UNIVERSITI PUTRA MALAYSIA

PRODUCTION OF PALM-BASED DIACYLGLYCEROL OLEIN AND STEARIN THROUGH DRY FRACTIONATION OF PALM-BASED DIACYLGLYCEROL FAT AND ITS APPLICATIONS AS COOKING OIL AND BAKERY SHORTENING

RAZAM ABD LATIP

FBSB 2012 37

PRODUCTION OF PALM-BASED DIACYLGLYCEROL OLEIN AND STEARIN THROUGH DRY FRACTIONATION OF PALM-BASED DIACYLGLYCEROL FAT AND ITS APPLICATIONS AS COOKING OIL AND BAKERY SHORTENING

By

RAZAM ABD LATIP

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Doctor of Philosophy

April 2012

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

PRODUCTION OF PALM-BASED DIACYLGLYCEROL OLEIN AND STEARIN THROUGH DRY FRACTIONATION OF PALM-BASED DIACYLGLYCEROL FAT AND ITS APPLICATIONS AS COOKING OIL AND BAKERY SHORTENING

By

RAZAM ABD LATIP

April 2012

Chairman : Professor Lai Oi Ming, PhD

Faculty : Faculty of Biotechnology and Biomolecular Sciences

This work was aimed at developing a novel fractional crystallisation process of palm-based diacylglycerol (PDAG) fat for production of palm-based diacylglycerol olein (PDAGL) and palm-based diacylglycerol stearin (PDAGS) for applications as cooking oil and bakery shortening. In the first part of this work, the effect of crystallisation temperature (Ct), cooling rate (Cr) and agitation speed (As) on physical and chemical properties of PDAGL and PDAGS were studied. It was noted that as Cr increased, the amount of palmitic acid, C16:0 and oleic acid, C18:1 in PDAGL increased (from 35.0 to 37.2%) and decreased (from 47.1 to 45.3%), respectively, resulting in decrease in iodine value (IV) (from 58.8 to 52.3). Similar trend was observed when Ct is increased, the amount of C16:0 increased from 33.5 to 38.7% and C18:1 decreased from 49.1 to 44.6%. Fast cooling produced PDAGS with lower amount of saturated fatty acid C16 and hence, contributed to higher IV. There is no correlation between physical and chemical properties of PDAGL and

PDAGS with different As. Crystallisation process parameters namely Cr, Ct and As were optimized using dual response surface methodology (RSM) in lab scale. The optimal crystallisation process parameters were 1.0 °C/min of Cr, 46 rpm of As and 37°C of Ct which yielded approximately 70 wt % of PDAGL with 58 IV. The optimal crystallisation process parameters can be further scaled-up to a 50 kg crystalliser for production of PDAGL with similar IV and percentage yield.

The oxidative stability of PDAG oil and its olein fraction were investigated at 120 °C by the rancimat method with and without addition of antioxidants. Heat stability test was conducted at 90°C for 5 days. Compared with TAG-based oils, the PDAG-based oil displayed lower oxidative stability due to lower content of tocopherols. The oxidative stability of PDAGL improved with addition of 1000 ppm tocopherols, 1000 ppm citric acid, 200 ppm tertiary butyl hydroquinone (TBHQ) and mixture of 100 ppm BHT and 100 ppm BHA. Among all antioxidants, natural antioxidant, tocopherol and synthethic antioxidant, TBHQ showed highest oxidative stability improvement to the oil. The induction period (IP) of PDAGL increased from 10.26 ± 0.28 to 13.58 ± 0.43 and 19.72 ± 0.36 h with addition of 1000 ppm tocopherol and 200 ppm TBHQ, respectively. The stability of palm olein (POL), PDAGL without antioxidant and with 1000 ppm tocopherol (PDAGL(T)) and 200 ppm TBHQ (PDAGL(Q)) under deep-frying conditions were investigated. PDAGL exhibited better IP than POL. However, the free fatty acid (FFA) increased 3 times faster in PDAGL compared to POL. The rate of FFA formation in PDAGL was 0.7 times lower when antioxidants were added. However, no significant difference ($P>0.05$) in FFA content was observed in PDAGL and PDAGL(Q). The initial IP of PDAGL

