UNIVERSITI PUTRA MALAYSIA

STUDY ON RECOVERY AND UTILIZATION OF VALUABLE COMPONENTS FROM GLYCEROL RESIDUE

YONG KUANG CHIH

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

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To my family,

For their unremitting encouragement and support.

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

STUDY ON RECOVERY AND UTILIZATION OF VALUABLE COMPONENTS FROM GLYCEROL RESIDUE

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Chairman: Associate Professor Dzulkefly Kuang Abdullah, Ph.D.

Faculty: Science and Environmental Studies

The Malaysian palm-based oleochemicals industry is growing rapidly and producing an increasing array of products like fatty acid methyl esters, fatty alcohols and glycerine. In the production of these oleochemicals, by-products are produced in which many of them are potentially useful. One of the by-products is glycerol residue which is generated by a glycerol refining plant (the glycerine source is from methanolysis of palm kernel oil). Glycerol residue is a waste under Schedule Waste S181 of the Environmental Regulations in Malaysia. Currently, this waste is disposed off in landfills with the cost of about RM700.00/tonne. This research was therefore undertaken to characterize the glycerol residue, and to recover and utilize its valuable components. It was found that thirteen batches of glycerol residue, GR1 to GR13, showed variation in the contents of glycerol, ash, moisture and matter organic non-glycerol (MONG). Salt (63.7%), glycerol (19.7%) and MONG (12.9%, mainly as soap) were the three main

valuable components of glycerol residue, accounting for 96.3% of the residue, and the rest of 3.7% was moisture.

Seven methods based on chemical and physical treatments (Route 1 to Route 7) were developed to recover crude glycerine, crude fatty acid and salt from glycerol residue. The most simple and efficient method was Route 7 which was technically optimized from Route 6, and involved; acidification, filtration, decantation and evaporation. The most optimum condition of chemical treatment was to acidify the glycerol residue with dilute sulfuric acid (6%, v/v) to pH range of 4 to 5. Typical compositions of the recovered components (by Route 7) from GR9-20 and GR9-21 samples were: 24.7 wt.% and 30.1 wt.% crude glycerine, 7.1 wt.% and 7.9 wt.% crude fatty acid, and 75.8 wt.% and 74.4 wt.% salt respectively. The typical compositions of the recovered crude glycerines, GR9-20CG and GR9-21CG, were: 53.7% and 55.5% glycerol, 12.2% and 12.4% ash, 6.6% and 10.7% water, 27.5% and 21.4% MONG, and pH 4.1 and 4.4 respectively.

The crude glycerines (GR9-20CG and GR9-21CG) were vacuum distilled at 120°C to 137°C and 1.8 to 5.0 x 10^{-1} mbar pressure to produce distilled glycerine (42.0 wt.% and 42.6 wt.% respectively) and distilled bottom (DB) (47.9 wt.% and 46.4 wt.% respectively). The typical characteristics of distilled glycerine (DG) from both GR9-20DG and GR9-21DG samples were: 96.0% and 96.8% glycerol, 0.12% and 0.09% ash, 0.5% and 0.2% water, 3.4% and 2.9% MONG, 3.8 of pH, 51.0 and 66.0 of colour (Hazen), and 1.2591 and 1.2603 of relative density (20°C) respectively. The typical

compositions of distilled bottoms (DB) were: 22.3% and 24.8% glycerol, 26.8% and 25.4% ash, 0.7% and 1.0% moisture, 50.2% and 48.8% MONG, and pH 7.5 and 8.4, both for GR9-20DB and GR9-21DB samples respectively. Further analysis of distilled bottom using HPLC and GC revealed that distilled bottoms (averages of samples GR7-16DB, GR7-17DB, GR8-18DB, GR8-19DB, GR9-20DB and GR9-21DB) contained 36.9% and 28.2% diglycerol, 3.6% and 2.6% triglycerol, and 0.2% and 0.3% tetraglycerol respectively.

Based on thirteen batches of glycerol residue, GR1 to GR13, the content of the isolated crude fatty acids (CFA) varied considerably, but averaged 7.2%. The main components of the crude fatty acids isolated from glycerol residue were C12:0 (40.3%), C8:0 (30.8%) and C10:0 (9.8%). The chemical characteristics of the CFA (based on GR1-3F, GR2-4F, GR4-13F and GR7-16F) samples were: acid value 319.4, saponification value 317.8, iodine value 3.5 and unsaponifiable matter 0.1%. The typical composition of the recovered salt (averages of samples GR7-16S, GR7-17S, GR8-18S, GR8-19S, GR9-20S and GR9-21S) was: 68.8% sodium chloride, 11.3% sodium sulfate, 7.5% of weight loss on heating at 110°C, and pH (5%) of 2.9 to 4.8. Results showed that molecular distillation was an efficient method to purify crude medium chain triglycerides (MCTs) which were synthesized from the recovered fatty acids and glycerol. The properties of the purified MCTs were close to commercial MCTs specification.

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

KAJIAN PENGELUARAN DAN PENGGUNAAN KOMPONEN BERGUNA DARIPADA SISA GLISEROL

Oleh

YONG KUANG CHIH

Julai 2002

Pengerusi: Profesor Madya Dzulkefly Kuang Abdullah, Ph.D.

