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MANAGING 3-MONOCHLOROPROPANE-1,2-DIOL (3-MCPD) ESTERS DURING PALM OIL REFINING

MUSFIRAH ZULKURNAIN

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By

MUSFIRAH ZULKURNAIN

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Chair: Professor Tan Chin Ping, PhD

Faculty: Faculty of Food Science and Technology

Contamination with 3-monochloropropane-1,2-diol esters (3-MCPD) in a palm oil physical refining process was studied, and their analytical, chemical and processing factors were determined for mitigation purposes. For monitoring purposes, two disputable indirect methods, acid transesterification and alkaline transesterification method were compared, and the best method for the determination of 3-MCPD esters in oil samples using gas chromatography-tandem mass spectrometry (GC-MS/MS) was validated in-house. The acid transesterification method showed better analytical relevance over the alkaline transesterification method, with a method detection limit (MDL) of 0.006 mg/kg, a method quantification limit (MQL) of 0.019 mg/kg and excellent recovery (93-105%) and precision (%RSD) (1.3-4.2%). Palm oil was found to contain the highest levels of 3-MCPD esters (2.36 ± 0.12 mg/kg) compared with other types of refined vegetable oil. The quantification of industrial palm oil samples at different stages of the refining process confirmed major formation of 3-MCPD esters during the deodorization stage and the formation of a small amount (11.2%) during the pre-treatment stage.

Subsequently, factors that contribute to formation of 3-MCPD esters in the palm oil refining process were assessed, including the effect of different crude palm oil (CPO) quality and refining parameters at all stages of the refining process. Poor quality CPO with a high phosphorus content (8.8 ppm) and a low deterioration of bleachability index (DOBI) value (2.4) gave a remarkably high formation of 3-MCPD esters. Utilizing D-optimal design, the effects of the degumming methods (water degumming and acid degumming) and different bleaching adsorbents (n=4) were studied relative to the minor components of palm oil that are likely to be the precursors of the 3-MCPD esters. Water degumming and bleaching with synthetic magnesium silicate significantly (p<0.05) reduced the level of 3-MCPD esters compared with other bleaching adsorbents, possibly due to the removal of precursors of 3-MCPD ester prior to deodorization step. Only phosphorus content exhibited a significant correlation (p<0.05) with the level of 3-MCPD ester (R^2=0.686), suggesting that phospholipids might be one of the precursor. The formation of 3-MCPD esters in the refining process also showed dependence on the temperature of the deodorization step.

The physical refining process was modified with the incorporation of a water degumming and washing step in addition to acid degumming. The synergistic effects of the combination of the adsorbents magnesium silicate and activated clay were utilized for the bleaching step. The modified process was then optimized using response surface methodology (RSM), with five processing parameters: water dosage (0-5%), acid degumming dosage (0-1%), degumming temperature (40-80 °C), bleaching earth dosage (0-1%) and deodorization temperature (220-280 °C), to obtain the greatest reduction in the formation of 3-MCPD esters with an acceptable

final refined bleached and deodorized (RBD) palm oil quality. Large reduction in 3-MCPD ester formation was observed with increasing water degumming percentage above 3%, reducing degumming temperature and increasing bleaching clay dosage. The color removal was significantly (p<0.05) influenced by increasing in all of the processing factors except bleaching clay dosage. The oil stability index (OSI) was significantly (p<0.05) contributed by increasing in acid dosage and degumming temperature, and decreasing in clay dosage and deodorization temperature. Incorporation of water degumming not affected the OSI value. The optimized conditions were 3.5% water dosage, 0.1% acid dosage, a degumming temperature of 60 °C, 0.3% bleaching earth dosage and a deodorization temperature of 260 °C. These conditions resulted in 87.2% reduction in 3-MCPD esters, from 2.948 mg/kg in RBD palm oil refined conventionally to 0.374 mg/kg, with color and OSI values of 2.4 R and 14.3 hrs, respectively. Model verification using one sample t-test at p<0.05 demonstrated the suitability of the established models in explaining the responses as function of the processing parameters.

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

MENGURUSKAN 3-MONOCHLOROPROPANE-1,2-DIOL (3-MCPD) ESTER DALAM PROSES PENULENAN FIZIKAL MINYAK KELAPA SAWIT

Oleh

MUSFIRAH ZULKURNAIN

Mei 2012

Pengerusi: Profesor Tan Chin Ping, PhD

Fakulti: Fakulti Sains dan Teknologi Makanan

Pecemaran karsinogen 3-monochloropropane-1,2 diol (3-MCPD) dalam proses penulenan fizikal minyak kelapa sawit telah dikaji dan kajian analitikal 3-MCPD ester, faktor kimia dan faktor pemprosesannya telah ditentukan untuk mencari penyelesaian permasalahan ini. Untuk tujuan pemantauan, dua kaedah yang dipertikaikan, kaedah transesterifikasi asid dan kaedah transesterifikasi alkali dibandingkan secara analitikal dan kaedah yang terbaik untuk kuantifikasi 3-MCPD ester di dalam sampel minyak telah ditentusahkan dengan menggunakan gas kromatografi tandem mass spektrometer (GC-MS/MS). Kaedah transesterifikasi asid menunjukkan relevansi analitikal lebih baik mengatasi kaedah transesterifikasi alkali dengan had kaedah pengesanan (MDL) pada 0.006 mg/kg, had kaedah kuantifikasi pada 0.019 mg/kg dan perolehan (93-105%) dan kepersisan (1.3-4.2%) yang cemerlang. Minyak kelapa sawit ditemui mengandungi amaun 3-MCPD ester tertinggi (2.36 ± 0.12 mg/kg) berbanding minyak masak tersaring lain. Kuantifikasi sampel minyal sawit daripada industri pada semua peringkat penulenan mengesahkan

pembentukan major 3-MCPD ester adalah pada peringkat nyahbau dan hanya sedikit (11.2%) penghasilan terdapat pada peringkat pra-rawatan.

