UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF LIGHT COLOUR MEDIUM CHAIN TRIGLYCERIDES FROM PALM KERNEL OIL PRODUCTS

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By

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The synthesis of light colour medium chain triglycerides (MCTs) from medium chain fatty acids (MCFAs) and glycerol was investigated in this study. The production of light colour medium chain triglycerides is tedious and consists of several purification steps. This causes an increase in production cost and its economic viability. In this study, homogeneous catalyst, homogeneous catalysts with an absorbent and heterogeneous catalyst were used in an effort to establish methods to minimise cost. Catalyst was used in order to reduce the reaction temperature, time and produce higher percentage conversion of MCTs, whereas absorbent helps in producing light colour MCTs.

The results showed that the use of homogeneous catalyst reduced the temperature and time of the reaction with higher conversion rate of MCTs, but the product obtained was dark in colour. However, with the presence of absorbent, the colour of the product obtained improved tremendously to almost colourless.

Several steps of purification such as distillation and alkali treatment helps in obtaining a better quality MCTs.

A commercial heterogeneous catalyst used in this study required 180°C temperature and 5 to 7 hours reaction time. The colour of the MCTs produced was yellowish due to the heterogeneous catalytic activity. One of the advantages of using heterogeneous catalyst was it could be used repeatedly for several reactions, and in the current study the catalytic activity decreased slightly after using for six times. Due to the different phases of the heterogeneous catalyst and the reactants, the purification steps were much simpler and easier to produce better colour MCTs.

The reaction rate for the esterification of MCFAs and glycerol in this current study was second order with respect to the MCFAs reactant. The rate order was determined at different temperature and conditions. The temperatures studied were at 120°C, 130°C,140°C, 150°C and 180°C. The same conditions were used with homogeneous catalyst without or with absorbent and heterogeneous catalyst with 0.6% and 2.0% active side. The total reaction time for reaction rate studies was 3 hours, 5 hours and 7 hours.

In the scale-up studies, three experiments were carried out with the optimised conditions obtained from previous experiments. The yield of MCTs obtained ranged from 64.7% to 73.0%. After distillation and alkali washing treatment, the percentage of MCTs increased from 72.2% to 89.9%.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan Ijazah Master Sains.

SINTESIS TRIGLISERID RANTAI SEDERHANA BERWARNA CERAH DARI HASILAN MINYAK ISIRONG SAWIT

Oleh

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Sintesis trigliserid rantai sederhana (TRS) berwarna cerah dari asid lemak berantai sederhana (ALBS) dengan gliserol telah dijalankan dalam kajian ini. Penghasilan TRS berwarna cerah adalah sukar dan memerlukan beberapa langkah penulenan. Ini menyebabkan kos bertambah dan mengurangkan potensi ekonominya. Dalam kajian ini, mangkin homogen, mangkin homogen dengan penyerap dan mangkin heterogen telah digunakan bagi mengurangkan kos. Tujuan mangkin digunakan dalam sintesis ini ialah bagi merendahkan suhu tindak balas, masa dan memperolehi kadar peratusan penukaran kepada TRS yang lebih tinggi. Penyerap pula menolong menghasilkan TRS yang berwarna lebih cerah.

Keputusan yang diperolehi menunjukkan bahawa suhu dapat dikurangkan dengan menggunakan mangkin homogen dengan kadar penghasilan TRS yang tinggi tetapi hasil yang diperolehi berwarna gelap. Dengan kehadiran penyerap, hasil yang didapati adalah lebih baik dengan warna yang jernih. Langkah penulenan seperti penyulingan dan peneutralan alkali membantu mendapatkan TRS yang lebih baik.

Mangkin heterogen pula memerlukan tindakbalas dengan suhu 180°C dan masa tindak balas diantara 5 hingga 7 jam. Warna TRS yang diperolehi berwarna kekuningan disebabkan oleh aktiviti mangkin tersebut. Satu kelebihan mangkin heterogen ini ialah ia boleh digunakan berulang kali. Dalam kajian ini, ia boleh digunakan sehingga enam kali berturut-turut sebelum keaktifannya mula menurun. Proses penulinan adalah lebih mudah dan ringkas kerana mangkin heterogen berlainan fasa dengan TRS yang memudahkan pemisahan mangkin.

