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Preparation of Palm Oil Methyl Esters for Alkenyl Succinic Anhydride Production

(Penyediaan Metil Ester Minyak Sawit untuk Penghasilan Suksinik Anhidrida)

NUR AZREENA IDRIS*, LOH SOH KHEANG, CHOO YUEN MAY & BOEY PENG LIM

ABSTRACT

The fractions of fatty acid methyl esters (FAME) i.e. crude palm oil methyl esters (CPOME), RBD palm olein methyl esters (RBD Palm Olein ME) and used frying oil methyl esters (UFOME) rich in unsaturated fatty esters were used to prepare alkenyl succinic anhydrides (ASA). The fractions were obtained via fractional distillation that separated the unsaturated fatty esters from the saturated fatty esters. The fractions with the highest content of unsaturated fatty esters were reacted with maleic anhydride (MA) for 8 hours at 240°C with the MA/FAME ratio of 1.5. The reaction was conducted without catalyst and solvent. The crude alkenyl succinic anhydride (ASA) obtained was purified by column chromatography. The purified compound was characterised by FTIR.

Keywords: Alkenyl succinic anhydride; fatty acid methyl esters; fractional distillation; unsaturated fatty esters

ABSTRAK

Ester metil daripada pelbagai sumber seperti ester metil sawit mentah, ester metil sawit olein dan ester metil minyak sawit terpakai yang mempunyai kandungan ester tak tepu yang tinggi digunakan untuk menyediakan alkenil suksinik anhidrida (ASA). Ester metil tersebut diperolehi melalui proses penyulingan berperingkat yang akan memisahkan ester tepu dan tak tepu. Bahagian yang mempunyai kandungan ester tepu paling tinggi akan di tindak balaskan dengan maleik anhidrida (MA) selama 8 jam pada suhu 240°C dengan nisbah MA/ME 1.5. Tindak balas dilakukan tanpa katalis dan pelarut. ASA mentah yang diperoleh ditulenkan dengan kaedah kolum kromatografi dan dicirikan menggunakan FTIR.

Kata kunci: Alkenil suksinik anhidrida; ester lemak tak tepu; metal ester asid lemak; penyulingan berperingkat

INTRODUCTION

The most common way to produce methyl esters (biodiesel) is by transesterification of vegetable oil and an alcohol to yield fatty acid methyl esters (FAME) and glycerol in the presence of catalyst (Choo 2004). Since the production of biodiesel is more expensive than petroleum-based diesel fuel, researchers have to find ways to diversify the utilisation of methyl esters other than as diesel (Choo et al. 2005). As direct applications of FAME are very limited, further fractionation of methyl esters would contribute to many value added products.

Fractional distillation has become the most important separation method. This method is used on the industrial scale for separation of C_{16} and C_{18} from palm oil. Most distillation units feature high vacuum with no allowance for air leakage, effective heating to achieve short contact time and a good circulation for effective mass transfer between vapor and condensate (Alexandre et al. 2007). The fractional distillation is employed to separate the saturated fractions from unsaturated fractions. There were high interests in the use of unsaturated vegetable oil as it can undergo various chemical syntheses. One of them is the preparation of alkenyl succinic anhydride (ASA) through Diels-Alder reaction.

ASA are reaction products of olefinically unsaturated hydrocarbon with maleic anhydride (MA) (Joaquin 2003; Joaquin et al. 2003). In this study, the unsaturated hydrocarbon was the unsaturated fractions of the methyl esters obtained from fractional distillation. The application of ASA prepared will depend on the structure and carbon chain length. The objective of this work to prepare ME for ASA production.

MATERIALS AND METHOD

MATERIALS

Methyl esters were prepared through transesterification from different sources of oil such as crude palm oil, RBD palm olein and used frying oil. Methanol was supplied by Mallinckrodt Chemicals, (Phillipsburg, USA), sodium hydroxide by APS. Chemicals (Auckland, New Zealand), maleic anhydride and standard methyl oleate by Aldrich-Sigma (St. Louis, USA). These chemicals were used as received.

PREPARATION OF CPOME, RBD PALM OLEIN ME AND UFOME

CPO, RBD palm olein and used frying oil were treated with the catalyst, sodium hydroxide. The catalyst was first

dissolved in methanol. The reaction mixture was stirred and heated to 60°C for 30 min under reflux. Thin layer chromatography (TLC) was used to monitor the completion of the reaction. After the reaction was completed, the mixture was allowed to cool down. The mixture consisted of two layers; the upper layer (esters) and the lower layer (glycerol). The layers were separated in a separating funnel. The yellowish ester layer was washed several times with hot distilled water until neutral and vacuum-dried for fuel characterisation.

