UNIVERSITI PUTRA MALAYSIA

CRYSTALLIZATION OF PALM OIL-BASED 9,10-DIHYDROXYSTEARIC ACID EMPLOYING ISOPROPYL ALCOHOL AS SOLVENT

GREGORY KOAY FENG LING

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By

GREGORY KOAY FENG LING

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

April 2007

This thesis is specially dedicated to
My beloved parents, Stanislaus and Agnes
My siblings, Anthony and Clement
&
All my love ones
For standing by me through thick and thin

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

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Chairman: **Associate Professor Luqman Chuah Abdullah, PhD**

Faculty: **Engineering**

9,10-dihydroxystearic acid (DHSA) was derived from commercial grade palm oil based crude oleic acid. It was derived through the epoxidation of the unsaturation present in the oleic acid with performic acid in the presence of sulphuric acid and hydrogen peroxide, followed with in-situ hydrolysis of the epoxide with hydrogen donor such as water. DHSA promises great potential in the personal care industry. It has the prospective to act as a multipurpose intermediate in the synthesis of fine chemical products such as decorative cosmetics. However, the impurities present in DHSA could lead to skin irritation and thus the crude DHSA produced need to endure purification process in order to be qualified as an additive for the cosmetic industry. Solvent crystallization was chosen as the path in preparing DHSA crystals of at least 80% purity and of high desirability.

The objective of this research was to study the effects of temperature and of solvent quality and quantity on the solvent crystallization of DHSA. On detailing the effects of temperature, four aspects were scrutinized: weight based crystal yield, particle size distribution (PSD), quality of purified DHSA crystals and crystallization operation efficiency. PSD, crystal morphology and quality of purified DHSA crystals were scrutinized when detailing the effects of solvent quality and quantity.

In the course of carrying out the research work, a crystallization unit was fabricated. The detailed design and operation of the crystallization unit were described. This research, through gas chromatography (GC), PSD, Fourier Transform – Infra Red (FT-IR) and scanning electron microscopy (SEM) analysis, revealed that solvent crystallization of DHSA was best carried out with the cooling temperature of 20°C, 80% isopropyl alcohol (IPA) concentration and $\frac{\text{crude dihydroxystearic acid}}{\text{solvent}}$ ratio of 1.0:1.0.

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

PENGHABLURAN ASID 9,10-DIHIDROKSISTEARIK BERASASKAN MINYAK SAWIT MENGGUNAKAN ISOPROPIL ALKOHOL SEBAGAI PELARUT

Oleh

GREGORY KOAY FENG LING

April 2007

Pengerusi: **Profesor Madya Luqman Chuah Abdullah, PhD**

Fakulti: **Kejuruteraan**

Asid 9,10-dihidroksistearik (DHSA) dihasilkan daripada asid oleik mentah yang berasaskan minyak sawit bergred dagangan. Ia dihasilkan melalui proses mengepoksidasikan ketidaktepuan yang wujud dalam asid oleik dengan asid performik. Proses ini dijalankan dalam kehadiran asid sulfurik dan hidrogen peroksida. Seterusnya, proses hidrolisis dijalankan secara *in-situ* keatas epoksida yang terhasil dengan penderma hidrogen seperti air. DHSA mempunyai potensi yang baik dalam industri penghasilan barangan penjagaan diri. Ia mempunyai prospek untuk menjadi pengantara pelbagaiguna dalam sintesis bahan kimia halus seperti bahan kosmetik untuk tujuan perhiasan diri. Namun, bahan cemar yang hadir boleh mengakibatkan kesan sampingan. Oleh itu, DHSA mentah perlu dinyahcemarkan supaya ia boleh digunakan sebagai aditif dalam industri kosmetik. Proses penghabluran dengan bantuan pelarut telah dipilih untuk menghasilkan hablur DHSA berketulenan 80% dan ke atas serta mempunyai permintaan yang tinggi dalam pasaran.

Objektif kajian ini ialah untuk mengkaji kesan suhu dan kesan kualiti dan kuantiti bahan pelarut ke atas penghabluran DHSA. Dalam mengkaji kesan suhu, empat aspek telah diperinci: jumlah penghasilan hablur, taburan saiz zarah (PSD), kualiti hablur DHSA yang telah ditulenkan dan kecekapan operasi penghabluran. PSD, morfologi hablur dan kualiti hablur DHSA diperinci semasa mengkaji kesan kualiti dan kuantiti bahan pelarut.

