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Synthesis of Palm Oil-Based Diethanolamides

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Abstract In this work, Epoxidized Palm Olein (EPO_o) was blended with Refined Bleached Deodorized Palm Kernel Olein ($RBDPKO_o$) in a range of 10–100% (w/w) to react with diethanolamine (DEA) with a 1:3 molar ratio to produce diethanolamides that retained some epoxides. The epoxidized diethanolamides are proposed as a new type of vegetable oil derived polyols for rigid polyurethane. The optimal reaction temperature is 110 °C for 5 h. In addition, the optimal amount of starting materials were determined to be 40% (w/w) of EPO_o blended with 60% (w/w) of $RBDPKO_o$. The diethanolamides appeared as non-viscous liquid at room temperature with a viscosity of 990.08 cP at 25 °C and 427.09 cP at 40 °C, a cloud point of 21 °C, a pour point of 12 °C and 0.78% of retained oxirane oxygen contents (OOC). The hydroxyl and the amine values of the diethanolamides were determined as 351.85 mg KOH/g sample and 4.5 mg KOH/g sample, respectively. In addition, chemical elucidation of the diethanolamides with functional epoxides was carried out using Gas Chromatography (GC) and Gas Chromatography Mass Spectrometry (GCMS) for the purpose of process development and quality control.

Keywords Epoxidized diethanolamides · Non-viscous · Gas Chromatography Mass Spectrometry (GCMS) · Gas Chromatography (GC)

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Introduction

Fatty alkanolamides, namely monoalkanolamide and dialkanolamide can be prepared by reacting fatty acids or fatty acid methyl esters with alkanolamine at elevated temperatures [1]. Recently, secondary fatty amides have been synthesized using triacylglycerides from tallow and tripalmitin to react with amine, such as ethanolamine, diethanolamine, ethylenediamine, diethylenediamine, and others [2]. Kolancilar also reported the preparation of ethanolamides from laurel oil of black olive-sized fruits of *Laurus nabilis* L. [3].

The alkanolamides are usually used as non-ionic surfactant in the household and cosmetic industries. However, it is well-known that alkanolamides, i.e., diethanolamides synthesized from natural oils can be utilized to produce rigid polyurethane foam. They can be prepared by reacting diethanolamine (DEA) with natural glycerides, such as soybean, linseed, peanut, and safflower oil [4]. Some efforts had been made to modify the diethanolamides for rigid polyurethane production. Khoe et al. reported the use of hydroxymethylated oil in the synthesis of diethanolamide polyols to increase the number of hydroxyl groups and to improve their distribution [5]. The hydroxymethylated diethanolamides contained five primary hydroxyl groups per fatty acid. In another study, carboxylated oils and fatty acids from linseed and soybean oil were used to synthesize modified diethanolamides with increased distribution of primary hydroxyl groups in the polyols [6]. When diethanolamides produced from hydroxymethylated and carboxylated oils blended with Quadrol (*N, N, N′, N′*-tetrakis [2-hydroxypropyl] ethylenediamine), the mixture produced better rigid polyurethane foam compared to those without addition of Quadrol. In addition, the synthesis of diethanolamides using palm oil has also been reported.

Badri et al. prepared diethanolamides by reacting Refined Bleached Deodorized Palm Kernel Olein (RBDPKO$_o$) with diethanolamine (DEA) in the presence of potassium acetate as catalyst [7]. Sieved empty fruit bunch fibers (EFB) from palm tree were added as an organic filler in order to improve the mechanical properties of the rigid polyurethane foam.

In this work, we described a convenient method to prepare chemically modified diethanolamides from palm oil products. A series of epoxidized diethanolamides were produced by using varying amounts of Epoxidized Palm Olein (EPO$_o$) and RBDPKO$_o$ to react with DEA. The newly synthesized diethanolamides, consisting of reactive epoxy compounds, are proposed to have extra cross-linking sites to allow the epoxides to react with diisocyanates to form oxazolidones during polyurethane foam production [8]. The formation of oxazolidone linkage can only happen at room temperature with the presence of an appropriate catalyst [9]. We believe that the addition of oxazolidone linkages in the rigid polyurethane foam will improve the mechanical properties of the foam. However, the production of rigid polyurethane foam by using these newly synthesized epoxidized diethanolamides will be described in another paper. Thus, the objectives of this work were to determine the optimum ratio between the two raw materials, which are EPO$_o$ and RBDPKO$_o$, reaction conditions, and also the chemical elucidation of the diethanolamides using Gas Chromatography (GC) and Gas Chromatography Mass Spectrometry (GCMS).

