UNIVERSITI PUTRA MALAYSIA

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By

TRI HARYATI

Dissertation Submitted in Fulfilment of the Requirements
for the Degree of Doctor of Philosophy in the
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Dedicated to my beloved husband
Lalang Buana, my daughters
Rika, Ratna, Ririn and
my father H.M. Salim

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LIST OF ABBREVIATIONS

A	area
AOCS	American Oil Chemists' Society
BSI	British Standards Institute
C8	caprylic acid
C9	pelargonic acid
C10	capric acid
C13	tridecanoic acid
C14	myristic acid
C16	palmitic acid
C18	stearic acid
C18-1	oleic acid
C18-2	linoleic acid
CP	cloud point
CPO	crude palm oil
CV	coefficient of variance
DG	diglyceride
DSC	differential scanning calorimetry
FAD	fatty acid distillate
FFA	free fatty acid
FTIR	Fourier transform infrared
g	gram

GLC	gas liquid chromatography
HF	heat flow
HMG	high melting glyceride
HPLC	high performance liquid chromatography
IUPAC	International Union of Pure and Applied Chemistry
IV	iodine value
L	linoleic acid
LMG	low melting glyceride
M	myristic acid
m	metre
mg	milligram
min	minute
mL	millilitre
mm	millimetre
MMM	trimyristoyl glycerol
MP	melting point
MPL	myristoyl-palmitoyl-linoleoyl glycerol
MPOPC	Malaysian Palm Oil Promotion Council
MSE	mean square error
mW	milliwatt
NIR	near infrared
NMR	nuclear magnetic resonance

O	oleic acid
°C	degree celcius
OOO	trioleoyl glycerol
OPO	dioleoyl-2-palmitoyl glycerol
OPP	dipalmitoyl-1-oleoyl glycerol
OPS	oleoyl-palmitoyl-stearoyl glycerol
OSP	oleoyl-stearoyl-palmitoyl glycerol
OSS	distearoyl-1-oleoyl glycerol
P	palmitic acid
PEP	dipalmitoyl-2-elaidioyl glycerol
PLO	palmitoyl-linoleoyl-oleoyl glycerol
POO	dioleoyl-1-palmitoyl glycerol
POP	dipalmitoyl-2-oleoyl glycerol
PORAM	Palm Oil Refiners Association of Malaysia
PORIM	Palm Oil Research Institute of Malaysia
POS	palmitoyl-oleoyl-stearoyl glycerol
PPL	dipalmitoyl-3-linoleoyl glycerol
PPM	dipalmitoyl-3-myristoyl glycerol
PPO	dipalmitoyl-3-oleoyl glycerol
PPP	tripalmitoyl glycerol
PPS	dipalmitoyl-3-stearoyl glycerol
PSO	palmitoyl-stearoyl-oleoyl glycerol

PSP	dipalmitoyl-2-stearoyl glycerol
PSS	distearoyl-1-palmitoyl glycerol
RBD	refined, bleached and deodorised
RI	refractive index
RSM	response surface methodology
S	stearic acid
S3	trisaturated
SAS	statistical analysis system
SES	distearoyl-2-elaidioyl glycerol
SFC	solid fat content
SFI	solid fat index
SOS	distearoyl-2-oleoyl glycerol
SPO	stearoyl-palmitoyl-oleoyl glycerol
SPS	distearoyl-2-palmitoyl glycerol
SSO	distearoyl-3-oleoyl glycerol
SSS	tristearoyl glycerol
TG	triglyceride
U3	triunsaturated
uL	microlitre
w/w	weight/weight

Abstract of dissertation presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

DEVELOPMENT AND APPLICATIONS OF DIFFERENTIAL SCANNING CALORIMETRIC METHODS FOR PHYSICAL AND CHEMICAL ANALYSIS OF PALM OIL

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TRI HARYATI

June 1999

Chairman : Professor Yaakob B. Che Man, Ph. D.

Faculty : Food Science and Biotechnology

Fractionation is accomplished by exploiting different crystallisation point of triglyceride (TG). This theoretical basis exposes the importance of thermal behaviour of the palm oil on the success of the fractionation process as well as the use of differential scanning calorimeter (DSC) for analysing some palm oil parameters. In this study, new methods to determine melting point (MP), cloud point (CP), iodine value (IV), and the composition of TG groups of palm oil were developed. The methods were then applied for monitoring chemical transesterification.

The appropriate running conditions of DSC for analysing palm oil were heating and cooling rate of 5°C/min, holding time of 5 minutes and sample weight of 2.3 - 18.4 mg. Regression models to calculate MP, CP, and IV of standard methods

were developed. For MP, the offset temperature from the heating thermogram was used to develop the model, while for CP and IV, the models used onset temperature and energy, respectively, from cooling thermogram. Using similar theoretical background as in IV, models to calculate trisaturated and triunsaturated TG concentration were developed. Regression models were developed to calculate trisaturated TG using energy in cooling thermogram and triunsaturated TG using energy either in cooling or heating thermograms. The study have shown that all DSC methods developed were more consistent than the standard AOCS methods.

Redistribution of the fatty acids was achieved through chemical transesterification. Using response surface methodology, trisaturated TG obtained from high performance liquid chromatography (HPLC) increased 2.1 times and triunsaturated TG increased 1.88 times from the original. Using DSC, the increase was 2.14 times for trisaturated and 1.92 times for triunsaturated.

Overall, this study have shown that DSC can be used to determine MP, CP, IV and TG group composition. The advantages of these methods are that they are rapid and convenience than the conventional methods and without using toxic chemicals and, therefore, more useful for process control, non-hazardous to the health of the analyst and environmentally friendly. Furthermore, DSC provides thermal profile which is an important reference for fractionation process. The most important advantage is that all of these parameters can be determined using only a single heating or cooling thermogram.

Abstrak disertasi yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi syarat untuk ijazah Doktor Falsafah

PENGEMBANGAN DAN PENERAPAN KAEDAH-KAEDAH *DIFFERENTIAL SCANNING CALORIMETRY* UNTUK ANALISA SIFAT-SIFAT FIZIKAL DAN KIMIA DALAM MINYAK SAWIT

Oleh

TRI HARYATI

Jun 1999

Pengerusi : Profesor Yaakob B. Che Man, Ph. D.

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Pemeringkatan minyak sawit dilaksanakan berdasarkan perbezaan takat kristal trigliserida (TG). Asas teori ini memperlihatkan kepentingan ciri-ciri terma dalam kejayaan proses pemeringkatan dan penggunaan peralatan *differential scanning calorimeter* (DSC) untuk menganalisa parameter kualiti minyak sawit. Dalam kajian ini, kaedah baru untuk menentukan takat lebur (MP), takat awan (CP), nilai iodin (IV) dan komposisi kumpulan TG dalam minyak sawit telah dibina. Selanjutnya, kaedah baru ini telah diterapkan dalam pengawasan transesterifikasi.

Keadaan operasi yang sesuai bagi DSC untuk minyak sawit adalah dengan kadar pemanasan dan penyejukan pada 5°C/min, masa penahanan selama 5 min dan berat sampel 2.3-18.4 mg. Model regresi untuk mengira MP, CP dan IV kaedah