



UNIVERSITI PUTRA MALAYSIA

**PREPARATION OF FATTY AMIDES FROM METAL SOAPS
UNDER MICROWAVE IRRADIATION**

LEE YEAN KEE

FSAS 2002 60

**PREPARATION OF FATTY AMIDES FROM METAL SOAPS
UNDER MICROWAVE IRRADIATION**

By

LEE YEAN KEE

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfillment of the Requirements for Degree of Master of Science**

December 2002



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

**PREPARATION OF FATTY AMIDES FROM
METAL SOAPS UNDER MICROWAVE IRRADIATION**

By

LEE YEAN KEE

December 2002

Chairman: Associate Professor Dr. Karen Badri

Faculty: Science and Environmental Studies

An efficient, high yield method of preparation of pure fatty amides was found through this research. From the 3-reactant system that consists of fatty sodium soap, a source of ammonia (or amine) and ammonium chloride, the fatty amides were formed when they were premixed and sealed in a glass vessel and then exposed to microwave irradiation. Primary amides were formed from the reaction of fatty sodium soap, urea or ammonium carbonate and ammonium chloride, whereas secondary amides were formed from the reaction of fatty sodium soap, amines and ammonium chloride. Primary amides successfully synthesized through this method are myristamide, palmitamide, oleamide and stearamide, whereas secondary amides synthesized from this method are *N*-butyl myristamide, *N*-butyl palmitamide, *N*-butyl stearamide, *N*-hexadecyl myristamide, *N*-hexadecyl palmitamide, and *N*-hexadecyl stearamide. Product identification was done through IR, NMR and CHN. The syntheses of myristamide and palmitamide were optimized by varying the irradiation time, reactant ratio and volume of reaction vessels. These optimized conditions were used for other primary amides syntheses. It was found that the best reactant ratio (sodium soap: urea: ammonium chloride) is 1:0.5:1 with 2.5 cm³ volume of reaction vessel when 0.5 g of reactant mixture were irradiated for 9 minutes. In the two or three-reactant systems

involving fatty acids and, or sodium soap with urea or ammonium carbonate as the source of ammonia, the presence or absence of ammonium chloride in these reactant mixtures were studied. The reaction involving soaps required the three-reactant system, where ammonium chloride is present in the reactant mixture. A kinetic study of the synthesis of palmitamide was done. The decomposition of sodium palmitate was found to fit first order kinetics and hence a reaction mechanism was proposed. Palm oil soap was also used in the amide syntheses and mixtures of primary amides were successfully synthesized from the reaction between palm oil soap, urea and ammonium chloride.

Abstrak yang dikemukakan kepada senat Unversiti Putra Malaysia bagi memenuhi keperluan Ijazah Master Sains

**PENYEDIAAN AMIDA ASID LEMAK DARIPADA
SABUN LOGAM MELALUI RADIASI GELOMBANG MIKRO**

Oleh

LEE YEAN KEE

Disember 2002

Pengerusi : Profesor Madya Dr. Karen Badri

Falkuti: Sains dan Pengajian Alam Sekitar

Satu cara penyediaan amida tulen yang efisien telah ditemui dalam kajian ini. Daripada 3 jenis bahan tindak balas, iaitu sabun natrium asid lemak, sumber ammonia (atau amina) dan ammonium klorida, amida dapat dihasilkan apabila campuran tersebut ditera dalam tiub kaca dan didedahkan kepada radiasi gelombang mikro. Amida primer telah dihasilkan daripada campuran sabun natrium asid lemak, urea atau ammonium karbonat dan ammonium klorida, manakala amida sekunder dihasilkan daripada campuran sabun natrium asid lemak, amina dan ammonium klorida. Melalui cara ini, amida primer yang telah dihasilkan ialah miristamida, palmitamida, oleamida dan stearamida, manakala amida sekunder yang telah dihasilkan ialah *N*-butil miristamida, *N*-butil palmitamida, *N*-butil stearamida, *N*-hexadesil miristamida, *N*-hexadesil palmitamida dan *N*-hexadesil stearamida. Analisis IR, NMR dan CHN dijalankan bagi menentukan struktur amida yang dihasilkan. Penghasilan miristamida dan palmitamida dioptimumkan dengan mengubah jangkamasa radiasi, nisbah antara bahan tindak balas dan isipadu tiub kaca. Keadaan optimum ini digunakan untuk menghasilkan pelbagai jenis amida primer yang lain. Didapati bahawa peratus hasil yang terbaik diperolehi daripada nisbah 1:0.5:1 (sabun