Experimental Procedures

Materials

RBDPKO$_o$ (specifications: iodine value = 26 I$_2$ mg/100 g sample, free fatty acid = 0.10 mg KOH/g sample, saponification value = 250 mg KOH/g sample) was obtained from Kempas Oil Sdn Bhd and EPO$_o$ (specifications: oxirane oxygen contents = 3.0%, acidity = 1.1 mg KOH/g sample, iodine value = 0.65 I$_2$ mg/100 g sample) was obtained from the pilot plant of Advanced Oleochemicals Technology Division (AOTD) of Malaysian Palm Oil Board (MPOB). Reagents: DEA (BASF), dimethylformamide (J.T. Baker), tetrahydrofuran (MERCK), isopropyl alcohol (J.T. Baker), N, O-bis(trimethylsilyl)trifluoroacetamide, 98+% (BSTFA) (ACROS ORGANICS), hydrobromic acid, 33 wt% solution in glacial acetic acid (ACROS ORGANICS), glacial acetic acid (J.T. Baker), were used as purchased. Chemicals: sodium acetate (MERCK), eosin Y (ACROS ORGANICS), silver nitrate (DU LAB) and gelatin (MERCK) were used as purchased. Standards: methyl esters from C$_{6:0}$ to C$_{18:2}$ (Cognis (M) Sdn. Bhd.), fatty acid from C$_{8:0}$ to C$_{18:2}$

(SIGMA CHEMICALS), monoglycerides from C$_{8:0}$ to C$_{18:1}$ (SIGMA CHEMICALS) and diglycerides from C$_{8:0}$ to C$_{18:1}$ were also used as purchased.

Synthesis of Diethanolamides

The reaction was carried out in a 1-L Pyrex glass reaction flask submerged in a silicone bath. The reaction flask was equipped with a mechanical stirrer, thermometer and condenser. About 10–100% (w/w) of EPO$_o$ was blended with RBDPKO$_o$ to react with DEA at a molar ratio of 1:3 [palm oil triacylglyceride (TAG):DEA]. The reaction was carried out at different temperatures ranging from 100 to 180 °C for 7 h. Samples of the reaction mixture were withdrawn hourly to determine total amine value and oxirane oxygen contents.

Indicator Method for Total Amine Value Determination

The total amine value is defined as the milligrams of potassium hydroxide equivalent to the basicity in one gram of sample. The analysis was based on the AOCS official method [10] but modified by dissolving 1.0 g of sample in 100 mL of isopropyl alcohol in order to obtain a more significant color change at the end point of the titration.

Oxirane Oxygen Content (OOC)

The OOC was not determined using the standard hydrobromic acid in acetic acid method [11]. This is because the presence of DEA traces would form amine–bromide complexes with HBr and interfere with the results of the determination test. The OOC was instead determined by using the back titration method described by Durbetaki [12]. The formation of amine–bromide complexes will be converted to amine acetate by sodium acetate. The procedure was as followed: 0.5 g sample was dissolved in 10 mL of glacial acetic acid in a 250-mL Erlenmeyer flask. Then, 25 mL of 0.1 M hydrobromic acid in glacial acetic acid, 20 mL of 0.1 M sodium acetate, 6 drops of eosin Y indicator and 0.1 g gelatin were added to the flask. Lastly, 30 mL water was added before the sample was titrated with 0.1 M silver nitrate to an orange-crimson end point. A blank was carried out by adding 25 mL of 0.1 M hydrobromic acid and 35 mL of 0.1 M sodium acetate, and titration was done as described above. The OOC was calculated from the following formula:

$$\%OOC = \frac{(V_1 - V_2) \times M \times 1.6}{W}$$

where, V_1 was the volume (mL) of silver nitrate used in the titration of the blank, V_2 was the volume (mL) of silver nitrate used in the titration of the sample, W was the weight of the sample in gram and M was the molarity of the hydrobromic acid solution.