Dalam pada menjalankan kerja kajian ini, seunit mesin penghablur telah dibina. Rekabentuk dan cara mengoperasikan mesin penghablur ini telah diterangkan secara terperinci. Analisis kromatografi gas (GC), PSD, Penukaran Fourier – Infra Merah (FT-IR) dan penelitian mikroskopi dengan elektron (SEM), menunjukkan bahawa penghabluran DHSA paling sesuai dijalankan pada suhu 20°C dengan alkohol isopropil berkepekatan 80% dan DHSA mentah:bahan pelarut bernisbah 1.0:1.0.

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Last but not least, I thank my parents, siblings, all my family members and all my love ones for their continuous prayers, love and support throughout my course of study.

I certify that an Examination Committee has met on 18 April 2007 to conduct the final examination of Gregory Koay Feng Ling on his Master of Science thesis entitled "Crystallization of Palm Oil-Based 9,10-Dihydroxystearic Acid Employing Isopropyl Alcohol as Solvent" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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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.

GREGORY KOAY FENG LING

Date: 28 DECEMBER 2006

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LIST OF ABBREVIATIONS

AOTD	Advanced Oleochemical Technology Division
BTSFA	Bis(trimethylsilyl)trifluoroacetamide
CSD	Crystal size distribution
CSTR	Continuous stir tank reactor
DHSA	Dihydroxystearic acid
DMF	N,N-Dimethylformamide
D [3,2]	Surface weighted mean diameter
D [4,3]	Volume weighted mean diameter
FFA	Free fatty acids
FT-IR	Fourier Transform – Infra Red
G	Growth rate
GC	Gas chromatography
HCOOH	Performic acid
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid
IPA	Isopropyl alcohol
J	Nucleation rate
J_i^+	Adsorption rate of component i
J_i^-	Desorption rate of component i
KBr	Potassium bromide
KCl	Potassium chloride

KNO_3	Potassium nitrate
L_D	Lag time
L_s	Steady state geometric mean crystal diameter
$L'(t)$	Geometric mean size of fat crystals' size distribution with time
MPOB	Malaysian Palm Oil Board
N	Population density
NaCl	Sodium chloride
Na_2SO_4	Sodium sulphate or sodium sulphate anhydrous
PKO	Palm kernel oil
PSD	Particle size distribution
RI	Reflective index
Rt	Retention time
SEM	Scanning electron microscopy
TAG	Triacylglycerols
T_c	Crystallization temperature
TMS	Trimethylsilyl
T_m (K) or T_m	Melting point or melting temperature
X_i	Average mesh size
XRD	X-ray diffraction
a_{eq}	Chemical activity at equilibrium state
a_{ss}	Chemical activity at supersaturated state
d_v	Volume diameter
d_s	Surface diameter

d_{sv}	Surface volume diameter
d_d	Drag diameter
d_f	Free falling diameter
d_{St}	Stokes' diameter
d_a or d_p	Projected area diameter
d_c	Perimeter diameter
d_A	Sieve diameter
d_F	Feret's diameter
d_M	Martin's diameter
d_R	Unrolled diameter
h_i	Induction time
k_i	Volume percent
n	Number density per volume of crystals or total volume percent, 100
s	Standard deviation
$s_{\max}$	Maximum fraction of solid fat
$s(t)$	Fraction of solid fat at time t
x	Solubility of solute at temperature T (K)
x_{eq}	Chemical activity of ideal solution at equilibrium state
x_{ss}	Chemical activity of ideal solution at supersaturated state
x_i^l	Molar fraction of component i at arbitrary point
$x_{i,eq}^l$	Molar fraction of component i at equilibrium liquid state
x_i^s	Concentration of component i at solid surface

x_j^s	Concentration of component *j* at solid surface
ΔG_c	Activation free energy of nucleation
ΔG_d	Activation free energy of diffusion
ΔH	Change in enthalpy
ΔH_m	Molar heat of melting
ΔT	Supercooling value
λ	Nominal induction time
μ	Maximum increase rate in fraction solid fat
μ_{eq}	Chemical potential at equilibrium state
μ_{ss}	Chemical potential at supersaturated state
v	Growth rate
σ	Supersaturation or crystal/melt interface free surface energy
τ_c	Time constant associated with crystallization

CHAPTER 1

INTRODUCTION

1.1 Oleochemicals

Oleochemicals are chemicals derived from biological oils and fats via the splitting of triglycerides into their constituent fatty acid derivatives and glycerol or via modification of oils and/or fats. The oils and/or fats may be of vegetable (*e.g.* castor oil, coconut oil, corn oil, cottonseed oil, groundnut oil, linseed oil, olive oil, palm kernel oil (PKO), palm oil, rapeseed oil, sesame oil, soybean oil, sunflower oil, etc.), animal (*e.g.* butter, lard and grease, edible and non edible tallow, etc.) or marine (*e.g.* fish oil) origin. Oleochemicals are analogous to petrochemicals. In other words, similar chemicals may be synthesized from petroleum. The most basic oleochemicals are fatty acids, fatty methyl esters, fatty alkyl esters, fatty alcohols, fatty amines and glycerol (Ahmad *et al.*, 2000a).

