

CHAPTER II

EXPERIMENT

2.1 INSTUMENTS AND EQUIPMENTS

The infrared spectra were recorded on a Nicolet Impact 410 Fourier-Transform Infrared Spectrophotometer.

The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Model ACF200 Fourier-transform NMR Spectrometer using tetramethylsilane (TMS) as an external standard. The chemical shift (δ) report are given in part per million down field from TMS.

Mass spectra were determined using a Fisons Instruments model Trio-2000 GC-Mass Spectrometer.

The ozone was generated by electric discharge in an oxygen stream using a Fischer Ozone Generator Model 500m.

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2.2 REAGENTS AND MATERIALS

Reagents and raw materials were obtained from various suppliers as shown in Table 2

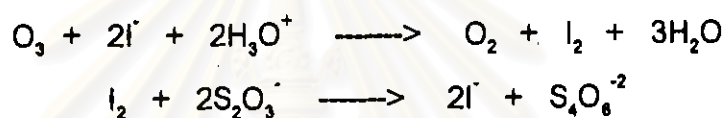
Table 2 Sources of chemicals

Materials	Company
Palm oil	Morakot Industrial
Hydrogen Peroxide	Carlo Erba
Formic acid	Baker
Sulfuric acid	Baker
Hexane	Merck
Methanol	Merck
Ethanol	Merck
Isopropanol	Merck
Butanol	Merck
2-ethyl-1-hexanol	Merck
Ferric chloride	Fluka
Hydroxylamine	Fluka
hydrochloric acid	Baker
Chloroform	Fluka
Sodium sulfate (anhydrous)	Fluka
Iodine	BHD chemical™
Potassium iodide	Baker

2.2.1 Other substances

Merck TLC sheet (silica gel 60 F254 precoated) was used for thin layer chromatography. Merck silica gel 60 (particle size 70-230 mesh) was used for column chromatography.

2.3 DETERMINATION THE AMOUNT OF OZONE



The ozone was passed through a solution of 50 ml of 5 % potassium iodide in aqueous acetic acid (1:1 V/V) by flow rate of 20 kg/cm³ for 5 minutes. The titration was liberated iodine (20ml) with 0.1 M sodium thiosulfate using starch as an indicator. The yield of ozone was calculated as 0.0076 mole/hour.

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2.4 PREPARATION OF ACIDS BY OZONOLYSIS

Palm oil (8.82 g, 0.012 mole) was dissolved in 20 ml of hexane and methanol in reaction vessel. The reactor, provided with a stirrer, a gas-inlet tube, gas vent, was placed in an ice bath to maintain the reaction temperature at 0 °C and ozone was introduced into the mixture for 2 hours (mole per mole of palm oil). The reaction was monitored by thin layer chromatography (TLC) (20 % chloroform in hexane as eluent), then the TLC plate was put in iodine chamber. Methanol and hexane were removed by rotary evaporator. To the solution, 9 ml of 90 % formic acid and 5 ml of 35 % hydrogen peroxide were added, and heated was cautiously. After the spontaneous reaction has ceased (30 minutes), the reaction mixture was refluxed for 30 minutes. The mixture was cooled to room temperature, separated (water in lower layer). The residue containing mostly carboxylic acid (7.93 g, 90 %) was used in the next experiment without purification.

Palm oil

¹³C-NMR (CDCl₃) δ (ppm) (Fig. 1) : 173.1 (CH₂-C=O), 172.1 (CH-CO), 130.0 (=CHCH₂), 128.5 (=CHCH₂), 69.0 (CH-O), 62.1 (CH₂-O), 34.1 (CH₂-C=O), 31.9, 29.3, 24.9, 22.7, 14 (CH₂'s chain).

Acids

FT-IR (KBr) ν (cm⁻¹) (Fig. 2) : 3600 (-OH stretching), 2923, 2853 (-CH aliphatic), 1730 (O=C stretching), 1180 (O-C stretching).

$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm) (Fig. 3) : 180.5 (COOH), 173.1 ($\text{CH}_2\text{-CO}$), 172.1(CH-CO), 69.0 (CH-O), 62.1 ($\text{CH}_2\text{-O}$), 34.1 ($\text{CH}_2\text{-C=O}$), 31.9, 29.3, 24.9, 22.7, 14(CH_2 ' s chain).