Fourier Transform Infrared (FTIR) Spectral Analysis

Nicolet FTIR, Model: Magma-IR 550 spectrometry, series II was used to monitor the functional groups of the synthesized products. The sample was coated onto potassium bromide pellets. An average of 16 scans were recorded for every sample.

Hydroxyl Value Determination

The hydroxyl value is defined as the milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of sample. The hydroxyl value was determined by following the AOCS Official Method [13].

Viscosity Measurement

The viscosity of the diethanolamides was measured by a Brookfield DV-III Programmable Rheometer at 25 °C and 40 °C. To determine the viscosity, a small amount of test sample (approximately 0.25 g) was placed on the cone plate of the Rheometer. Test data was gathered automatically by the computer program.

Cloud Point and Pour Point Measurement

The cloud point and pour point of the diethanolamide products were determined based on the AOCS Official Method Cc 6–25 and ASTM D 97–87 methods [14, 15]. Each sample was prepared in triplicate and the average values were rounded to the nearest degree. The measurement of the pour point was done with resolution of the specified 3 °C increment.

GC Analysis

The samples were prepared by dissolving 0.01 g of diethanolamides samples in 1 mL of dimethylformamide and 0.5 mL BSTFA was then added. The mixture was shaken vigorously and warmed at 45 °C for 1 h before analyzing by GC. This procedure allowed the silylation of the

samples to take place. The sample was then transferred to a 2-mL auto-sampler vial for injection into the GC system. *Validation.* There were no standards for fatty diethanolamide, therefore secondary standards were synthesized from methyl esters, such as methyl caproate ($C_{6:0}$), methyl caprylate ($C_{8:0}$), methyl caprate ($C_{10:0}$), methyl laurate ($C_{12:0}$), methyl myristate ($C_{14:0}$), methyl palmitate ($C_{16:0}$), methyl stearate ($C_{18:0}$), and methyl oleic ($C_{18:1}$). These esters were reacted with DEA at 110 °C for 5 h. In addition, monoglycerides standards ($C_{8:0}$–$C_{18:1}$), diglycerides standards ($C_{8:0}$–$C_{18:1}$), and also fatty acid standards ($C_{8:0}$–$C_{18:2}$) were derivatized by BSTFA before they were used to identify the by-products and the partial glycerides that the reaction might have yielded. *Condition.* The SGE HT-5, Polymide clad, 12 m × 0.53 mm × 0.15 μm column was used in the gas chromatograph study. The injection was made at 80 °C, held for 8 min and the temperature of the injector and column oven was raised by 5 °C/min to 220 °C. The inlet temperature and the detector temperature were 250 °C. Helium gas was used as the carrier gas and the flow rate for the column was 27.0 mL/min. Nitrogen gas was used as the makeup gas.

GCMS Analysis

Mass spectrometric analysis was carried out on an Agilent 5973 Network Mass Selective detector interfaced to an Agilent 6890 Series gas chromatograph with a septum-equipped programmable Agilent 783 Series injector. The HP-5 ms column, 30 m × 0.25 mm id, 0.25-μm film was used in the gas chromatographic study and was connected directly to the electron impact (EI) source (70 eV). The injection was made at 80 °C, held for 50 min and the temperature of the injector and column oven was raised by 5 °C/min to 270 °C. The inlet pressure of the helium carrier gas was 8.67 psi and the flow rate was 1 mL/min when the MSD detector was used. The inlet temperature was 280 °C whereas the auxiliary set point was 290 °C. The samples were dissolved in tetrahydrofuran, derivatized with BSTFA and then warmed at 45 °C for 1 h before analyzing by EI-GCMS.

