UNIVERSITI PUTRA MALAYSIA

PREPARATION OF FATTY AMIDES FROM METAL SOAPS UNDER MICROWAVEIRRADIATION

LEE YEAN KEE

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 cm^3 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 tuib 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 diperoleh 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 mengikuti 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

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

α	Alpha
β	Beta
brs	Broad singlet
brd	Broad doublet
^{13}C	Carbon-13
cm	Centimeter
δ	Chemical shift in ppm
^{o}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).

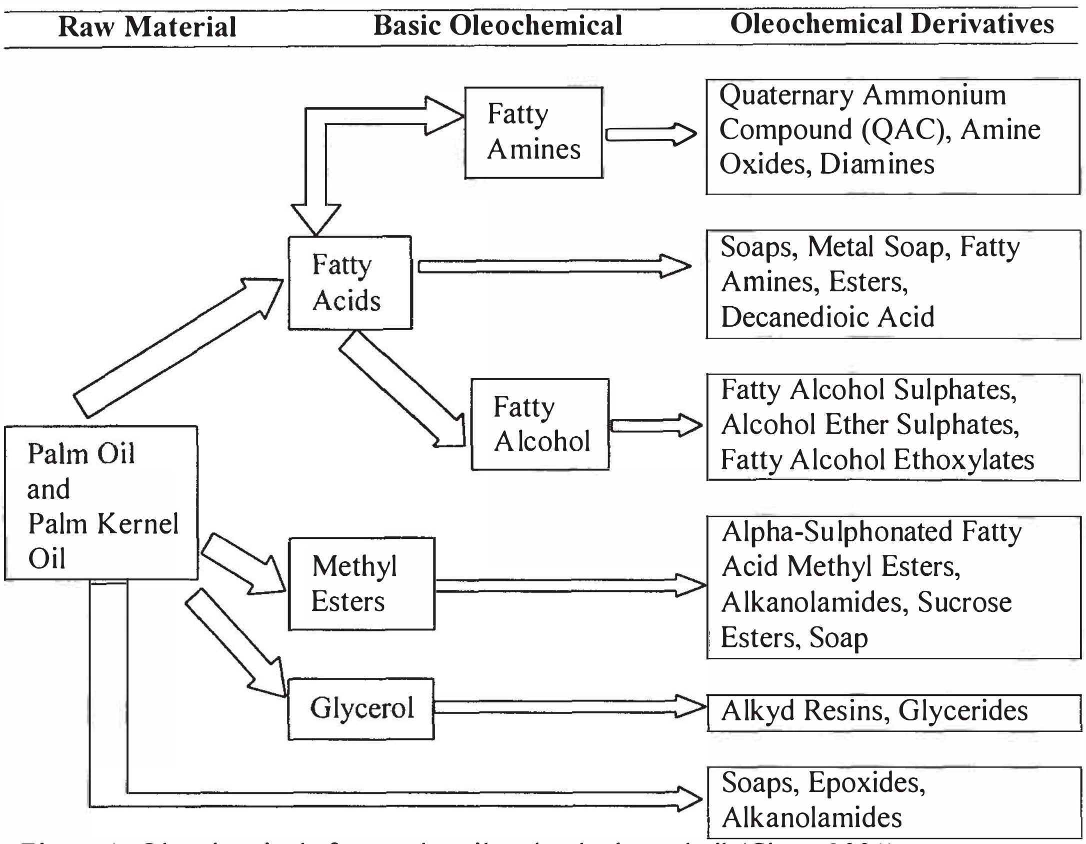

Figure 1: Oleochemicals from palm oil and palm kernel oil (Choo, 2001)

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

(Souce: 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):

$$\begin{array}{ccccccc} CH_2COOR & & & & RCOONa & & CH_2OH \\ | & & & & & & | \\ CHCOOR' & + & 3\ NaOH & \longrightarrow & R'COONa & + & CHOH \\ | & & & & & & | \\ CH_2COOR'' & & & & R''COONa & & CH_2OH \\ \text{Oil/Fat} & & \text{Caustic soda} & & \text{Sodium Soaps} & & \text{Glycerol} \end{array} \qquad [1]$$

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):

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O \qquad [2]$$

$$2RCOOH + K_2CO_3 \longrightarrow 2RCOOK + H_2O + CO_2 \qquad [3]$$

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 (Lidstrőm *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 lead 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