(9.95 ± 0.04 h) was increased upon addition of tocopherol (14.55±0.05 h) and TBHQ (17.83 ± 0.04 h). PDAGL(T) showed slower reduction in the IP throughout frying process as compared to PDAGL(Q). However, additions of antioxidants to PDAGL showed no significant effect ($P>0.05$) in polymerized-glyceride (PG) and anisidine value (AV) produced throughout the frying due to oxidization of the antioxidants upon heating, thus decreasing their antioxidant activities. It can be concluded that PDAGL is suitable as cooking oil but not for industrial frying oil.

The physicochemical properties including phase, melting and crystallisation behavior of shortening systems produced from PDAGS with palm-mid fraction (PMF), POL and sunflower oil (SFO) were studied. The results showed that PDAGS and PMF were hard fats while SFO was a softer oil than POL. Due to sharp melting points of PMF, the SFC profile of PDAGS/PMF was able to achieve the desired level of solid fat especially at body temperature for food application. The binary mixtures of PDAGS/SFO had very low SFC at temperature below 35^{o}C as compared to PDAGS/POL. The melting profiles of PDAGS/PMF, PDAGS/POL and PDAGS/SFO had completely different low melting fraction (LMF) and medium melting fraction (MMF) but almost similar high melting fraction (HMF). Thermodynamic analysis of liquidus line showed that all binary mixtures of PDAGS/ PMF, PDAGS/POL and PDAGS/SFO had ideal mixing behavior where the calculated liquidus line reproduced well with the experimental points in phase diagram. The iso-solid diagram constructed showed that no eutectic behavior existed in all binary mixtures. However, the iso-solid lines of PDAGS/POL lacked structural complementary between high and low percentage of SFC line, while PDAGS/SFO not well constructed at high percentage of SFC line. The results from X-Ray

Diffractometer (XRD) analysis showed that both binary mixtures of PDAGS/PMF and PDAGS/SFO were crystallized in β'+β polymorphs at X_{PDAGS} = 0.4 to X_{PDAGS} = 0.5, while all the binary mixtures of PDAGS/POL were crystallized in β polymorphs. Overall analyses results gave indication that PDAGS and PMF blend was the most suitable fat blend to be used as bakery shortening.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENGHASILAN OLEIN DAN STEARIN DIASILGLISERIDA MINYAK SAWIT MELALUI PROSES FRAKSINASI KERING LEMAK DIASILGLISERIDA MINYAK SAWIT BAGI APLIKASI SEBAGAI MINYAK MASAK DAN LELEMAK BAKERI

Oleh

RAZAM ABD LATIP

April 2012

Pengerusi : Profesor Lai Oi Ming, PhD

Fakulti : Fakulti Bioteknologi dan Sains Biomolekul

Kajian ini bertujuan untuk menghasilkan satu proses baru fraksinasi untuk lelemak diasilgliserida minyak sawit (PDAG) bagi penghasilan olein diasilgliserida minyak sawit (PDAGL) dan sterin diasilgliserida minyak sawit (PDAGS) untuk diaplikasikan sebagai minyak masak dan lelemak bakeri. Pada peringkat awal kajian ini, pengaruh suhu pengkristalan (Ct), kadar penyejukan (Cr) dan kelajuan kitaran (As) terhadap sifat fizikal dan kimia PDAG dan PDAGS telah dikaji. Peningkatan Cr, menyebabkan peningkatan jumlah asid palmitik, C16 (dari 35.0 kepada 37.2%) dan penurunan (dari 47.1 kepada 45.3%) jumlah asid oleik, C18:1 di dalam PDAGL menyebabkan nilai iodin (IV) yang lebih rendah. Keadaan yang serupa dapat diperhatikan apabila Ct meningkat, di mana jumlah C16 meningkat daripada 33.5% kepada 38.7% dan C18:1 menurun daripada 49.1% kepada 4.6%. Penyejukan cepat menghasilkan PDAGS dengan jumlah lemak tepu, C16 yang lebih rendah, maka menghasilkan IV yang tinggi. Tiada korelasi antara sifat fizikal dan