Results and Discussion

Synthesis of Diethanolamides

The reaction was carried out by blending different amount ranging from 10 to 100% (w/w) of EPO_o to $RBDPKO_o$ as the starting material. The oil mixture was then reacted with DEA at molar ratio of 1:3 (palm oil TAG:DEA) (Scheme 1). Glycerol was being produced as the by-product

Scheme 1 Reaction scheme of the synthesization of diethanolamide. R_1, R_2, R_3 are the alkyl chains with or without epoxide(s) functionality
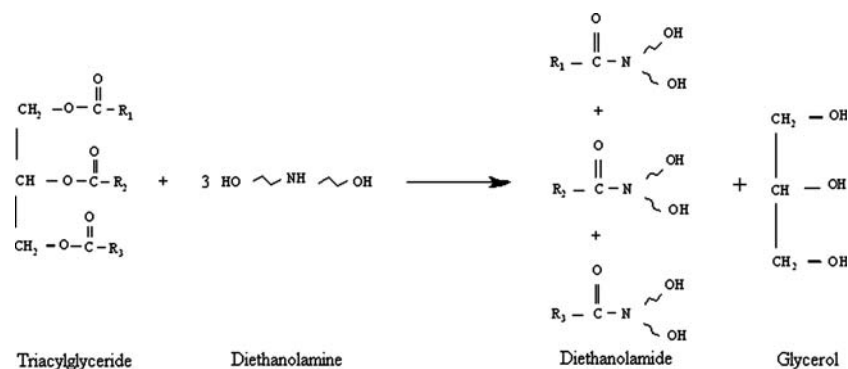
of the reaction. However, it was not removed from the reaction mixture because it can help in cross-linking during the production of rigid polyurethane foam.

The optimum reaction temperature and reaction duration were first studied by reacting 10% (w/w) of EPO_o and 90% (w/w) of $RBDPKO_o$ with DEA at temperature ranging from 100 °C to 180 °C for 7 h. The reaction mixture was initially immiscible and separated into two layers, with the oil on the upper layer while the DEA stood at the bottom layer. When the two immiscible layers became homogenous, the epoxidized diethanolamides were formed. Sample was taken from the lower layer of the reaction mixture to study the changes of the amine value. The total amine value of the reaction mixture decreased throughout the reaction and when the reaction mixture became a single, homogenous phase, a sharp drop in amine content was observed (Table 1). This indicated the formation of diethanolamides and it occurred more rapidly at a higher reaction temperature. When the reaction was carried out at lower temperatures, e.g., at 100 °C, the mixture remained as two immiscible layers even after refluxing for 7 h.

The OOC of the reaction mixture was also determined in this work and the epoxy functionality decreased more rapidly at higher reaction temperature (Fig. 1). The OOC of the diethanolamides, synthesized at 110 °C for 7 h managed to retain 0.15% of OOC, whereas those that were reacted at 180 °C for 7 h only managed to retain 0.05% of OOC. From the results, 110 °C (R2) of reaction temperature and 5 h of reaction duration were determined as the optimum reaction conditions for the synthesis of diethanolamides due to the lowest amine value (4.7 mg KOH/g sample) and the highest OOC (0.19%) obtained. The retained epoxy ring is expected to provide additional cross-linking sites by forming oxazolidone during the preparation of rigid polyurethane foam.

Nevertheless, oxazolidone can only be formed by reacting epoxides with an isocyanate group at elevated temperatures [8]. However, oxazolidone-isocyanurate foam can be prepared at room temperature by adding Lewis acid–Lewis base complexes [9]. Many different types of catalysts in the reaction between 9, 10-epoxyoctadecane and phenylisocyanate to form oxazolidone have been