Kadar tindak balas pengesteran ALBS dengan gliserol dalam kajian ini adalah order kedua berpandukan kepada reaktan ALBS. Penentuan hukum kadar tersebut dilakukan pada suhu dan keadaan tindakbalas yang berlainan. Suhu yang digunakan ialah 120°C, 130°C,140°C, 150°C dan 180°C. Keadaan tindak balas pula ialah dengan mangkin homogen, mangkin homogen dengan penyerap dan mangkin heterogen dengan 0.6% dan 2.0% tapak aktif. Masa tindak balas ialah 3 jam, 5 jam dan 7 jam.

Kajian pada skala yang lebih besar telah dijalankan sebanyak 3 kali dengan menggunakan keadaan tindak balas optimum hasil dari kajian terdahulu. Peratusan TRS yang dihasilkan adalah diantara 64.7% hingga 73.0%. Selepas penyulingan dan rawatan alkali peratusan TRS bertambah kepada 72.2% hingga 89.9%.

CHAPTER I

INTRODUCTION

Oleochemicals Industry in Malaysia

Palm oil has become Malaysia most important economic agricultural product and its development has been remarkable. Starting as a semi-wild crop in West Africa, it has now developed into the second largest oil crops in the world after soybean. This is possible due to the highest yield per unit area at 3.60 tonnes/ha, compared to soybean at 0.46 tones/ha (Jalani and Cheah, 1997).

Due to increase in land cultivation of palm oil and highest yield per planted area, Malaysia managed to export 7,211,909 tonnes of palm oil earning RM 9,232.1 million and 465,442 tonnes of palm kernel oil with RM 862.5 million earning in 1996 (PORLA, 1997).

Oleochemicals are chemicals derived from oils and fats and often classified into two categories, basic oleochemicals and derivatives. Basic oleochemicals are fatty acids, methyl esters, fatty alcohol and fatty amines with glycerol being an important by-product (Ong *et al.*, 1989).

Malaysia has 15 oleochemicals plants producing various types of oleochemicals with a total capacity of about 1 million tonnes per annum. This made Malaysia the third largest oleochemicals producer in the world and contributes about 20% share of the total world supply (Kifli *et al.*, 1995). More than 90% of these basic oleochemicals are exported to industrialised countries where they are further processed into intermediates and finally consumer products. It would be of tremendous benefit to Malaysia if the consumer products were produced locally for value addition of the basic oleochemicals (Kang, 1997).

The Objectives Of the Present Research

Palm oil and palm kernel oil are used for the production of oleochemicals in Malaysia. Palm kernel oil (crude and processed) contributed 70% of the total production (Yusof, 1997). Palm kernel oil is similar to coconut oil, making them suitable alternative raw materials for various oleochemicals applications (Oba and Nakamura, 1997). Palm kernel oil (also known as lauric oils) contains short and medium chain fatty acids from carbon 6 (caproic acids) to carbon 18:2 (linolenic acids) with carbon 12 (lauric acids) as the major carbon chain length which constitute 45% - 50% in the palm kernel oil.

In the distillation and fractionation process of the fatty acids from palm kernel oil, the short and medium chain length of carbon 6 (caproic acids) to carbon 10 (capric acids) were distilled off in the fractionation column. The presence of short chains acids often cause of soapy off-flavour and colour reversion in soap. Normally they are discarded as by-products from the oleochemicals plants.

In the late forties, a method of using the short and medium chain fatty acids (MCFAs) of caproic acids to capric acids ($C_6 - C_{10}$) was discovered. Esterification between MCFAs and glycerol with and without catalyst produced medium chain triglycerides (MCTs) (Babayan, 1968).