natrium asid lemak: urea: ammonium klorida) dengan isipadu tuib kaca 2.5 cm^3 apabila 0.5 g campuran bahan tindak balas diradiasi selama 9 minit. Kehadiran atau ketiadaan ammonium klorida dalam campuran bahan tindak balas ini telah dikaji dalam sistem 2 jenis dan 3 jenis bahan tindak balas yang melibatkan penggunaan asid lemak atau sabun natrium, dimana urea atau ammonium karbonat bertindak sebagai sumber ammonia. Didapati bahawa tindak balas yang melibatkan penggunaan sabun memerlukan sistem 3 jenis bahan tindak balas, dimana perlunya kehadiran ammonium klorida dalam campuran bahan tindak balas. Kajian kinetik penghasilan palmitamida juga dijalankan, dimana penguraian natrium palmitat didapati mengikut tertib pertama. Susulan daripada ini, satu mekanisme tindak balas telah dicadangkan. Sabun yang diperolehi daripada minyak kelapa sawit juga telah digunakan untuk menghasilkan amida. Campuran amida primer telah disintesiskan menerusi sabun minyak kelapa sawit, urea dan ammonium klorida.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest appreciation to my chairman, Assoc. Prof. Dr. Karen Badri and members of the supervisory committee, Prof. Dr. Badri Muhammad and Dr. Abd. Rahman Manas for their unfailing help, guidance and advice throughout the study.

I am also very grateful to the staff of the Chemistry Department of UPM, En. Zainal Zahari, Pn. Rusnani Amiruddin, En. Zainal Kassim, En. Nordin Ismail, En. Ismail Yasin, En. Abbas Abd. Rahman, En. Narzari Ahamad and En. Isharuddin Misron for their co-operation and help during the study. My sincere thanks also extended to my labmates, Chea Ling, Boon Hui, Mizawati and Khairi as working partners throughout the project. I am also very thankful to the financial sponsorship provided by UPM under the PASCA Scheme.

Last but not least, I am also indebted to my family and my friends who have always encouraged and supported me.

I certify that an Examination Committee met on 2nd December 2002 to conduct the final examination of Lee Yean Kee on his Master of Science thesis entitled "Preparation of Fatty Amides from Metal Soaps under Microwave Irradiation" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidates be awarded the relevant degree. Members of the Examination Committee are as follow:

Taufiq Yap Yun Hin, Ph.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

Karen Badri, Ph.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Badri Muhammad, Ph.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Abdul Rahman Manas, Ph.D

Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)



SHAMSHER MOHAMAD RAMADILI, Ph.D.

Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: **8 JAN 2002**

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

Karen Badri, Ph.D.

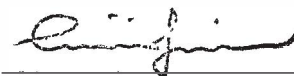
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairperson)

Badri Muhammad, Ph.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Abdul Rahman Manas, Ph.D.

Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)



AINI IDERIS, Ph.D.
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: **13** FEB 2003

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



LEE YEAN KEE

Date: 24/12/2002

TABLE OF CONTENTS

		Page
ABSTRACT		2
ABSTRAK		4
ACKNOWLEDGEMENTS		6
APPROVAL		7
DECLARATION		9
LIST OF TABLES		13
LIST OF FIGURES		14
LIST OF ABBREVIATIONS		18
 CHAPTER		
I	INTRODUCTION	20
	Palm Based Oleochemicals	20
	Fatty Acids	21
	Fatty Nitrogen Compounds	22
	Soaps	22
	Microwave Irradiation as a Powerful Tool in Organic Synthesis	23
	The Advantages and Uses of Microwave Heating in Industry	24
	Summary	27
II	LITERATURE REVIEW	28
	Fatty Acid Amides	28
	Nomenclature	29
	Physical Properties	31
	Chemical Properties	32
	Natural Occurrence	33
	Commercial Value and Uses	34
	Synthesis of Amides	36
	Manufacture of Amides	43
	Unsubstituted Amides	43
	Substituted Amides	45
	Analysis of Amides	49
	Titration Method	49
	Thin-Layer-Chromatography (TLC)	49
	Infrared Spectroscopy (IR)	50
	Nuclear Magnetic Resonance Spectroscopy (NMR)	52
	Gas Chromatography-Mass Spectrometry (GC-MS)	53
	Microwave Technology in Organic Synthesis	54
	Origin of the Microwave Effects	55
	Microwave Irradiation	55
	Heating Effect	57
	Dielectric Heating	57
	Superheating Effect	60
	The Development of Microwave-Assisted Organic Reactions	61