ANALYSIS OF CPOME, RBD PALM OLEIN ME AND UFOME

The oil and its esters were analysed for peroxide value, FFA content, carotene content, and iodine value according to PORIM Test Method p2.5 (1995) and p3.2a (1993). The fatty acid compositions were determined according to ISO 5508: Animal and Vegetable Fat and Oil Analysis (1990) by Gas-Liquid Chromatography of Methyl Esters of Fatty Acids. Analysis was carried out with a Hewlett Packard 5890 Series II gas chromatography equipped with a flame ionisation detector and split injector. A fused silica capillary column (60 m × 0.25 mm) coated with a highly polar stationary phase, Supelco SP2340 (0.2 μm) was used with programmed temperature profile as follows: 185°C, injector temperature: 240°C, detector 240°C, split ratio of 1:100, carrier gas: helium at 2.0 mL min^{-1}.

The viscosity was measured by using an Automated Multi Range Viscometer HVM 472 (Walter Herzog, Germany) at 40°C. All the measurements were performed in duplicate and only means were reported. The density was measured at 25°C using Mattler Toledo DE 40 Density Meter and oxidative stability was measured using the Model 743 Rancimat (Metrohm AG, Herisau, Switzerland) at 110°C. Samples (3 g) was analysed under a constant airflow of 10 litres hr^{-1} and 110°C temperatures of the heating blocks. All the measurements were performed in duplicate and only means reported.

FRACTIONAL DISTILLATION OF METHYL ESTERS (ME)

The distillation of ME was performed in a round bottomed, one neck flask with a temperature controller, a received flask connected to a vacuum gauge and a condenser. A pump connected to the condenser provided vacuum. The crude ME was fed to the flask. The distillates were collected at 50 to 60, 80°C to 120 and 60 to 90°C respectively and the distillation was terminated when all distillates were collected.

CHARACTERIZATION OF ME FRACTIONS

The fatty acid compositions were determined according to ISO 5508: Animal and Vegetable Fat and Oil Analysis (1990) by Gas-Liquid Chromatography of Methyl Esters of Fatty. Analysis was carried with a Hewlett Packard 5890 Series II gas chromatography equipped with a flame ionization detector and split injector. A fused silica capillary column (60 m × 0.25 mm) coated with a highly polar stationary phase, Supelco SP2340 (0.2 μm) was used with programmed temperature profile as follows: 185°C, injector temperature: 240°C, detector 240°C, split ratio: 1:100, carrier gas: helium at 2.0 mL min^{-1}.

PREPARATION OF ASA

The unsaturated fatty esters with mostly methyl oleate were reacted with MA. The reaction mixture was heated at 240°C for 8 hours with MA/ME molar ratio of 1.5 under nitrogen atmosphere in a three-necked reactor equipped with magnetic stirrer and a condenser heated at 65°C. Then, the mixture was allowed to cool to room temperature. The crude product obtained was purified by column chromatography 50 cm lenght, using silica gel 60 (0.063-0.200 mm) as sorbent and a mixture of acetone and hexane with ratio of 7:3 as eluent.

CHARACTERIZATION AND IDENTIFICATION OF ASA

The IR spectra were recorded on a Perkin Elmer FT-IR spectrometer.

RESULTS AND DISCUSSIONS

CHARACTERIZATION OF METHYL ESTERS

Methyl esters obtained from CPO, RBD Palm Olein and UFO were analyzed under a series of test that met the specification of standard EN 14214 (European Standard for Biodiesel). Their physical properties are tabulated in Table 1.

TABLE 1. Physical properties of various palm oil and their esters

Properties	CPO		RBD PALM OLEIN		UFO	
	OIL	ESTERS	OIL	ESTERS	OIL	ESTERS
FFA, %	2.63	0.74	0.56	0.19	0.88	0.12
Moisture content, %	0.328	0.134	0.135	0.078	0.098	0.079
Iodine value,	48.08	32.16	35.71	33.96	55.09	50.20
Oxidation stability 110°C, hrs	33.41	16.39	9.10	15.94	28.11	11.02
Density	0.9096	0.8683	0.9110	0.8745	0.9094	0.8765
Viscosity	40°C	46.25	4.5472	43.08	4.5995	40.18

FRACTIONAL DISTILLATION OF METHYL ESTERS

Fractional Distillation of CPOME In the fractional distillation of CPOME, 3 fractions of methyl esters were obtained at different temperatures as showed in Table 2. The percentage recovery of CPOME via fractional distillation was 89.31%.

TABLE 2. Fractions of CPOME distillate

Fractions	Temperature (°C)	Yield (g)
1	58- 60	82.000
2	120-158	326.98
3	160-180	62.659

Of the 3 fractions distilled, fraction 3 had the most unsaturated carbon chain (C18:1 and C18:2) which could be used to produce ASA (Table 3). The other two fractions had more saturated ester. The ASA obtained from methyl ester of fraction 3 and MA was a viscous dark brown product.