kimia PDAGL dan PDAGS pada As yang berbeza. Parameter proses pengkristalan seperti Cr, Ct dan As telah dioptimumkan melalui Kaedah Tindakbalas Permukaan (RSM) dalam skala makmal. Parameter optima bagi proses pengkristalan PDAG adalah 1.0 ^{o}C/min bagi Cr, 46 rpm bagi As dan 37^{o}C bagi Ct yang mana menghasilkan lebih kurang 70% daripada berat PDAGL dengan IV 58. Parameter untuk proses pengkristalan yang optimum boleh digunakan pada skala yang lebih besar sehingga pengkristal 50 kg untuk menghasilkan PDAGL dengan IV dan peratusan penghasilan yang sama.

Kestabilan oksidatif minyak PDAG dan PDAGL tanpa dan dengan penambahan antioksida telah dijalankan pada suhu 120^{o}C menggunakan kaedah ransimat. Manakala ujian kestabilan haba telah dijalankan pada suhu 90^{o}C selama 5 hari. Berbanding dengan minyak berasaskan TAG, minyak berasaskan PDAG menunjukkan kestabilan oksidatif yang lebih rendah disebabkan kandungan tokoferol yang rendah. Kestabilan oksidatif PDAGL meningkat dengan penambahan 1000 ppm tokoferol, 1000 ppm citric asid, 200 ppm tertiari butil hidrokuinon (TBHQ) dan campuran dari 100 ppm BHT dan 100 ppm BHA. Di antara semua antioksida, antioksida semulajadi tokoferol dan antioksida sintetik TBHQ menunjukkan peningkatan kestabilan oksidatif tertinggi bagi minyak yang diuji. Tempoh induksi (IP) untuk PDAGL meningkat dari 10.26$\pm$0.28 ke 13.58$\pm$0.43 dan 19.72$\pm$0.36 h dengan penambahan 1000 ppm tokoferol dan 200 ppm TBHQ. Kestabilan POL, PDAGL tanpa antioksida dan PDAGL dengan 1000 ppm tokoferol (PDAGL(T)) dan 200 ppm TBHQ (PDAGL(Q)) telah dikaji di bawah keadaan pengorengan penuh. PDAGL menunjukkan IP yang lebih baik dari POL. Walaubagaimanapun, FFA telah meningkat 3 kali lebih cepat dalam PDAGL

berbanding POL. Kadar pembentukan FFA dalam PDAGL adalah 0.7 kali lebih rendah apabila ditambah antioksida. Namun begitu tiada perbezaan yang ketara (P>0.05) didapati bagi kandungan FFA bagi PDAGL dan PDAGL(Q). IP awal untuk PDAGL (9,95 $\pm$ 0,04 h) telah meningkat ketika penambahan tokoferol (14,55 0.05 h) dan TBHQ (17,83 0,04 h). PDAGL(T) menunjukkan penurunan yang perlahan dalam IP semasa proses pengorengan berbanding dengan PDAGL(Q). Namun, penambahan antioksida pada PDAGL tidak menunjukkan kesan ketara (P>0.05) pada PG dan AV yang dihasilkan semasa pengorengan berikutan pengoksidaan keatas antioksida semasa pemanasan sehingga menyebabkan penurunan aktiviti antioksida mereka. Ianya boleh disimpulkan bahawa PDAGL adalah sesuai sebagai minyak masak tetapi tidak sesuai sebagai minyak goreng berskala industri.