Kemudian, faktor-faktor yang menyumbang kepada pembentukan 3-MCPD ester dalam proses penulenan minyak kelapa sawit telah dikaji, termasuk kesan pelbagai kualiti minyak kelapa sawit mentah (CPO) dan parameter penulenan pada setiap peringkat proses penulenan minyak. Kualiti CPO yang rendah dengan kandungan fosforus yang tinggi (8.8 ppm) dan niali DOBI (2.4) yang rendah menghasilkan amaun 3-MCPD ester yang luar biasa tinggi. Dengan menggunakan reka bentuk D-optimal, kesan kaedah nyahgum (nyahgum air dan nyahgum asid) dan pelbagai penjerap peluntur (n=4) telah diselidik relatif kepada komponen minor dalam minyak sawit yang berpotensi menjadi prekusor 3-MCPD ester. Nyahgum air and meluntur dengan megnesium silikat sintetik telah menurunkan amaun 3-MCPD ester dengan signifikan (p<0.05) berbanding penjerap peluntur lain barangkali kerana penyingkiran prekusor 3-MCPD ester sebelum peringkat nyahbau. Hanya kandungan fosforus menunjukan hubungkait (R^2=0.686) yang signifikan (p<0.05) dengan amaun 3-MCPD ester, mencadangkan bahawa fosfolipid mungkin merupakan prekusor tersebut. Penghasilan 3-MCPD ester dalam proses penulenan juga menunjukkan pergantungan terhadap suhu peringkat nyahbau.

Proses penulenan fizikal telah diubahsuai dengan menambahkan peringkat nyahgum air dan pembasuhan pada peringkat nyahgum asid. Kesan sinergi penggabungan penjerap peluntur megnisium silikat dan penjerap bumi asid telah digunakan untuk peringkat pelunturan. Proses yang telah diubahsuai kemudian dioptimumkan menggunakan kaedah permukaan responsi (RSM), dengan lima parameter proses:

dosis air (0-5%), dosis asid (0-0.1%), suhu peringkat nyahgum (40-80 °C), dosis penjerap bumi asid (0-1%) dan suhu peringkat nyahbau (220-280 °C), untuk mendapatkan pengurangan penghasilan 3-MCPD ester yang terbanyak dengan kualiti minyak kelapa sawit tertapis, terluntur dan ternyahbau (RBD) yang diterimapakai. Pengurangan 3-MCPD ester dengan jelas diperhatikan dengan peningkatan dosis air melebihi 3%, pengurangan suhu peringkat nyahgum dan peningkatan dosis penjerap bumi asid. Perlunturan warna dipenaruhi dengan signifikan (p<0.05) oleh peningkatan semua faktor pemprosesan yang dikaji. Nilai OSI disumbangkan secara signifikan (p<0.05) oleh peningkatan dosis asid dan suhu peringkat nyahgum, dan pengurangan dosis penjerap bumi asid dan suhu peringkat nyahbau. Penambahan peringkat nyahgum air tidak mempengaruhi nilai OSI. Kondusi optimum proses tersebut adalah 3.5% dosis air, 0.1% dosis asid, pada suhu peringkat nyahgum 60 °C, 0.3% dosis penjerap bumi asid dan pada suhu peringkat nyahbau 260 °C. Ini telah menghasilkan 87.2% pengurangan penghasilan 3-MCPD ester, daripada 2.948 mg/kg dalam minyak sawit RBD yang diproses secara konvensional kepada 0.374 mg/kg, dengan warna pada 2.4 R dan nilai OSI sebanyak 14.3 jam.Verifikasi model menggunakan ujian-t satu sampel menunjukkan nilai ujikaji tersebut bersetuju pada signifikasi p<0.05 yang menunjukkan kesesuaian model tersebut untuk menghuraikan responnya sebagai fungsi paramater proses.

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I certify that a Thesis Examination Committee has met on **14th May 2012** to conduct the final examination of Musfirah Zulkurnain on her thesis entitled "**Managing 3-Monochloropropane-1,2-diol (3-MCPD) Esters during Palm Oil Refining**" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science degree.

Members of the Thesis Examination Committee were as follows:

Nazamid Saari, PhD
Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Chairman)

Jinap Selamat, PhD
Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Internal Examiner)

Badlishah Sham Baharin, PhD
Associate Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Internal Examiner)

Miskandar Mat Sahri, PhD
Product Development & Advisory Services Division
Malaysian Palm Oil Board
Malaysia
(External Examiner)

_____

SEOW HENG FONG, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of **Master of Science**. The members of the Supervisory Committee were as follows:

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

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

Yaakob Che Man, PhD
Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and 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 is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

MUSFIRAH ZULKURNAIN

Date: 14 May 2012.

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