III	MATERIALS AND METHODS	69
	General Experimental	69
	Microwave Oven	69
	Fourier-Transform Infrared Spectroscopy (FTIR)	70
	Nuclear Magnetic Resonance Spectroscopy (NMR)	70
	Analysis of the Carbon, Hydrogen and Nitrogen Composition (CHN)	70
	Gas Chromatography (GC)	70
	Melting Point Apparatus	71
	Gas Chromatography-Mass Spectrometry (GC-MS)	71
	Production of Amides	71
	Preparation of Sodium Soap	71
	Primary Amides	72
	Secondary Amides	74
	Optimization of the Product Yield	76
	Generalized Reaction	77
	Comparison between Two-Reactant and Three-Reactant Systems	77
	Kinetic Study of Production of Palmitamide under Microwave Irradiations	79
	Synthesis of Primary Amide Mixture from Palm Oil Soap	79
IV	RESULTS AND DISCUSSION	
	Preparation of Sodium Soap	80
	Production of Amides	81
	Primary Amides	82
	Myristamide	82
	Palmitamide, Oleamide and Stearamide	84
	Secondary Amides	85
	<i>N</i> -Butyl Myristamide	85
	<i>N</i> -Butyl Palmitamide, <i>N</i> -Butyl Stearamide, <i>N</i> -Hexadecyl Myristamide, <i>N</i> -Hexadecyl Palmitamide, <i>N</i> -Hexadecyl Stearamide	88
	Summary	89
	Optimization of the Myristamide Synthesis	89
	Time of Irradiation	89
	The Ammonium Chloride Ratio	92
	The Volume of Reaction Vessels	93
	Optimization of Palmitamide Synthesis	95
	Time of Irradiation	95
	The Ammonium Chloride Ratio	100
	Generalized Reaction	102
	Using the Condition Optimized from Synthesis of Myristamide	102
	Using the Condition Optimized from Synthesis of Palmitamide	103
	Comparison between Two-Reactant and Three-Reactant Systems	104
	The Role of Ammonium Chloride in the Reactions Involving Fatty Acid	104
	The Role of Ammonium Chloride in the Reactions Involving Sodium Soap	107

	Reaction between Palmitic Acid or Sodium Palmitate and Ammonium Chloride	110
	Summary	112
	Kinetic Study of Production of Palmitamide	113
	Decomposition of Sodium Palmitate	118
	Summary	121
	Proposed Mechanism of Reaction	121
	Comparison between Conventional Heating Method and Microwave Heating Method in the Synthesis of Amides	122
	Synthesis of Primary Amides Mixtures from Palm Oil Soap	124
V	CONCLUSION	128
	BIBLIOGRAPHY	130
	APPENDICES	139
	VITA	177