1.2 Fatty Acids

In chemistry, a fatty acid is a carboxylic acid. A fatty acid is characterized by the number of carbon atoms in the carbon chain, ranging generally from caproic acid with six carbon atoms to behenic acid with 22 carbon atoms. Most of the natural fatty acids have an even number of carbon atoms. Fatty acids without double bonds are called saturated fatty acids. They are generally solids (Dieckelmann and Heinz, 1988).

Saturated fatty acids also do not contain other functional groups along the carbon chain. The term 'saturated' refers to hydrogen, in that all carbons (apart from the carboxylic acid [-COOH] group) contain as many hydrogen atoms as possible.

Fatty acids with double bonds are unsaturated and generally liquids (Dieckelmann and Heinz, 1988). One or more alkene functional groups exist along the carbon chain, with each alkene substituting a singly-bonded '$-CH_2-CH_2-$' part of the chain with a doubly bonded '-CH=CH-' part. The two hydrogen atoms that are bound to the doubly bonded carbon atoms can occur in either *cis*- or *trans*- configuration.

1.3 Palm Oil and Palm Kernel Oil as Sources of Fatty Acids

In tallow, C_{16} and C_{18} fatty acids dominate; in coconut oil, C_{12} and C_{14} acids are more prevailing (Dieckelmann and Heinz, 1988). Thus, tallow and coconut oil are traditionally used as feed stocks for oleochemicals of chain lengths 12, 14, 16, 18 and 18:1. Prior to 1985, tallow was an important raw material for the oleochemical industry. However, during the period 1985-1995, the significance of tallow was greatly reduced. This was due to the following three factors:

- Minimal increase in the world's production (about 25% increase in 10 years);
- Suspected relationship between human disease and materials of animal origin and thus, the reluctance of manufacturers to use tallow;

- The negative perception among consumers on the use of animal derived oleochemicals for consumer products, particularly in personal care products.

For the ensuing years, no increase or even a decrease in tallow production and use was foreseen and it was expected that tallow would play a less important role in the oleochemical industry in the future.

In a similar fashion, prior to 1985, coconut oil was the most important source of C_{12} and C_{14} fatty acids for the oleochemical industry. However, during the period of 1985-1995, the global production of coconut oil increased by only 10% and the production was not expected to increase significantly in the foreseeable future. Thus, the significance of coconut oil for the oleochemical industry was also expected to be diminished somewhat in the future (Ahmad *et al.*, 2000a).

For the corresponding period, both palm oil and PKO enjoyed steady and heartening growth in Malaysia. In 1985, the production of crude palm oil and crude PKO stood at 4,134,463 and 511,908 tons per annum respectively and by the year 1994, the production increased to 7,810,546 and 1,036,538 tons per annum respectively. There was almost a 90% increase for crude palm oil production and over 100% increase for crude PKO production. For the ensuing 10 years, the production increase was almost 80% for crude palm oil and almost 60% for crude PKO. In 2004, the production of crude palm oil stood at 13,976,182 tons per annum while the production of crude PKO stood at 1,644,445 tons per annum (MPOB, 2005). The annual production of oil palm products in Malaysia for the period 1975-2004 is shown in Table 1.1.

Table 1.1: Malaysian annual production of oil palm products for 1975 – 2004 (Malaysian Palm Oil Board – MPOB, 2005)

Year	Crude palm oil (tons)	Crude PKO (tons)
1975	1,257,573	108,260
1980	2,573,173	222,285
1985	4,134,463	511,908
1990	6,094,622	827,233
1995	7,810,546	1,036,538
2000	10,842,095	1,384,685
2004	13,976,182	1,644,445

This mass production not only put Malaysia in the global map as both the world top producer and exporter of palm oil but also as the world third major producer and top exporter of 17 biological oils and fats besides elevating the status of palm oil as the world second most produced biological oils and fats, ranking right behind soybean oil (MPOB, 2005).

Insignificant increase in tallow production allowed the emergence of palm oil as a new source of C_{16} and C_{18}. As the centre of growth of oleochemicals gradually shifts to the ASEAN region, palm oil would equally replace tallow and its usage would therefore markedly increase (Yusof *et al.*, 1996; Ahmad *et al.*, 2000a). Coconut oil used to enjoy a unique position in the oleochemical industry due to its fatty acid composition, particularly lauric acid which is highly regarded in the cosmetics and detergent industry. However, this position is threatened with the emergence of PKO as the sole alternative source of commercially available lauric oils. For Malaysian oleochemical