Table 1 Effect of temperature on amine value in the synthesis of diethanolamides

Reaction (h)	Amine Value (mg KOH/g sample)								
	R1[a] 100 °C	R2[a] 110 °C	R3[a] 120 °C	R4[a] 130 °C	R5[a] 140 °C	R6[a] 150 °C	R7[a] 160 °C	R8[a] 170 °C	R9[a] 180 °C
0.0	595.2	520.0	480.0	410.0	383.1	353.0	328.0	304.4	22.6[b]
0.5	575.1	388.0	345.4	320.0	315.2	290.3	264.0	14.7[b]	13.2
1.0	552.0	305.0	281.0	250.0	220.0	180.8	13.2[b]	10.5	12.8
2.0	543.0	212.0	200.3	8.2[b]	9.6[b]	10.3[b]	10.4	10.6	12.5
3.0	531.8	110.0	104.4	5.5	6.2	7.7	11.5	10.6	11.7
4.0	484.3	27.7	5.6[b]	4.7	5.9	7.0	10.7	12.4	11.3
5.0	481.9	4.7[b]	4.9	4.2	4.8	5.5	12.1	11.9	9.5
6.0	374.3	3.2	2.3	3.4	4.4	4.4	11.2	8.7	7.2
7.0	220.1	3.8	2.9	3.8	4.2	4.4	11.3	6.4	4.2

[a] Diethanolamides (Sample R1 to R8) synthesized from 10% (w/w) of EPO_o and 90% (w/w) of $RBDPKO_o$ with DEA at molar ratio of 1:3 (palm oil TAG:DEA) at different temperature

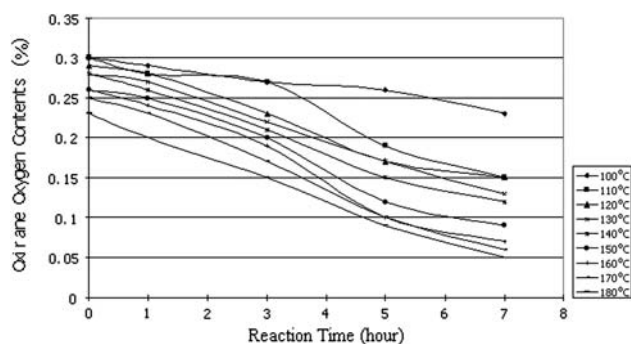[b] The reaction mixture started to become homogenous

Fig. 1 Oxirane oxygen contents at different reaction temperature. Starting material: 10% EPO_o and 90% RBDPKO_o (w/w)

investigated [16]. Other study reported on improved compressive strength of epoxy modified polyurethane rigid foams by reacting epoxy resin, isocyanate, and additives at 80 °C for 24 h [17]. There is a potential of oxazolidone in assisting the cross-linking of polyurethane foam, therefore we propose a new synthesis by introducing epoxy compounds into diethanolamides. We believe that the thermal conductivity, hardness and compressive strength of the polyurethane foam could be improved.

The FTIR study was used to monitor the reaction of diethanolamides. Figure 2 shows that the sample undergone significant changes, particularly in the gradual appearance of the peak of C=O stretch for tertiary amide at around 1,648 cm^{-1}. Another significant change was the gradual appearance of the broad peak, OH band at around 3,400 cm^{-1}. These changes indicated the gradual formation of the diethanolamides.

Next, EPO_o was blended with RBDPKO_o, in different percentages, to determine the optimal amount of EPO_o and RBDPKO_o to be used as starting material. The OOC, amine value, viscosity, cloud point, pour point, and hydroxyl

value of the synthesized products were determined (Table 2). The OOC of the samples increased proportionately with the increasing amount of EPO_o blended to RBDPKO_o and this was due to the contribution of epoxides by the EPO_o.

The hydroxyl value is also important as it determines the suitability of the diethanolamides in the production of rigid or flexible polyurethane foam. The synthesized diethanolamides exhibit high hydroxyl values in the range of 330–350 mg KOH/g sample (Table 2). The hydroxyl values is found to be quite similar to the hydroxyl values (300–370 mg KOH/g sample) of the carboxylated diethanolamides and palm oil-based diethanolamides used in the production of rigid polyurethane foams [6, 7].