2.5 PREPARATION OF DIESTERS

Solution of acid (from 2.4) in 2 ml of sulfuric acid was stirred at room temperature for half hour, then 20 ml of methanol was added. The reaction mixture was refluxed for 2 hours. The upper layer of the mixture was removed and was extracted the aqueous layer with ether. The combination of ether extract and crude esters was washed with water, then with saturated sodium bicarbonate solution until ethervesence cease, and finally with water, dry with anhydrous sodium sulfate. The ether was removed with rotary evaporator and concentrated to obtain the crude product (6.82 g) as yellow liquid.

The experiment was replaced with different alcohols such as ethanol, isopropanol, butanol, and 2-ethyl-1-hexanol.

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2.6 SEPARATION OF ESTER COMPOUNDS

All ester compounds (20 : 1 w/w of silicagel per ester compounds) were purified using silica gel column chromatography (20 % chloroform in hexane).

Table 3 The results of separation of crude esters by column chromatography

Type of esters	Fraction no.	Compounds no.
Methyl	5-7	1
	9-10	2
	12-13	3
Ethyl	4-6	4
	7-9	5
	12-14	6
isopropyl	5-7	7
	8-10	8
	12-13	9
Butyl	6-8	10
	10-12	11
	15-16	12
2-ethyl-hexyl	4-6	13
	8-10	14
	13-14	15

2.7 CHARACTERIZATION AND PROPERTIES OF ESTER COMPOUNDS

Compound 1

The compound 1 was a colorless liquid, b.p. 170 °C and $R_f = 0.73$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 4) : 2923, 2853 (C-H stretching), 1739 (O=C stretching), 1470 (CH_2 methylene group), 1369 (CH_3 methyl group), 1230-1100 (C-O stretching).

^{13}C -NMR (CDCl_3) δ (ppm) (Fig. 5) : 174.28, 51.42, 34.02, 32.01, 29.02, 25.01, 22.82, 14.00.

^1H -NMR (CDCl_3) δ (ppm) (Fig. 6) : 3.63 (s), 2.27 (t), 1.58 (m), 1.23 (m), 0.85(t).

Mass (m/e) (% relative intensity) (Fig. 8) : 270 (M^+) (5), 239 (3), 74 (100).

Compound 2

The compound 2 was a colorless liquid, b.p. 150 °C and $R_f = 0.37$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 9) : 2923, 2853 (C-H stretching), 1739 (O=C stretching), 1470 (CH_2 methylene group), 1369 (CH_3 methyl group), 1230-1100 (C-O stretching).

^{13}C -NMR (CDCl_3) δ (ppm) (Fig.10) : 174.24, 51.20, 34.01, 28.80, 24.82, 22.80.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm) (Fig. 11) : 3.59 (s), 2.23 (t), 1.55 (p), 1.25 (m), 1.18 (m).

Mass (m/e) (% relative intensity) (Fig. 12) : 216 (M^+), 185 (20), 111 (36), 74 (55).

Compound 3

The compound 3 was a yellow liquid, b.p. 80°C and $R_f = 0.29$ (Silica gel, $\text{CHCl}_3 : \text{C}_6\text{H}_{14}$ 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 13) : 2929, 2848 (C-H stretching), 1734 (O=C stretching), 1470 (CH_2 methylene group), 1369 (CH_3 methyl group), 1230-1100 (C-O stretching).

$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm) (Fig. 14) : 174.02, 51.20, 34.0, 32.00, 29.20, 25.02, 22.45, 14.01.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm) (Fig. 15) : 3.61 (s), 2.25 (t), 1.56 (p), 1.26 (m), 1.21 (m), 0.83 (m).

Mass (m/e) (% relative intensity) (Fig. 16) : 72 (M^+) (1), 141 (10), 74 (100).

Compound 4

The compound 4 was a colorless liquid, b.p. 190°C and $R_f = 0.64$ (Silica gel, $\text{CHCl}_3 : \text{C}_6\text{H}_{14}$ 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 17) : 2929, 2848 (C-H stretching), 1734 (O=C stretching), 1465 (CH_2 methylene group), 1363 (CH_3 methyl group), 1230-1100 (C-O stretching).

