18 fatty acid samples. The sample is placed in a beaker and heated on a hot plate at a specified temperature over a certain time. The temperature of hot plate is determined by using a thermometer. The loss in weight during the heating is calculated by the difference in sample weight before and after heating. This method is not suitable for the following: hydroxylated fatty acids because the boiling point of this compound is lower than  $100^\circ\text{C}$ ; highly unsaturated fatty acids because high temperature can form dimer of a polymer compound; and short-chain fatty acids (lower than 14 carbon atoms) because they have high volatile matter contents.

The moisture contents of fatty acids in this survey were low, *i.e.* below 0.2%.

### Fatty Acid Composition

Fatty acid composition can indicate the purity of the fatty acids and can be used to determine the types of fatty acids. The saturated and unsaturated fatty acids with 8 to 24 carbon atoms are quantitatively determined by gas chromatography (GC) through their corresponding methyl esters. Fatty acids exhibit strong hydrogen bonding and the carboxylic groups interacts strongly with the stationary phase used in this analysis, thus resulting in peak tailing, and the quantitative results are not reliable (Frank *et al.*, 2001).

A reference standard mixture of fatty methyl esters of known composition is used to identify the various component fatty acids, by comparing the retention times of the corresponding peaks of the sample with those of the reference mixture.

A summary of the fatty acid compositions is shown in *Table 3* for samples surveyed in 2003 and 2006, whereas *Table 5* shows the fatty acid composition of samples as published in 2001.

### CONCLUSION

It was found that the quality parameters of the eight fatty acids analysed in 2003 and 2006 were similar to those reported in 2001. Thus, the fatty acid producers in Malaysia have constantly been producing good quality fatty acids since 1998.

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