Fractional Distillation of RBD Palm Olein ME In the fractional distillation of RBD Palm Olein ME, 4 fractions of methyl esters were obtained at different temperatures as showed in Table 4. The percentage recovery of RBD Palm Olein ME via fractional distillation was 84.25%.

Of the 4 fractions distilled, fraction 3 had the most unsaturated carbon chain (C18:1) which could be used to produce ASA (Table 5). The other three fractions had more saturated ester. The ASA obtained from methyl ester of fraction 3 and MA were of a viscous dark brown products.

Fractional Distillation of UFOME In the fractional distillation of UFOME, 2 fractions of methyl esters were obtained at different temperature as showed in Table 6. The percentage recovery of UFOME via fractional distillation was 96.5%.

Of the 2 fractions distilled, fraction 1 had the most unsaturated carbon chain (C18:1) which could be used to produce ASA (Table 7). The other fractions had a slightly lower concentration of C18:1 ester chain. The ASA obtained from methyl ester of fraction 1 and MA were of a viscous dark brown products.

TABLE 3. Analysis of FAC for distilled CPOME

CPOME	C12	C14	C16	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	TOTAL
1	0.96	4.65	69.59	0.23	1.80	18.17	4.51	0.10	0.00	100.00
2	0.00	0.31	49.76	0.15	3.90	36.72	8.84	0.17	0.15	100.00
3	0.00	0.00	3.68	0.00	9.68	71.49	14.52	0.54	0.09	100.00

TABLE 4. Fractions of RBD palm olein ME distillate

Fractions	Temperature (°C)	Yield (g)
1	108-126	30.5363
2	86-188	89.2261
3	188-204	86.1628
4	118-160	45.1447

TABLE 5. FAC analysis for RBD palm olein ME

Fraction	C12	C14	C16	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	TOTAL
1	0.61	6.29	48.26	2.37	36.96	5.15	0.36	0.00	0.00	100.00
2	0.21	3.03	82.13	0.12	9.38	4.40	0.44	0.11	0.00	100.00
3	0.64	0.40	0.00	0.84	0.00	92.10	1.10	3.44	0.00	100.00
4	0.00	0.00	26.26	0.42	67.06	0.00	1.88	4.38	0.13	100.00

TABLE 6. Fractions of UFOME distillate

Fractions	Temperature (°C)	Yield (g)
1	60- 90	423.0
2	90-110	62.9

TABLE 7. FAC analysis for distilled UFOME

UFOME	C12	C14	C16	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	TOTAL
1	0.16	0.84	23.66	0.72	7.86	65.37	0.39	0.86	0.07	100.00
2	0.13	0.67	20.48	0.64	6.61	55.68	14.41	1.26	0.05	100.00

It can be concluded that the fractionated methyl esters consist of a mixture of saturated and unsaturated carbon chain. All of the fractions have more unsaturated carbon chain (18:1, 18:2) than saturated carbon chain (16:0).

Preparation of ASA The percentage yield of the ASA from CPOME, RBD Palm Olein ME and UFOME were 80.53%, 81.67% and 79.67%. From the FTIR spectra for ASA from CPOME, three distinctive absorption peaks at 1711.43 cm^{-1} and 1740.29 cm^{-1} were observed indicating the presence of C=O and 972.99 cm^{-1} represented a five-membered cyclic anhydride. While for ASA from RBD Palm Olein ME, the C=O were presented at 1861.49 cm^{-1} and 1782.78 cm^{-1}. The five membered cyclic anhydride confirming the anhydride functional group was indicated at 916.79 cm^{-1}. As for ASA from UFOME, the distinctive peaks were observed at 1862.29 cm^{-1} and 1786.33 cm^{-1} for C=O, and 917.16 cm^{-1} for a five membered cyclic anhydride.

CONCLUSION

Vegetable-derived methyl esters are renewable sources that can be used as substitute to the petroleum fuels. They have comparable properties when crude palm oil, RBD palm olein and used frying oil were used as the raw materials. They were reacted by basic catalyzed transesterification using sodium hydroxide and methanol as the solvent. So, they can be used as diesel substitutes for unmodified diesel engines and help in keeping the environment greener. The overall conversion of the methyl esters was more than 96%.

Characterisation of ASA using FTIR showed significant peaks that were comparable with peaks obtained by previous researchers. Upon comparison, the product obtained had similarities with both of the raw materials that are ME and MA. These should be expected since the reaction product is a combination of both.

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Nur Azreena Idris*, Loh Soh Kheang & Choo Yuen May
Malaysian Palm Oil Board
No. 6, Persiaran Institusi
43000 Kajang, Selangor
Malaysia

Boey Peng Lim
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia
11800 Minden, Penang
Malaysia

*Corresponding author; email: azreena@mpob.gov.my

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