$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm) (Fig. 18) : 174.01, 60.01, 34.25, 31.98, 29.20, 25.02, 22.84, 14.02.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm) (Fig. 19) : 4.05 (q), 2.25 (t), 1.58 (p), 1.23 (m), 1.19 (m), 0.83 (m).

Mass (m/e) (% relative intensity) (Fig. 21) : 284 (M^+) (1), 239 (3), 88 (100).

Compound 5

The compound 5 was a colorless liquid, b.p. 180 °C and $R_f = 0.38$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 22) : 2934, 2853 (C-H stretching), 1734 (O=C stretching), 1470 (CH_2 methylene group), 1373 (CH_3 methyl group), 1230-1100 (C-O stretching).

$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm) (Fig.23) : 173.82, 60.05, 34.84, 29.02, 24.92.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm) (Fig. 24) : 4.10 (q), 2.32 (t), 1.62 (p), 1.23 (m), 1.19 (m).

Mass (m/e) (% relative intensity) (Fig. 25) : 244 (M^+), 199 (93), 88 (48).

Compound 6

The compound 6 was a yellow liquid, b.p. 120 °C and $R_f = 0.25$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 26) : 2918, 2853 (C-H stretching), 1734 (O=C stretching), 1470 (CH_2 methylene group), 1438 (CH_3 methyl group), 1230-1100 (C-O stretching).

$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm) (Fig. 27) : 174.02, 60.02, 34.01, 32.01, 29.02, 25.01, 22.78, 14.01.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm) (Fig. 28) : 4.05 (q), 2.26 (t), 1.57 (p), 1.23 (m), 1.26 (m), 1.19 (m), 0.85 (t).

Mass (m/e) (% relative intensity) (Fig. 29) : 186 (M^+) (0.5), 141 (11), 88 (100).

Compound 7

The compound 7 was a colorless liquid, b.p. 210°C and $R_f = 0.70$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 30) : 2923, 2853 (C-H stretching), 1739 (O=C stretching), 1470 (CH_2 methylene group), 1363 (CH_3 methyl group), 1230-1100 (C-O stretching).

$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm) (Fig. 31) : 173.82, 67.81, 34.82, 32.01, 29.20, 25.01, 22.82, 22.24, 14.01.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm) (Fig. 32) : 4.97 (h), 2.23 (t), 1.58 (p), 1.23 (m), 0.85 (t).

Mass (m/e) (% relative intensity) (Fig. 34) : 298 (M^+) (1), 239 (16), 102 (49).

Compound 8

The compound 8 was a colorless liquid, b.p. 175°C and $R_f = 0.65$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 35) : 2929, 2859 (C-H stretching), 1734 (O=C stretching), 1460 (CH_2 methylene group), 1363 (CH_3 methyl group), 1230-1100 (C-O stretching).

^{13}C -NMR (CDCl_3) δ (ppm) (Fig. 36) : 174.02, 67.81, 34.54, 29.18, 25.40, 22.02.

^1H -NMR (CDCl_3) δ (ppm) (Fig. 37) : 4.92 (h), 2.31 (t), 1.62 (p), 1.23 (m), 1.19 (m).

Mass (m/e) (% relative intensity) (Fig.38) : 272 (M^+), 213 (3), 111 (4), 102 (3).

Compound 9

The compound 9 was a yellow liquid, b.p. 135°C and $R_f = 0.19$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 39) : 2923, 2848 (C-H stretching), 1734 (O=C stretching), 1465 (CH_2 methylene group), 1363 (CH_3 methyl group), 1230-1100 (C-O stretching).

^{13}C -NMR (CDCl_3) δ (ppm) (Fig.40) : 174.01, 67.63, 34.83, 32.5, 29.20, 25.32, 22.82, 21.97, 14.10.

^1H -NMR (CDCl_3) δ (ppm) (Fig. 41) : 4.95 (h), 2.22 (t), 1.57 (p), 1.23 (m), 1.18 (m), 1.17 (m), 0.84 (t).

Mass (m/e) (% relative intensity) (Fig. 42) :206 (M^+), 141 (3), 102 (3).

Compound 10

The compound 10 was a colorless liquid, b.p. $>220^{\circ}\text{C}$ and $R_f = 0.66$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 43) : 2923, 2853 (C-H stretching), 1739 (O=C stretching), 1465 (CH_2 methylene group), 1363 (CH_3 methyl group), 1230-1100 (C-O stretching).