The main objective of this research is to study the production of low colour MCTs by esterification of MCFAs and glycerol. The study covers the used of homogeneous catalyst, homogeneous catalyst with absorbent and a commercial heterogeneous catalyst. The study were divided into 3 phases:

1. Laboratory study on the optimisation conditions of the esterification by homogeneous catalyst, homogeneous catalyst with absorbent and heterogeneous catalyst.
2. Study on the effect of temperature on the reactions rate, and
3. Scale-up study on the esterification and purification of MCTs.

The scope of the study includes the evaluation of the medium chain triglycerides produced, reaction time, reaction temperature and purification steps.

CHAPTER II

LITERATURE REVIEW

Oleochemicals from Palm Oil and Palm Kernel Oil

Oleochemicals are chemicals derived from oils and fats and can be divided into two groups, basic oleochemicals and oleochemicals derivatives. The basic oleochemicals are fatty acids, methyl esters, fatty alcohol, fatty amines and glycerol as the valuable by-products (Ong *et al*., 1989). The basic oleochemicals which can be converted into oleochemicals derivatives that have a large variety of end uses are shown in Table 1 (Salam *et al*., 1998).

Palm Oil And Palm Kernel Oil As Raw Materials

In oleochemical industry, tallow and coconut oil have been the traditional raw materials used in the production of fatty acids with the chain length of C_{16} – C_{18} and C_{12} – C_{14}, respectively. Oleochemicals or derivatives based on C_{12} - C_{14} and C_{16} - C_{18} chain length have a variety of uses.

Due to similarity in carbon chain length, the traditional raw materials are now being replaced by palm stearin; palm kernel and other palm oil products and comparison of their carbon chain length are own in Table 2. (Appalasami and Vries, 1991).

Table 1: Basic Oleochemicals Products and Their Derivatives

Raw materials	**Oils and Fats**				
Basic Oleochemicals	Fatty acids	Fatty esters	Fatty alcohols	Fatty amines	Glycerol
Uses of basic oleochemicals	Plasticiser/ Stabiliser Rubber products Cosmetic	Lubricant Grease Platiciser for plastics Cosmetic	Prevent water evaporation	Anti-slip Anti-block Water repellents Foam stabiliser Ore floatation Anti-rust	Humectants in several end uses
Derivatives	Sodium and other metallic salts MCTs	Sulphonated methyl ester	Fatty alcohol sulphates Fatty ethoxylates	Quaternary ammonium compounds	Mono and di-glycerides Polyglycerol esters
Uses of Derivatives	Soaps Animal feeds Infant foods Cosmetics Plasticers/ Stabilisers Internal lube	Detergent	Washing and cleaning products	Conditioners Softeners Antimicrobials	Emulsifiers in food and non food applications

Table 2: The Fatty Acids Composition Of Oleochemicals Derived from Palm Oil, Palm Kernel, Palm Stearin, Coconut Oil and Tallow

Fatty acids	Palm oil	Palm kernel oil	Palm Stearin	Coconut oil	Tallow
Caproic acid	-	0 1 – 0 5	-	0 1 – 0 8	-
Caprylic acid	-	3 4 – 5 9	-	3 0 – 6 0	-
Capric acid	-	3 3 – 4 4	-	6 0 – 10 0	-
Lauric acid	0 1 – 1 0	46 3 - 51 1	0 1 – 0 6	44 0 - 52 0	0 1 – 0 2
Myristic acid	0 9 – 1 5	14 3 -16 8	1 1- 1 9	13 0 - 11 0	0 1 – 8 0
Palmitic acid	41 8 - 46 8	6 5 – 8 9	47 2 -73 8	8 0 – 11 0	24 0 - 30 0
Stearic acid	4 2 – 5 1	1 6 – 2 5	4 4 – 5 6	0 1– 3 0	14 0 - 25 0
Oleic acid	37 3 - 40 8	13 2 - 16 4	15 6 - 37 0	5 0 – 3 0	40 0 – 49 0
Linolenic acid	6 1 – 9 1	2 2 – 3 3	3 2 – 9 8	0 0 – 3 0	0 1 – 5 0
Others	0 0 – 1 0	traces - 0 9	0 1 - 1 0	0 0 – 1 0	0 0 – 1 0