LIST OF TABLES

Table		Page
1	Fatty acid composition (%) of palm oil and palm kernel oil	22
2	Fatty amide (RCONH ₂) nomenclature	30
3	Dielectric constants and loss tangent values from some solvents relevant to organic synthesis	60
4	Boiling points of some typical polar solvents (°C)	61
5	Chemical shifts of myristamide from ¹ H NMR	83
6	IR assignment of palmitamide, oleamide and stearamide in cm ⁻¹	86
7	Chemical shifts of <i>N</i> -butyl-myristamide from ¹ H NMR	88
8	IR spectra assignment of the secondary amides in cm ⁻¹	89
9	Percentage yield (palmitamide) at different irradiation times	96
10	Percentage yield from different kinds of sodium soap with ratio 1: 1: 0.8 (soap:urea:NH ₄ Cl)	102
11	Percentage yields from different kinds of sodium soap with ratio 1: 0.5: 1 (soap:urea:NH ₄ Cl)	103
12	Percentage yield from different combinations of reactants	105
13	Percentage yield, by-product and conversions from different combination of reactants	109
14	Data for palmitic acid, palmitamide and the calculated percentage of sodium palmitate unreacted	118
15	Correlation coefficient of the kinetic plot	119
16	Data for first order kinetic plot (decomposition of sodium palmitate)	119
17	Kinetic details from various reactants and different temperatures	123
18	Molecular weight, theoretical and experimental values (%C, %H, %N) of primary amides and secondary amides.	139
19	Chemical shifts of palmitamide from ¹ H NMR	146
20	Chemical shifts of oleamide from ¹ H NMR	146
21	Chemical shifts of stearamide from ¹ H NMR	146
22	Melting point of primary amides	146
23	Chemical shifts of <i>N</i> -butyl palmitamide from ¹ H NMR	152
24	Chemical shifts of <i>N</i> -butyl stearamide from ¹ H NMR	152
25	Chemical shifts of <i>N</i> -hexadecyl myristamide from ¹ H NMR	152
26	Chemical shifts of <i>N</i> -hexadecyl palmitamide from ¹ H NMR	153
27	Chemical shifts of <i>N</i> -hexadecyl stearamide from ¹ H NMR	153
28	Melting point of secondary amides	153
29	Percentage of myristamide yielded at different times of irradiation	154
30	Percentage yield (myristamide) from different ratios of NH ₄ Cl to sodium myristate	157
31	Percentage yield using different volumes of reaction vessels	166
32	Product details (palmitamide) from different ratios of NH ₄ Cl to sodium palmitate	170
33	Total percentage yield and yield of by-product after different irradiation times	173
34	Details of GC-MS trace of products extracted by chloroform	174

LIST OF FIGURES

Figure		Page
1	Oleochemicals from palm oil and palm kernel oil	21
2	Heating patterns in conventional and microwave furnaces	55
3	Interaction of microwaves with materials	56
4	Effects of the electric field on the mutual orientation of dipolar molecules: a) without any electric field applied, b) continuous electric field applied and c) alternating electric field with a high frequency applied	58
5	IR spectrum of myristamide	83
6	Molecular structure of myristamide	83
7	¹ H NMR spectrum of myristamide	84
8	IR spectrum of <i>N</i> -butyl myristamide	86
9	Molecular structure of <i>N</i> -butyl myristamide	87
10	¹ H NMR spectrum of <i>N</i> -butyl myristamide	87
11	Percentage of myristamide yielded vs. time of irradiation	90
12	IR spectrum of crude product of myristamide	91
13	IR spectrum of residue	91
14	IR spectrum of the dried product extracted by petroleum ether during purification	92
15	Percentage yield vs. ratio of NH ₄ Cl to sodium myristate	93
16	Percentage yield vs. volume of vessel	94
17	Percentage yield of palmitamide vs. time of irradiation	96
18	Percentage of palmitic acid vs. time of irradiation	97
19	Percentage of conversion (soap reacted) vs. time of irradiation	97
20	IR spectrum of the crude product	98
21	IR spectrum of the dried product extracted by chloroform from the crude product	99
22	IR spectrum of the dried product extracted by petroleum ether (purification step)	99
23	IR spectrum of the residue after extraction	99
24	Graph of percentage yield of palmitamide vs. ratio of NH ₄ Cl to sodium palmitate	101
25	IR spectrum of crude product from PaU	105
26	IR spectrum of crude product from PaAc	105
27	IR spectrum of crude product from PaUAm	106
28	IR spectrum of crude product from PaAcAm	106
29	IR spectrum of crude product from PU	107
30	IR spectrum of crude product from PAc	108
31	IR spectrum of crude product from PUAm	108
32	IR spectrum of crude product from PAcAm	108
33	IR spectrum of crude product from PaAm	110
34	IR spectrum of the dried product extracted by chloroform from PaAm	111
35	IR spectrum of crude product from PAm	111
36	IR spectrum of the dried product extracted by chloroform from PAm	112
37	GC trace of P20SCHL	114
38	Mass spectrum of P20SCHL (retention time 8.197)	114

