UNIVERSITI PUTRA MALAYSIA

SOLVENT CRYSTALLIZATION OF PALM-BASED DIHYDROXYSTEARIC ACID

SUMAIYA ZAINAL ABIDIN @ MURAD.

SOLVENT CRYSTALLIZATION OF PALM-BASED DIHYDROXYSTEARIC ACID

By

SUMAIYA ZAINAL ABIDIN @ MURAD

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Partial Fulfilment of the Requirement for the Degree of Master of Science

July 2006

This thesis is dedicated to
My beloved parents, Zainal Abidin and Sadiah
My siblings, Irfan, Anis, Zuhair and Atifa
My gradma, Saunah Awang

SOLVENT CRYSTALLIZATION OF PALM-BASED DIHYDROXYSTEARIC ACID

By

SUMAIYA ZAINAL ABIDIN @ MURAD

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Partial Fulfilment of the Requirement for the Degree of Master of Science

July 2006

This thesis is dedicated to
My beloved parents, Zainal Abidin and Sadiah
My siblings, Irfan, Anis, Zuhair and Atifa
My gradma, Saunah Awang

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

SOLVENT CRYSTALLIZATION OF PALM-BASED DIHYDROXYSTEARIC ACID

By

SUMAIYA ZAINAL ABIDIN @ MURAD

July 2006

Chairman : Chuah Teong Guan, PhD

Faculty : Engineering

Palm based *9,10-threo* dihydroxystearic acid (DHSA) was produced from epoxidation of oleic acid with performic acid, followed by hydrolysis of the epoxide. It is widely used as ingredient in cosmetic industries. However, it is a requirement for low purity crude DHSA to undergo a purification stage in order to fulfil the stringent quality requirement in this field. Solvent crystallization has been employed with detailed examination to produce good quality crystallized product.

The objective of this research work is to carry out a preliminary and detailed study on the solvent crystallization of palm based DHSA. Preliminary study was done using two different solvents, ethanol and hexane, at several concentrations and cooling conditions. The chemical and physical product properties of the crystallized product are evaluated using gas chromatography (GC), crystal size distribution (CSD) and scanning electron microscopy (SEM). The preliminary studies suggested that crystallization of DHSA using ethanol has been successfully achieved and natural cooling mode gives better performance compared to rapid cooling mode, almost in

all aspects. However, crystallization of DHSA using hexane as solvent was unable to shape DHSA into crystal. It produced bulk solid DHSA with low purity percentage (79%).

Based on preliminary studies, an investigation on controlled cooling crystallization using a fabricated crystallizer has been conducted. This study focuses on various operating conditions, namely temperature (24°C, 26°C, 28°C), time (1 – 12 hours), seeding process (2.5, 5, 10grams) and cooling modes (natural and controlled crystallization). Effect of these parameters on crystal size distribution (CSD), purity and yield of crystallized product has been examined. Quality and quantity of crystals produced via the controlled cooling crystallizer are greatly influenced by the operating temperature. Higher working temperature produced crystals with higher purity and larger average crystal size. However, the yield is lower. Controlled crystallization process results in a better crystal properties compared to natural cooling crystallization, generally in almost all aspects. Furthermore, the addition of DHSA seed into the solution could reduce the purity of product and at the same time, as it could retard the crystal growth.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi sebahagian keperluan untuk ijazah Master Sains

PENGHABLURAN ASID DIHYDROXYSTEARIK YANG BERASASKAN KELAPA SAWIT MENGGUNAKAN BAHAN LARUT

Oleh

SUMAIYA ZAINAL ABIDIN @ MURAD

Julai 2006

Pengerusi : Chuah Teong Guan, PhD

Fakulti : Kejuruteraan

Asid 9,10-threo dihydroxystearik (DHSA) dihasilkan daripada proses epoksidasi antara asid oleic dan asid performik, dituruti dengan hidrolisis ke atas hasilan tersebut. DHSA digunakan secara meluas di dalam industri sebagai bahan asas dalam produk kosmetik. Oleh itu, DHSA mentah yang mempunyai kadar ketulenan yang rendah perlu melalui proses purifikasi bagi memenuhi keperluan kualiti yang ketat bagi setiap penghasilan produk dalam cabang ini. Penghabluran menggunakan bahan larut telah digunapakai dan kajian terperinci telah dijalankan untuk menghasilkan produk yang berkualiti tinggi.