There were also increment in the cloud point and pour point of the diethanolamides corresponding with the increasing amount of EPO_o used in the starting material. This similar trend was also noted in the viscosities of the products. When we examined the physical appearance of the diethanolamides at room temperature, we found that sample produced from blending more than 40% (w/w) EPO_o to RBDPKO_o would solidify slowly at room temperature. This is attributed to the palm olein-derived EPO_o which has a high proportion of long chain saturated fatty acids. Apart from that, EPO_o also appeared as semi-solid at room temperature because of the formation of epoxides at the unsaturated bonds of oleic and linoleic acids. By mixing RBDPKO_o, which has low melting temperature due to the high content of short and medium chain of saturated fatty acids [18] into EPO_o, a less viscous diethanolamides can be produced. Therefore, we summarized that 40% (w/w) of EPO_o blended with 60% (w/w) of RBDPKO_o is the optimal starting amount of the two materials to produce epoxidized diethanolamides with 0.78% of OOC,

Fig. 2 FTIR analysis on sample R2 to monitor the formation of OH band and C=O stretch of tertiary amide. R2: Diethanolamide polyols synthesized by 10% (w/w) of EPO_o and 90% (w/w) of RBDPKO_o with DEA at 3:1 (Palm oil TAG:DEA) molar ratio. Reaction conditions: reaction temperature, 110 °C; reaction time, 5 h
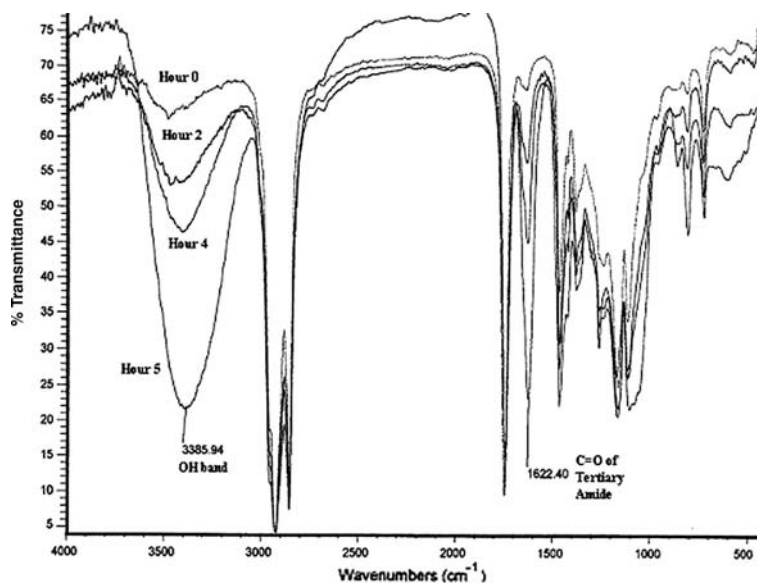
Table 2 Synthesis of diethanolamides at different percentage of EPO$_o$ to RBDPKO$_o$

Percentage of EPO$_o$:RBDPKO$_o$ (%) (w/w)	OOC[a] (%)		Amine value (mg KOH/g sample)	Hydroxyl value (mg KOH/g sample)	Viscosity (cP)		Cloud point, °C	Pour point, °C	Physical appearance at 25 °C
	H0[b]	H5[c]			25 °C	40 °C			
10:90	0.29	0.19	4.7	346.3	650.03	378.56	12	6	Liquid
20:80	0.57	0.38	5.2	333.1	718.29	310.61	12	6	Liquid
30:70	0.87	0.59	4.9	334.1	737.71	315.47	18	12	Liquid
40:60	1.18	0.78	4.5	351.9	990.08	427.09	21	12	Liquid
50:50	1.47	1.01	4.6	351.9	1339.52	465.92	24	15	Semi-solid
60:40	1.74	1.17	5.3	350.8	1417.18	470.77	30	18	Semi-solid
70:30	2.05	1.40	4.8	351.9	1640.43	572.69	33	24	Semisolid
80:20	2.36	1.63	4.9	338.7	2699.34	679.31	36	24	Semi-solid
90:10	2.53	1.71	5.0	350.5	4173.17	1218.19	36	27	Solid
100:0	2.98	2.03	4.8	354.8	4018.57	1164.80	36	30	Solid

[a] Oxirane oxygen content

[b] Sample before reaction was started at 110 °C

[c] Sample after 5 h of reaction

Table 3 Composition and retention time of trimethylsilyl derivatives of diethanolamides[a]