39	GC trace of P40SCHL	115
40	Mass spectrum of P40SCHL (retention time 8.996)	115
41	GC trace of P50SCHL2 (purified palmitamide)	116
42	Mass spectra obtained from GCMS on P50SCHL2 with the retention time at 8.965 (top) and 11.369 (bottom)	116
43	Percentage of sodium palmitate/palmitamide/palmitic acid vs. irradiation time	117
44	Percentage of sodium palmitate left vs. time of irradiation	119
45	First order kinetic plot (decomposition of sodium palmitate)	120
46	IR spectrum of extracted product (primary amides mixtures from palm oil soap)	125
47	IR spectrum of the residue (primary amides mixtures from palm oil soap)	126
48	GC chromatogram of products extracted by chloroform	126
49	IR spectrum of myristic acid	140
50	IR spectrum of palmitic acid	140
51	IR spectrum of oleic acid	140
52	IR spectrum of stearic acid	141
53	IR spectrum of sodium myristate	141
54	IR spectrum of sodium palmitate	141
55	IR spectrum of sodium oleate	142
56	IR spectrum of sodium stearate	142
57	IR spectrum of palmitamide	143
58	Molecular structure of palmitamide	143
59	¹ H NMR spectrum of palmitamide	143
60	IR spectrum of oleamide	144
61	Molecular structure of oleamide	144
62	¹ H NMR spectrum of oleamide	144
63	IR spectrum of stearamide	145
64	Molecular structure of stearamide	145
65	¹ H NMR spectrum of stearamide	145
66	IR spectrum of <i>N</i> -butyl palmitamide	147
67	Molecular structure of <i>N</i> -butyl palmitamide	147
68	¹ H NMR spectrum of <i>N</i> -butyl palmitamide	147
69	IR spectrum of <i>N</i> -butyl stearamide	148
70	Molecular structure of <i>N</i> -butyl stearamide	148
71	¹ H NMR spectrum of <i>N</i> -butyl stearamide	148
72	IR spectrum of <i>N</i> -hexadecyl myristamide	149
73	Molecular structure of <i>N</i> -hexadecyl myristamide	149
74	¹ H NMR spectrum of <i>N</i> -hexadecyl myristamide	149
75	IR spectrum of <i>N</i> -hexadecyl palmitamide	150
76	Molecular structure of <i>N</i> -hexadecyl palmitamide	150
77	¹ H NMR spectrum of <i>N</i> -hexadecyl palmitamide	150
78	IR spectrum of <i>N</i> -hexadecyl stearamide	151
79	Molecular structure of <i>N</i> -hexadecyl stearamide	151
80	¹ H NMR spectrum of <i>N</i> -hexadecyl stearamide	151
81	IR spectrum of the dried product extracted by chloroform from crude product	154
82	IR spectrum of crude product (ratio of NH ₄ Cl to sodium myristate = 0)	155

83	IR spectrum of crude product (ratio of NH ₄ Cl to sodium myristate = 0.4)	155
84	IR spectrum of crude product, M06A (ratio of NH ₄ Cl to sodium myristate = 0.6)	155
85	IR spectrum of crude product, M07A (ratio of NH ₄ Cl to sodium myristate = 0.7)	156
86	IR spectrum of crude product M08A (ratio of NH ₄ Cl to sodium myristate = 0.8)	156
87	IR spectrum of crude product, M09A (ratio of NH ₄ Cl to sodium myristate = 0.9)	156
88	IR spectrum of crude product, M10A (ratio of NH ₄ Cl to sodium myristate = 1.0)	157
89	IR spectrum of crude product (ratio of NH ₄ Cl to sodium myristate = 1.2)	157
90	IR spectrum of residue (ratio of NH ₄ Cl to sodium myristate=0.6)	158
91	IR spectrum of residue (ratio of NH ₄ Cl to sodium myristate=0.7)	158
92	IR spectrum of residue (ratio of NH ₄ Cl to sodium myristate=0.8)	158
93	IR spectrum of residue (ratio of NH ₄ Cl to sodium myristate=0.9)	159
94	IR spectrum of residue (ratio of NH ₄ Cl to sodium myristate=1.0)	159
95	IR spectrum of crude product (M12L)	160
96	IR spectrum of the dried product extracted by chloroform from M12L	160
97	IR spectrum of residue from M12L	160
98	IR spectrum of crude product (M13L)	161
99	IR spectrum of the dried product extracted by chloroform from M13L	161
100	IR spectrum of residue from M13L	161
101	IR spectrum of crude product (M14L)	162
102	IR spectrum of the dried product extracted by chloroform from M14L	162
103	IR spectrum of residue from M14L	162
104	IR spectrum of crude product (M15L)	163
105	IR spectrum of the dried product extracted by chloroform from M15L	163
106	IR spectrum of residue from M15L	163
107	IR spectrum of crude product (M16L)	164
108	IR spectrum of the dried product extracted by chloroform from M16L	164
109	IR spectrum of residue from M16L	164
110	IR spectrum of crude product (M17L)	165
111	IR spectrum of the dried product extracted by chloroform from M17L	165
112	IR spectrum of residue from M17L	165
113	IR spectrum of crude product (P0N, ratio of NH ₄ Cl to sodium palmitate = 0)	167
114	IR spectrum of crude product (P04N, ratio of NH ₄ Cl to sodium palmitate = 0.4)	167
115	IR spectrum of crude product (P08N, ratio of NH ₄ Cl to sodium palmitate = 0.8)	168