Objektif thesis ini adalah untuk menjalankan kajian asas dan terperinci ke atas penghabluran DHSA yang berasaskan kelapa sawit, dengan menggunakan bahan larut. Kajian asas mencangkupi dua jenis bahan larut, etanol dan heksana pada beberapa kepekatan dan persekitaran penghabluran yang berbeza. Keputusan kajian dianalisis menggunakan beberapa kaedah, diantaranya adalah gas kromatografi (GC), penyebaran saiz kristal (CSD) dan mikroskop pengimbas elektron (SEM). Kajian

asas ini memperlihatkan kejayaan menghablurkan DHSA menggunakan etanol sebagai bahan larut. Penghabluran semulajadi pula menghasilkan keputusan yang lebih baik, secara amnya dalam semua aspek. Walaubagaimanapun, penghabluran DHSA menggunakan heksana sebagai bahan larut tidak berjaya membentuk hablur DHSA, sebaliknya menghasilkan DHSA pada peratus ketulenan yang rendah (79%).

Berdasarkan daripada kajian asas, penyelidikan terperinci telah dijalankan dengan mengaplikasi kaedah penghabluran melalui penyejukan terkawal dimana sebuah penghablur telah direka khas bagi memenuhi keperluan tujuan ini. Kajian ini memberi tumpuan kepada beberapa pembolehubah, iaitu suhu (24°C, 26°C, 28°C), masa (1 – 12 jam), proses pembenihan (2.5, 5, 10 gram) dan persekitaran penghabluran (peghabluran semulajadi dan penghabluran terkawal) yang berbeza. Pembolehubah ini dikaji berdasarkan kesannya terhadap CSD, ketulenan dan perolehan produk yang telah terhablur. Suhu memberikan pengaruh yang besar ke atas kualiti dan kuantiti hablur yang dihasilkan. Pada suhu yang tinggi, proses ini menghasilkan hablur yang berketulenan tinggi degan purata saiz partikel yang lebih besar tetapi rendah dari segi perolehan. Secara kasarnya, penghabluran pada suhu terkawal menghasilkan produk yang lebih baik berbanding penghasilan produk melalui penghabluran pada suhu natural. Selain daripada itu, penambahan benih DHSA pada larutan pula menyebabkan penurunan dari segi ketulenan produk. Pada masa yang sama juga, ia boleh membantut pertumbuhan hablur.

ACKNOWLEDGEMENTS

Bismillahi ar-rahmaan ir-rahim

In the Name of Allah The Most Gracious and Most Merciful

Alhamdulillah, I am grateful for the opportunity to acknowledge the following for their contributions:

My advisor and chairmain of the supervisory committee, Dr. Chuah Teong Guan, my supervisory committee Assoc. Prof. Dr. Robiah Yunus, Dr. Salmiah Ahmad and Mr. Parthiban Siwayanan for their patience, support and guidance throughout my study.

All lecturers in Department of Chemical and Environmental Engineering especially Assoc. Prof. Dr. Thomas Choong Shean Yaw for the help and assistance that were given.

All staff in Advanced Oleochemical Technology Division, MPOB for their cheerfulness and assistance during my research work.

My colleagues in MPOB (Dila and Chua), and all those who were with me during ups and downs, thank you for the academic input and friendship. Not forgotten to my lovely housemates (Ayu, Nad and Enne) who were so helpful and supportive.