Faculti: Sains dan Pengajian Alam Sekitar

Industri oleokimia di Malaysia berkembang pesat dan mengeluarkan pelbagai jenis produk seperti ester metil asid lemak, alkohol lemak dan gliserin. Dalam pengeluaran bahan-bahan berkenaan, hasil sampingan dikeluarkan dan kebanyakan hasil sampingan ini mempunyai potensi untuk diguna semula. Salah satu daripada hasil sampingan ini adalah sisa gliserol yang dikeluarkan daripada kilang penulenan gliserol (sumber gliserol adalah dari proses metanolisis minyak isirong sawit). Sisa gliserol adalah sisa buangan dibawah '*Schedule Waste*' S181, Akta Perundangan Alam Sekitar di Malaysia. Pada masa kini, sisa ini dilupuskan dengan kos kira-kira RM 700.00/tan. Oleh itu, kajian ini dijalankan untuk menciri sisa gliserol berkenaan dan mengeluarkan serta mencari kegunaan untuk komponen berguna daripadanya. Keputusan daripada tiga belas '*batches*' sisa gliserol, GR1 hingga GR13, menunjukkan julat yang besar untuk kandungan gliserol, kandungan abu, kandungan lembapan dan MONG. Garam (63.7%),

gliserol (19.7%) dan MONG (12.9%, kebanyakannya adalah sabun) adalah tiga komponen utama sisa gliserol, jumlahnya mencapai 96.3% daripada sisa gliserol, dan 3.7% lagi merupakan lembapan.

Tujuh kaedah (Kaedah 1 ke Kaedah 7) berasaskan rawatan kimia dan fizik telah dikembangkan untuk mengeluarkan gliserin mentah, asid lemak mentah, dan garam daripada sisa gliserol. Kaedah yang paling ringkas dan efisien adalah Kaedah 7 yang dioptimakan daripada Kaedah 6, yang melibatkan; pengasidan, penurasan, '*decantation*' dan penyejatan. Keadaan paling optima untuk rawatan kimia adalah pengasidan sisa gliserol dengan larutan akuas asid sulfurik (6%, v/v) sehingga pH di antara 4 – 5. Komposisi tipikal komponen yang dikeluarkan dari sisa glycerol, sampel GR9-20 dan GR9-21 (melalui Kaedah 7) adalah masing-masing: 24.7 wt.% dan 30.1 wt.% gliserin mentah, 7.1 wt.% dan 7.9 wt.% asid lemak mentah, dan 75.8 wt.% dan 74.4 wt.% garam; manakala komposisi tipikal gliserin mentah dari sampel GR9-20CG dan GR9-21CG adalah: 53.7% dan 55.5% gliserol, 12.2% dan 12.4% abu, 6.6% dan 10.7% air, 27.5% dan 21.4% MONG, dan pH bernilai 4.1 dan 4.4 masing-masing.

Gliserin mentah (sampel GR9-20CG dan GR9-21CG) telah ditulenkan melalui penyulingan vakum pada suhu 120°C hingga 137°C dan tekanan 1.8 hingga 5.0 x 10^{-1} mbar untuk menghasilkan gliserin tersuling (42 wt.% dan 42.6 wt.%) dan sisa tersuling (47.9 wt.% dan 46.4 wt.%). Ciri-ciri tipikal gliserin tersuling (masing-masing bagi sampel GR9-20DG dan GR9-21DG) adalah: 96.0% dan 96.8% gliserol, 0.12% dan 0.09% abu, 0.5% dan 0.2% air, 3.4% dan 2.9% MONG, pH bernilai 3.8, 51.0 dan 66.0

untuk warna (Hazen), dan 1.2591 dan 1.2603 ketumpatan relatif (20°C). Komposisi tipikal sisa tersuling adalah: 22.3% dan 24.8% gliserol, 26.8% dan 25.4% abu, 0.7% dan 1.0% lembapan, 50.2% dan 48.8% MONG, dan pH bernilai 7.5 dan 8.4, masing-masing bagi sampel GR9-20DB dan GR9-21DB. Analisis lanjutan bagi sisa tersuling menunjukkan bahawa sisa tersuling (purata untuk sampel GR7-16S, GR7-17S, GR8-18S, GR8-19S, GR9-20S dan GR9-21S) mengandungi 36.9% dan 28.2% digliserol, 3.6% dan 2.6% trigliserol, dan 0.2% dan 0.3% tetragliserol, masing-masing ditentukan dengan menggunakan HPLC dan GC.

Berdasarkan tiga belas '*batches*' sisa gliserol, GR1 hingga GR13, yang dianalisis, kandungan asid lemak mentah yang dikeluarkan adalah amat berbeza, tetapi mempunyai nilai purata sebanyak 7.2%. Komponen utama dalam asid lemak mentah adalah C12:0 (40.3%), C8:0 (30.8%) dan C10:0 (9.8%). Sifat-sifat kimia untuk asid lemak mentah (berdasarkan sampel GR1-3F, GR2-4F, GR4-13F dan GR7-16F) adalah: 319.4 nilai asid, 317.8 nilai saponifikasi, 3.5 nilai iodin dan 0.1% bahan tak tersaponifikasi. Komposisi tipikal garam yang dikeluarkan (purata untuk sampel GR7-16S, GR7-17S, GR8-18S, GR8-19S, GR9-20S dan GR9-21S) adalah: 68.8% natrium klorida, 11.3% natrium sulfida, 7.5% kehilangan jisim dalam pemanasan pada suhu 110°C, dan pH (5%) yang bernilai antara 2.9 hingga 4.8. Keputusan menunjukkan penyulingan molekular adalah suatu kaedah yang efisien untuk menulen trigliserida berantai sederhana mentah yang disintesis daripada asid lemak dan glycerol yng dikeluarkan daripada sisa gliserin. Ciri-ciri MCTs tersuling adalah mencapai spesifikasi MCTs komersial.

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I certify that an Examination Committee met on 3rd July 2002 to conduct the final examination of Yong Kuang Chih on his Doctor of Philosophy thesis entitled "Study on Recovery and Utilization of Valuable Components from Glycerol Residue" 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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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy.

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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.

Yong Kuang Chih

Date: 16/7/2002

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