116	IR spectrum of crude product (P12N, ratio of NH ₄ Cl to sodium palmitate = 1.2)	168
117	IR spectrum of crude product (P06N, ratio of NH ₄ Cl to sodium palmitate = 0.6)	168
118	IR spectrum of crude product (P07N, ratio of NH ₄ Cl to sodium palmitate = 0.7)	169
119	IR spectrum of crude product (P09N, ratio of NH ₄ Cl to sodium palmitate = 0.9)	169
120	IR spectrum of crude product (P11N, ratio of NH ₄ Cl to sodium palmitate = 1.1)	169
121	IR spectrum of crude product from PI 108	171
122	IR spectrum of crude product from O1108	171
123	IR spectrum of crude product from PI 108	171
124	IR spectrum of crude product from M1051	172
125	IR spectrum of crude product from O1051	172
126	IR spectrum of crude product from S1051	172
127	GC chromatogram of products extracted by chloroform	174
128	Mass spectrum of peak 1 (top) with library match (bottom)(retention time = 12.552 min.)	175
129	Mass spectrum of peak 2 (top) with library match (bottom)(retention time = 13.375 min.)	175
130	Mass spectrum of peak 3 (top) with library match (bottom)(retention time = 14.755 min.)	175
131	Mass spectrum of peak 4 (top) with library match (bottom)(retention time = 15.960 min.)	176
132	Mass spectrum of peak 5 (top) with library match (bottom)(retention time = 18.179 min.)	176
133	Mass spectrum of peak 6 (top) with library match (bottom)(retention time = 18.365 min.)	176

LIST OF ABBREVIATIONS

α	Alpha
β	Beta
brs	Broad singlet
brd	Broad doublet
^{13}C	Carbon-13
cm	Centimeter
δ	Chemical shift in ppm
$^{\circ}\text{C}$	Degree in Celsius
d	Doublet
FID	Flame Ionization Detector
FTIR	Fourier-Transform Infrared Spectroscopy
γ	Gamma
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectroscopy
GHz	Giga Hertz
g	Gram
IR	Infrared
kbar	Kilo bar
kPa	Kilo Pascal
Ltd.	Limited
MHz	Mega Hertz
MPa	Mega Pascal
m	Meter

μm	Micro meter
MW	Microwave
ml	Milliliter
min	Minute
NMR	Nuclear Magnetic Resonance
ppm	parts per million
ppb	parts per billion
π	Pi
^1H	Proton
q	Quartet
qt	Quintet
st	Sextet
s	Singlet
tan	Tangen
TLC	Thin Layer Chromatography
t	Triplet
W	Watt

CHAPTER I

INTRODUCTION

Palm Based Oleochemicals

Malaysia is the world largest producer and exporter of palm oil. In 1998, about 8.3 million tonnes of crude palm oil were produced, together with 1.1 million tonnes of crude palm kernel oil. About 80% of the palm oil is used for food applications, while the remainder goes into non-food applications. Although it appears as a smaller percentage, the non-food sector is of increasing importance because of the higher added value of the derived products. The two main non-food uses are in the manufacture of oleochemicals and soaps (Choo, 2001).