I am especially grateful to mama (Sadiah Baharom) and abah (Zainal Abidin Bachok) for their never ending prayers and love. To my brothers, sisters, and not forgotten, Faiz Hamzah, whom supports never end.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CSD	=	crystal size distribution
DHSA	=	dihydroxystearic acid
FT-IR	=	fourier transform infra red
NBD	=	neutralized, bleached and deodorized
OHV	=	OH value
PKO	=	palm kernel oil
PKOo	=	palm kernel oil olein
PKOs	=	palm kernel oil stearin
PO	=	palm oil
RBD	=	refined, bleached and deodorized
RI	=	reflective index
SEM	=	scanning electron microscopy
TAG	=	triacylglycerol
XRD	=	X-ray diffraction
ϕ	=	general term of frequency (e.g. length,number,surface or volume)
c	=	concentration (%)
C'	=	constant, J m
d_{av}	=	arithmetic mean of particle diameter
d_i	=	mean diameter of size band I
D_s	=	mean diameter of the distribution
d_i	=	particle diameter
d_s	=	surface mean particle size
d_v	=	volume mean particle size
d_{vs}	=	volume surface mean particle size

E_j = light energy falling on any ring j, J

f = focal length of lens, m

G = growth rate (m/s)

h = thickness of the plate

J_0, J_1 = Bessel functions

k = wave number of incident light, 1/m

L = length

$L_{i,M}$ = measured size of size range i, m

L_s = initial seed size (mm)

L_{sp} = final seed size (mm)

N = number

Q_i = extinction coefficient of size band I

S = surface

S_c = seed surface area (cm^2)

s_{j1}, s_{j2} = radii of ring j in focal plane, m

T_{ij} = the light energy falling on any ring j due to a particle of size Li, J

V = volume

V_i = volume in size band I

W_c = theoretical crystallized mass (g)

W_i = weight percent of particles in size range i with calibration, %

W_s = seed mass (g)

x_0 = smallest particle in the distribution

x_∞ = largest particle in the distribution

x_g = geometric mean size

x_m = mean size

x_{NL}	=	length mean diameter by number
x_{NS}	=	surface mean diameter by number
x_{NV}	=	volume mean diameter by number
x_{SV}	=	mean size of surface distribution
x_{VM}	=	mean size of weight distribution
α	=	volume shape factor (dimensionless)
β	=	surface shape factor
λ	=	wavelength of He–Ne laser, m
ρ	=	crystal density (g/m^3)
σ	=	standard deviation of particle distribution
σ^2	=	variance of particle distribution
σ_g	=	geometric standard deviation

CHAPTER 1

INTRODUCTION

1.1 Hydroxy Fatty Acid

The industry has shown great interest in hydroxy fatty acid because of their different behavior compared with ordinary fatty acids (Weber *et al.*, 1995). Hydroxyl fatty acids and its derivatives have many applications such as additives in lubricants, in cosmetics and surfactants (Dahlke *et al.,* 1995). Castor oil is the main source of hydroxyl fatty acids but because of its unavailability in Malaysia, oleic acid is an alternative for the compound preparation. Palm oil contains around 40% of oleic acid, which can be obtained by splitting the oil/fat. Malaysian Palm Oil Board (MPOB) has successfully synthesized a new fatty acid derivative, which may have a great commercial potential, namely the dihydroxystearic acid (DHSA) (Rolia *et al.,* 1998).

1.2 Dihydroxystearic Acid (DHSA)

Dihydroxystearic acid is a hydroxyl fatty acid. It is produced from the epoxidation of oleic acid with peracetic acid. The resulting epoxide is hydrolyzed in an aqueous solution resulting in 9, 10-dihydroxystearic acid (Rolia *et al.*, 1998). The reaction is presented in Figure 1.1. The presence of hydroxyl and carboxylic group in the structure, provide various reaction sites for the preparation of many useful derivatives.