Peak No.[b]	Component	Retention time, min	%, w/w
1	Glycerol	0.846	21.76
2	DEA	1.554	0.79
3	Unknown	2.383	0.28
4	C$_{12}$ fatty acid	2.984	1.26
5	Unknown	4.065	0.48
6	C$_{14}$ fatty acid	4.729	0.21
7	C$_6$ diethanolamide	5.155	0.20
8	C$_{16}$ fatty acid	6.356	0.76
9	C$_8$ diethanolamide	6.744	2.34
10	Monolauroyl glycerol	7.996	0.85
11	C$_{10}$ diethanolamide	8.262	1.68
12	Unknown	9.200	0.52
13	Unknown	9.375	0.45
14	C$_{12}$ diethanolamide	9.847	19.46
15	Unknown	10.736	0.27
16	C$_{14}$ diethanolamide	11.109	6.22
17	Unknown	11.809	0.26
18	C$_{16}$ diethanolamide	12.447	13.53
19	C$_{18:2}$ + C$_{18:1}$ diethanolamide	13.395	9.28
20	C$_{18:0}$ diethanolamide	13.564	2.10
21	8-(3-octyl-oxiranyl)-octanoic acid bis-(2-hydroxy-ethyl)-amide	14.513	8.38
22	Unknown	14.670	0.23
23	Dilauroyl glycerol	15.166	1.03
24	8-[3-(3-Pentyl-oxiranylmethyl)-oxiranyl]-octanoic acid bis-(2-hydroxy-ethyl)-amide	15.454	1.11
25	Unknown	16.628	0.50
26	Dimyristoyl glycerol	16.738	0.44
27	Dipalmitoyl glycerol	17.833	4.38
28	Unknown	18.198	0.89
29	Unknown	18.397	0.34

[a] Diethanolamides synthesized from 40% (w/w) of EPO$_o$ and 60% (w/w) of RBDPKO$_o$ in reaction with DEA at molar ratio of 1:3 (palm oil TAG:DEA) at 110 °C for 5 h

[b] Peak from gas chromatogram of Fig. 3

Fig. 3 Typical gas chromatogram of trimethylsilyl-diethanolamide polyol derivatives. Raw material: 40% (w/w) of EPO_o and 60% (w/w) of $RBDPKO_o$. Reaction conditions: reaction temperature, 110 °C; reaction time, 5 h
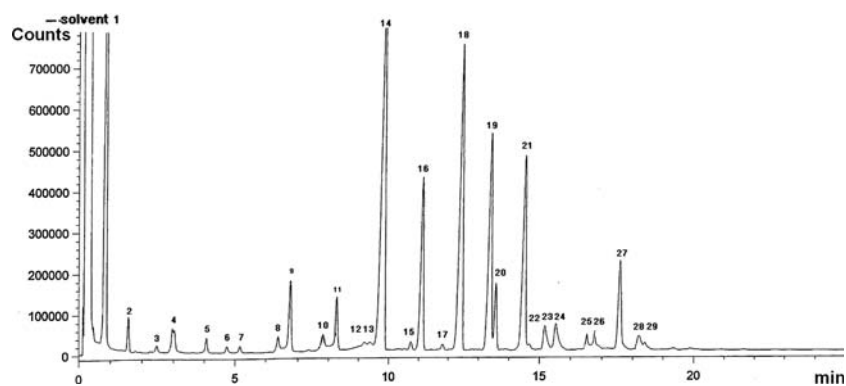

Table 4 Selected EI-GCMS fragment ions of trimethylsilyl derivatives of diethanolamide polyols[a]