^{13}C -NMR (CDCl_3) δ (ppm) (Fig. 44) : 173.67, 63.94, 34.82, 32.25, 30.81, 29.02, 25.02, 22.82, 19.22, 14.01, 13.82.

^1H -NMR (CDCl_3) δ (ppm) (Fig.45) : 4.02 (t), 2.24 (t), 1.58 (p) 1.28 (m), 1.22 (m), 1.16 (m), 0.84 (t).

Mass (m/e) (% relative intensity) (Fig. 47) : 312 (M^+) (3), 239 (20), 116 (10).

Compound 11

The compound 11 was a colorless liquid, b.p. 175°C and $R_f = 0.37$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig.48) : 2923, 2859 (C-H stretching), 1739 (O=C stretching), 1465 (CH_2 methylene group), 1363 (CH_3 methyl group), 1230-1100 (C-O stretching).

^{13}C -NMR (CDCl_3) δ (ppm) (Fig. 49) : 174.02, 64.02, 34.20, 30.81, 28.92, 25.01, 19.03, 13.86.

^1H -NMR (CDCl_3) δ (ppm) (Fig. 50) : 4.02 (t), 2.28 (t), 1.56 (p), 1.27 (m), 1.25 (m), 1.18 (m).

Mass (m/e) (% relative intensity) (Fig. 51) : 300 (M^+), 227 (97), 116 (5), 111 (29).

Compound 12

The compound 12 was a yellow liquid, b.p. 150 °C and $R_f = 0.29$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 52) : 2929, 2859 (C-H stretching), 1739 (O=C stretching), 1460 (CH_2 methylene group), 1438 (CH_3 methyl group), 1230-1040 (C-O stretching).

^{13}C -NMR (CDCl_3) δ (ppm) (Fig. 53) : 174.01, 63.94, 34.34, 31.85, 30.21, 29.01, 25.03, 22.82, 19.20, 14.02, 13.81.

^1H -NMR (CDCl_3) δ (ppm) (Fig. 54) : 4.03 (t), 2.25 (t), 1.58 (p), 1.28 (m), 1.23 (m), 0.85 (t).

Mass (m/e) (% relative intensity) (Fig. 55) : 312 (M^+) (3), 239 (20), 116 (10).

Compound 13

The compound 13 was a colorless liquid, b.p. >220 °C and $R_f = 0.65$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 56) : 2923, 2853 (C-H stretching), 1739 (O=C stretching), 1470 (CH_2 methylene group), 1363 (CH_3 methyl group), 1230-1040 (C-O stretching).

^{13}C -NMR (CDCl_3) δ (ppm) (Fig. 57) : 173.88, 66.72, 39.02, 34.22, 31.81, 30.20, 29.84, 29.02, 25.02, 23.98, 23.01, 22.82, 14.01, 13.85, 11.03.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm) (Fig. 58) : 3.94 (d), 2.26 (t), 1.58 (p), 1.35 (q), 1.31 (q), 1.26 (m), 1.22 (m), 0.87 (t), 0.85 (t).

Mass (m/e) (% relative intensity) (Fig. 60) : 412 (M^+), 283 (1), 171 (100), 112 (20).

Compound 14

The compounds 14 was a colorless liquid, b.p. $>220^\circ\text{C}$ and $R_f = 0.40$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 61) : 2923, 2848 (C-H stretching), 1739 (O=C stretching), 1470 (CH_2 methylene group), 1363 (CH_3 methyl group), 1230-1169 (C-O stretching).

$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm) (Fig. 66) : 174.02, 66.64, 39.01, 34.20, 30.22, 29.87, 29.03, 25.02, 23.96, 23.0, 23.01, 13.85, 11.01.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm) (Fig. 67) : 3.93 (d), 2.23 (t), 1.57 (p), 1.34 (h), 1.30 (m), 1.26 (m), 1.23 (m), 0.84 (t).

Mass (m/e) (% relative intensity) (Fig. 64) : 386 (M^+), 239 (20), 171 (5).

Compound 15

The compounds 15 was a yellow liquid, b.p. 180°C and $R_f = 0.37$ (Silica gel, CHCl_3 : C_6H_{14} 1:4).