Sifat fisiokimia termasuk fasa, peleburan dan penghabluran sistem lelemak yang dihasilkan daripada PDAGS dicampur dengan Minyak Sawit Pertengahan (PMF), Minyak Olein Sawit (POL) dan Minyak Bunga Matahari (SFO) telah dikaji. Hasil kajian menunjukkan PDAGS dan PMF merupakan lemak keras manakala SFO merupakan minyak yang lebih lembut berbanding POL. Disebabkan oleh takat lebur PMF yang tajam, profil SFC bagi PDAGS/PMF boleh mencapai tahap lemak pepejal yang diingini terutamanya pada suhu badan bagi aplikasi makanan. Campuran binari PDAGS/SFO mempunyai kandungan SFC yang sangat rendah pada suhu di bawah 35 ºC jika dibandingkan dengan PDAGS/POL. Profil peleburan PDAGS/PMF, PDAGS/POL dan PDAGS/SFO mempunyai pecahan peleburan rendah (LMF) dan pecahan peleburan pertengahan (MMF) yang berbeza sepenuhnya tetapi mempunyai hampir sama pecahan peleburan tinggi (HMF). Analisis termodinamik garisan cecair

menunjukkan kesemua campuran binari PDAGS/PMF, PDAGS/POL dan PDAGS/SFO mempunyai perilaku campuran ideal dimana kiraan garisan cecair dihasilkan semula lebih baik, dengan takat eksperimen dalam rajah fasa. Rajah iso-pepejal yang dihasilkan menunjukkan tiada perilaku eutektik wujud dalam campuran binari. Walaubagaimanapun, garisan iso-pepejal PDAGS/POL kekurangan struktur yang saling melengkapi antara peratus garisan SFC tinggi dan rendah, sementara garisan iso-pepejal PDAGS/SFO tidak dihasilkan dengan baik pada peratus garisan SFC yang tinggi. Hasil daripada analisa XRD menunjukkan bahawa kedua-dua campuran PDAGS/PMF dan PDAGS/SFO adalah penghabluran dalam pempolimorfan ß' + ß pada X_{PDAGS} = 0.4 kepada X_{PDAGS} =0.5, sementara kesemua campuran binari PDAGS/POL adalah penghabluran dalam pempolimorfan ß. Hasil analisa keseluruhan menunjukkan campuran PDAGS dan PMF adalah campuran yang paling sesuai untuk digunakan dalam lelemak bakeri.

ACKNOWLEDGEMENTS

With great thanks to Almighty Allah S.W.T and His mercy for giving me life and the opportunity to write this thesis as required.

I would like to take this opportunity to express my most sincere appreciation and deepest gratitude to Prof. Dr Lai Oi Ming of Faculty of Biotechnology and Biomolecular Sciences. Without her valuable guidance, advice, suggestions and constructive criticisms, I would not have been able to present my work and in the preparation of this thesis.

I offer my sincere thanks to other members of the Assoc. Prof. Dr. Tan Chin Ping of Faculty of Food Science and Technology, Dr. Kamariah Long of MARDI for their supervision, support and comments.

Special thanks and appreciation to my friends and staff of Sime Darby Research Sdn. Bhd. for their assistance in preparing this thesis. I would also like to acknowledge Sime Darby Research Sdn. Bhd. for approving my PhD studies and for the laboratory facilities made available in Sime Darby Jomalina Sdn. Bhd.

I also owe my special thanks to my beloved wife Aziah Lajis for her inspiration, moral encouragement, support, patience and sacrifices which had helped me in my undertakings and completing this research study.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Lai Oi Ming, PhD
Professor,
Faculty of Biotechnology and Biomolecular Sciences
Universiti Putra Malaysia
(Chairman)

Tan Chin Ping, PhD
Associate Professor,
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Member)

Kamariah Long, PhD
Deputy Director
Bio-Processing Programme,
Biotechnology Research Centre,
MARDI Head Quarters
(Member)

.....
BUJANG BIN KIM HUAT, PhD
Professor and Deputy Dean,
School of Graduate Studies
Universiti Putra Malaysia

Date :

DECLARATION

I declare that the thesis is my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously and it is not currently, submitted for any other degree at Universiti Putra Malaysia or other institutions.

.....

RAZAM ABD LATIP

Date : 20 April 2012

TABLE OF CONTENTS