Diethanolamide polyols	Retention time, min	Molecular weight of trimethylsilyl-diethanolamide polyol (MW)	Fragment ions, m/z
C6:0	24.51	347	347 $(M + TMS)^+$, 332, 214, 146, 73
C8:0	27.99	375	375 $(M + TMS)^+$, 360, 242, 146, 73
C10:0	31.30	403	403 $(M + TMS)^+$, 388, 270, 146, 73
C12:0	34.43	431	431 $(M + TMS)^+$, 416, 298, 146, 73
C14:0	37.33	459	459 $(M + TMS)^+$, 444, 326, 146, 73
C16:0	40.08	487	487 $(M + TMS)^+$, 472, 354, 146, 73
C18:1	42.31	513	513 $(M + TMS)^+$, 498, 380, 146, 73
C18:0	42.64	515	515 $(M + TMS)^+$, 500, 382, 146, 73
8-(3-octyl-oxiranyl)-octanoic acid bis-(2-hydroxy-ethyl)-amide	44.99	529	529 $(M + TMS)^+$, 514, 396, 146, 73
8-[3-(3-Pentyl-oxiranylmethyl)-oxiranyl]-octanoic acid bis-(2-hydroxy-ethyl)-amide	47.55	543	543 $(M + TMS)^+$, 528, 410, 146, 73

[a] Diethanolamide polyols synthesized by using raw material: 40% (w/w) of EPO_o and 60% (w/w) of $RBDPKO_o$ to react with DEA at a molar ratio of 1:3 (Palm oil TAG:DEA) at 110 °C for 5 h

351.09 mg KOH/g sample of hydroxyl value, 990.08 cP of viscosity at 25 °C, 427.09 cP of viscosity at 25 °C, 21 °C of cloud point and 12 °C of pour point.

Characterization of Diethanolamides

DMF and THF were found to be the most suitable solvent for diethanolamides. The diethanolamides with hydroxyl and amide functionalities were rather polar with low volatility and hence could not be injected directly to the chromatograph. For that reason, the diethanolamides were converted to the less polar trimethylsilyl derivatives prior to injection. Ryszard Piekos et al. reported the conversion of the ethanolamines to trimethylsilyl derivatives before gas chromatographic determination by reacting the mono-ethanolamines, diethanolamines, and triethanolamines with N, O-bis(trimethylsilyl) acetamide (BSA) [19]. In this work, we used BSTFA to convert the diethanolamide products to trimethylsilyl-diethanolamide products. When the trimethylsilyl-diethanolamide products were analyzed, the retention time between the products and the prepared secondary standards was comparable and most of the trimethylsilyl-diethanolamides, namely $C_{6:0}$, $C_{8:0}$, $C_{10:0}$, $C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{18:2}$, $C_{18:1}$, $C_{18:0}$, epoxidized $C_{18:1}$, and epoxidized $C_{18:2}$ diethanolamides, were identified. Additionally, glycerol, DEA, fatty acid, monoglycerides, and diglycerides were also identified. Gas chromatography results showed that the composition of the diethanolamide mixture, reacted from 40% (w/w) of EPO_o and 60% (w/w) of $RBDPKO_o$ at the optimum conditions (110 °C, 5 h) consisted of 64.30% (w/w) of diethanolamide products, 21.76% (w/w) of glycerol by-products, 2.23% (w/w) of fatty acids, 0.85% (w/w) of monoglycerides, 5.85% (w/w) of diglycerides, 4.22% (w/w) of unknown compounds, and 0.79% (w/w) of excessive DEA (Table 3, Fig. 3). Previous study has reported that the condensation of coconut oil with DEA during the production of coconut oil diethanolamide

yielded 2.8% (w/w) of diesteramine by-products through gas chromatographic determination [20]. We, thus, surmised that the 4.22% of unknown compounds were most likely diesteramine, N, N-bis (2-hydroxyethyl) piperazine(I), monoesteramine, monoesteramide, or diesteramide produced from the self-condensation of DEA and diethanolamide products at elevated temperature [21]. Subsequent characterization was carried out using GCMS analysis and the molecular weight and structure of the trimethylsilyl derivatized diethanolamide polyols were identified. Table 4 summarized the fragmentation patterns and relative intensities of the trimethylsilyl-diethanolamide products. The molecular ion (M+TMS)[+] for the epoxidized diethanolamides, namely 8-(3-octyl-oxiranyl)-octanoic acid bis-(2-trimethylsilanyloxyl-ethyl)-amide and 8-[3-(3-Pentyl-oxiranylmethyl)-oxiranyl]-octanoic acid bis-(2-trimethylsilanyloxyl-ethyl)-amide were recorded at m/z 529 and m/z 543, respectively.

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