Oleochemicals are chemicals derived from oils or fats. They are analogous to petrochemicals which are chemicals derived from petroleum. The hydrolysis or alcoholysis of oils or fats is the basis of the oleochemical industry. The hydrolysis of the triglycerides composing oils and fats produces various fatty acids and glycerol, whereas alcoholysis gives fatty acid esters and glycerol. Fatty acids or their esters can be used as the starting materials for making fatty alcohols and fatty nitrogen compounds. These products can be further modified to produce various derivatives. Hence oleochemicals are often divided into at least two categories, which are basic oleochemicals and their derivatives. The five basic oleochemicals are fatty acids, esters, alcohols, nitrogen compounds and glycerol (Figure 1) (Ong *et al.*, 1990).

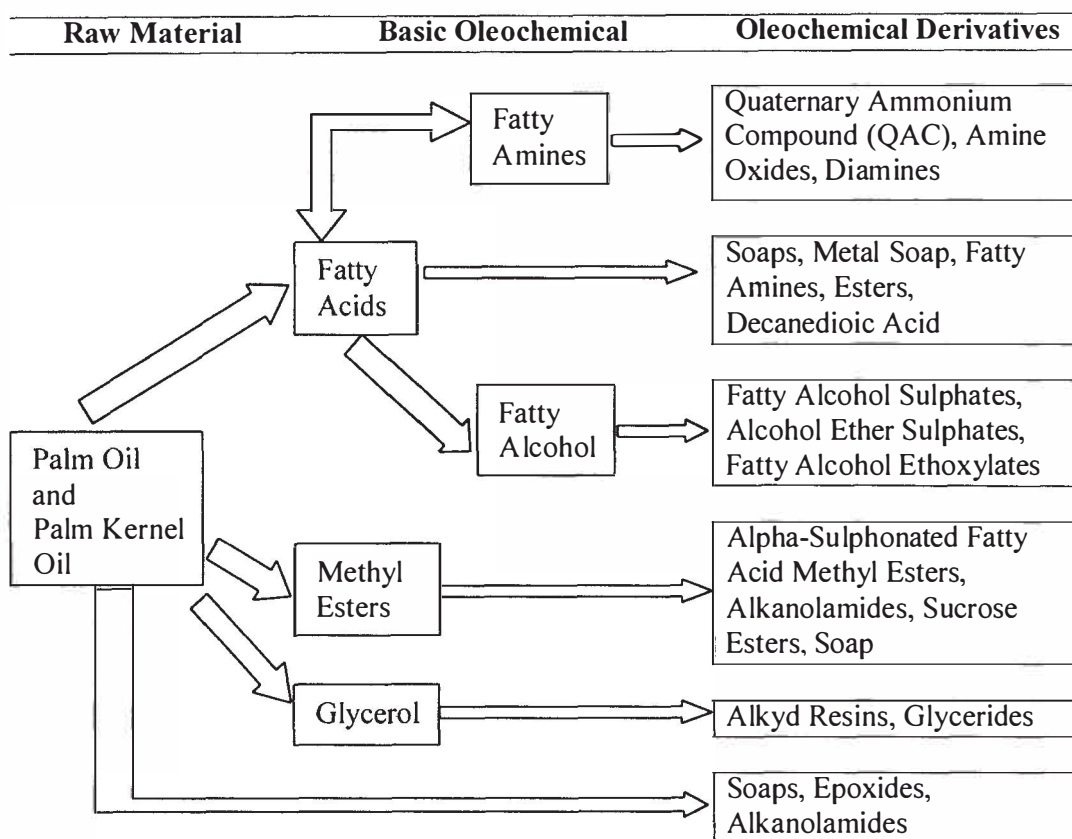


Figure 1: Oleochemicals from palm oil and palm kernel oil (Choo, 2001)

Fatty Acids

Various fatty acids can be obtained directly from palm oil and palm kernel oil by saponification, fat splitting or alcoholysis. Soap and glycerol are liberated by saponification and the soap is further treated with mineral acid to give free fatty acids. Fat splitting involves the hydrolysis of triglycerides to form free fatty acids and glycerol. In alcoholysis, fatty esters produced are treated with mineral acid to convert them to free fatty acids. Table 1 shows the fatty acid composition of palm oil and palm kernel oil.