FT-IR (KBr) ν (cm^{-1}) (Fig. 65) : 2929, 2848 (C-H stretching), 1734 (O=C stretching), 1470 (CH_2 methylene group), 1438 (CH_3 methyl group), 1230-1169 (C-O stretching).

$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm) (Fig. 62) : 174.02, 66.74, 39.42, 34.25, 32.02, 30.22, 29.92, 29.04, 25.30, 23.98, 23.02, 23.01, 14.02, 13.86, 11.05.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm) (Fig. 63) : 3.95 (d), 2.27 (t), 1.58 (p), 1.35 (h), 1.32 (q), 1.31 (q), 1.27 (m), 1.23 (m), 0.88 (t), 0.85 (t).

Mass (m/e) (% relative intensity) (Fig. 69) : 270 (M^+), 171 (43), 141 (100).

2.8 ESTER COMPOUNDS AS MARKER IN DIESEL FUEL

2.8.1 Preparation of mixed ester compounds in diesel fuel

Esters (1 g, mixture) were dissolved in diesel in 100 ml volumetric flask (10^4 ppm), diluted to 600-350 ppm (Table 4).

2.8.2 Test of ester compounds in diesel fuel (Colorimetric)

Test solution (0.2 ml) was placed in crucible then 0.2 ml of saturated alcoholic solution of hydroxylamine hydrochloride and 0.1 ml of saturated sodium hydroxide were added to this crucible. The mixture in the crucible was heated until it started to boil. After cooling, the mixture was acidified with 0.5 M hydrochloric acid, and 0.1 ml of 1 % ferric chloride. A more or less intense violet color appears.

Table 4 The concentration of ester compounds in diesel fuel

Ester compounds	Concentration (ppm)
Methyl	500
	450
	350
	300
Ethyl	500
	300
	250
	200
Isopropyl	500
	400
	350
	300
n-Butyl	600
	550
	500
2-ethyl-1-hexyl	500
	450
	400

2.8.3 Detection of ester compounds in diesel fuel by GC

Esters (1 g, mixture) were dissolved in diesel fuel in 100 ml volumetric flask. The concentration were 10000 ppm.

GC condition

Column : DB-1 capillary column 30 m x 0.25 ID x 0.25 μm

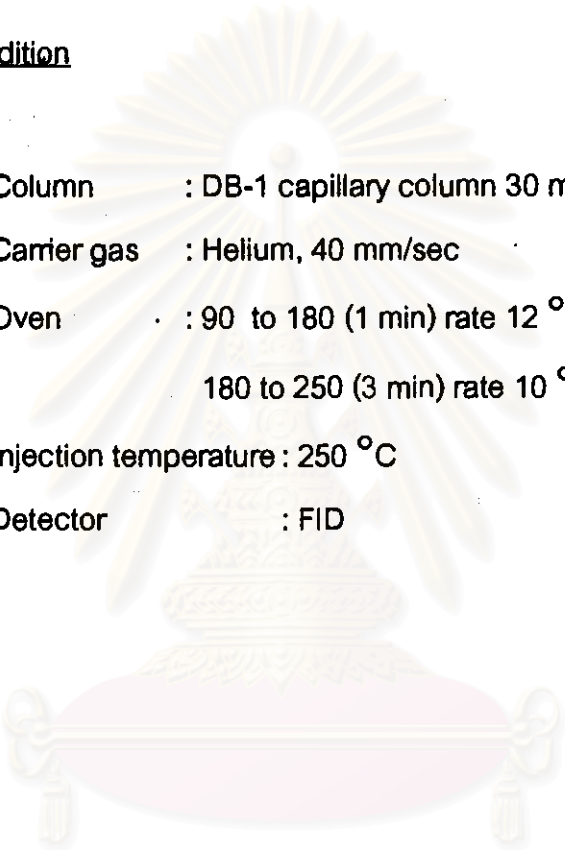
Carrier gas : Helium, 40 mm/sec

Oven : 90 to 180 (1 min) rate 12 $^{\circ}\text{C}/\text{min}$

180 to 250 (3 min) rate 10 $^{\circ}\text{C}/\text{min}$

Injection temperature : 250 $^{\circ}\text{C}$

Detector : FID



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