Table 1: Fatty acid composition (%) of palm oil and palm kernel oil

Fatty Acid	Carbon Number: Unsaturated Bond	Palm Oil	Palm Kernel Oil
Caproic	6:0	-	0.1-0.5
Caprylic	8:0	-	3.4-5.9
Capric	10:0	-	3.3-4.4
Lauric	12:0	0.1-1.0	46.3-51.1
Myristic	14:0	0.9-1.5	14.3-16.8
Palmitic	16:0	41.8-46.8	6.5-8.9
Palmitoleic	16:1	0.1-0.3	-
Stearic	18:0	4.2-5.1	1.6-2.6
Oleic	18:1	37.3-40.8	13.2-16.4
Linoleic	18:2	9.1-11.0	2.2-3.4
Others	-	0-1	Traces-0.9

(Source: Choo, 2001)

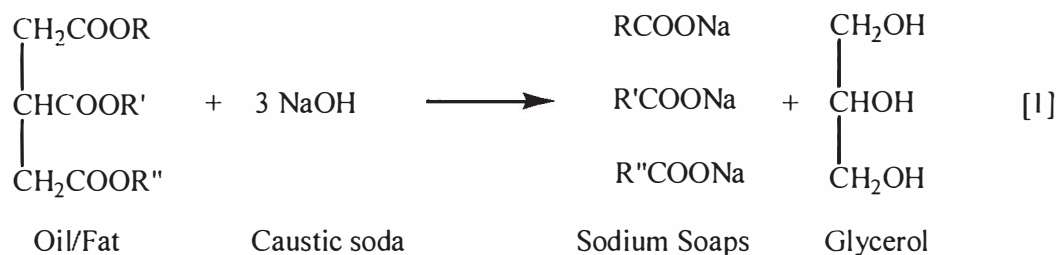
Fatty Nitrogen Compounds

The most common fatty nitrogen compounds are fatty amides, nitriles, amines and quaternary ammonium compounds. The most important of these are the quaternary ammonium compounds, colloquially known as 'Quats'. Lately manufacturers in developed countries have been voluntarily reducing or stopping the use of quats in softeners, etc. in view of recent findings that they may not be completely biodegradable (Kifli *et al.*, 1991), and although licenses have been issued in Malaysia, so far the commercial production of fatty nitrogen compounds has not started.

Soaps

Soaps are mixtures of metal salts (for instance, sodium salts) of fatty acids which can be derived from oils or fats by reacting them with sodium hydroxide at

80°-100 °C. The basic reaction in soap making is quite simple, where soap is produced together with glycerol (Marvin *et al.*, 1979):



The use of soap as a laundering agent and for cleansing the skin is many centuries old. Although modern detergents have almost eliminated the use of soap for home laundry purposes, soap is still the main ingredient in toilet bars for personal use (Richtler, and Knaut, 1991).

Pure fatty acid metal soap can be easily obtained by the reaction between a pure fatty acid and sodium or potassium hydroxide, oxides and carbonates (Formo *et al.*, 1979):



Microwave Irradiation as a Powerful Tool in Organic Synthesis

It has been known for a long time that microwaves can be used to heat materials. Its development in heating food has had more than 50 years history (Buffler, 1993). However, in the earliest version, the cost of its power systems was greater than conventional heating systems (Othmer, 1992). Magnetrons, the microwave generators, were improved and simplified in the 1970's, causing the prices

of domestic microwave ovens to fall considerably, and leading them to become a mass product (Lidström *et al.*, 2001).

The use of microwave heating in organic synthesis was pioneered by Gedye and co-workers in 1986. Since then, the number of annual publications on microwave-assisted organic synthesis has increased year by year. The availability of scientific microwave equipment over the last five years has further enabled the development of knowledge in this field. The publications report acceleration of a wide range of organic reactions to minutes and seconds from days and hours using conventional heating methods (Perreux and Loupy, 2001). From organic synthesis, the use of microwave is branched to drugs in the fields of combinatorial and automated medicinal chemistry, where increased rate of reaction is essential to meet the increasing requirements for new compound discoveries (Larhed and Hallberg, 2001).

The use of supported reagents which eliminates the need for a solvent has led to an increased number of reactions being studied under microwave irradiation. These solventless reactions, from which the support can often be recovered, are environmentally friendly. Recovery of support is leading to efficient and low waste reaction routes (Varma, 1999).

The Advantages and Uses of Microwave Heating in Industry

There are numerous advantages in productivity of microwave heating over conventional heating methods. The major advantage of using the microwave method is its high efficiency and speed of material processing compared to conventional

