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APPENDICES

APPENDIX A

Calculation in the Characterization of the Catalyst

1. Calculation of the sulfur content from XRF

Crumb rubber	100	g	had SO_3	3.010	g
SO_3	1	mol	=	80.000	g
Crumb rubber	100	g	had SO_3	0.038	mol

From the calculation, crumb rubber 100 g had 1.204 g of sulfur and 1.806 g of oxygen which equaled to 0.038 mol and 0.113 mol, respectively. The detected sulfur content from XRF found 0.380 mmol per 1 g of crumb rubber.

2. Calculation of the sulfur content from Bomb Calorimetry

The sulfur content of the original and oxidized crumb rubber was found by following the ASTM D3177, the standard for the estimation of sulfur content in coal. This calculation used the equation below;

$$Sulfur\ content\ (\%) = \frac{(A - B) \times 13.738}{C} \quad \text{(A1)}$$

where; *A* is weight of burned crucible with sample (g)

B is weight of empty crucible (g)

C is weight of sample (g)

Example;

CR-HNO_3(6M)	weight of burned crucible with sample	20.2920	g
	weight of empty crucible	20.2515	g
	weight of sample	0.8814	g
	sulfur content	0.63	% by mass

3. Calculation of the sulfur loss from the oxidation

$$Sulfur\ loss\ (\%) = \frac{(A - B)}{A} \times 100 \qquad (A2)$$

where;	*A*	is	the sulfur content of the original crumb rubber (g sulfur/g rubber)
	B	is	the sulfur content of the oxidized crumb rubber (g sulfur/g rubber)

Example;

CR-HNO_3 (6M)	the sulfur content of the original crumb rubber	0.0121	g sulfur/g rubber
	the sulfur content of the oxidized crumb rubber	0.0056	g sulfur/g rubber
	sulfur loss	54.0	%

4. Calculation of the swelling ratio

The swelling ratio of samples was measured by swelling test following ASTM D471. The swelling ratio (Q) was calculated according to the equation below;

$$Swelling\ ratio\ (Q) = \frac{M - M_0}{M_0} \qquad (A3)$$

where;	*M*	is	weight of the swollen sample (g)
	M_0	is	weight of the original sample (g)
	Q	is	swelling ratio

Example;

CR-HNO_3 (6M)	weight of the swollen sample in toluene	0.54	g
	weight of the original sample	0.21	g
	swelling ratio in toluene	1.55	

5. Calculation of the sol/gel content

The sol and gel content of samples were measured by the determination of gel fraction following ASTM D3616. The gel content was calculated after the weight of sample changed by the equation below;

$$Sol\,(\%) = \frac{W_0 - W_d}{W_0} \times 100 \tag{A4}$$

$$Gel(\%) = 100 - Sol\,(\%) \tag{A5}$$

where;	W_0	is	the initial mass of sample (g)
	W_d	is	the total dried mass of sample (g)
	Sol	is	the dissolved rubber fraction in the solvent (%)
	Gel	is	the undissolved rubber fraction in the solvent (%)

Example;

CR-HNO_3 (6M)	the initial mass of sample	0.2069	g
	the total dried mass of sample	0.1706	g
	the dissolved rubber fraction in the solvent	17.6	%
	the undissolved rubber fraction in the solvent	82.4	%

6. Calculation of the acid content from the titration

The acid content of the oxidized crumb rubber was measured by an acid-base titration method. The result of this part was represented as mmol/g of the oxidized crumb rubber which measured from the ion-exchange capacity or the acid content (H^+). The acid content was calculated from the equation below:

$$Acid\ content = \frac{A \times B}{C} \tag{A6}$$

where;	*A*	is	NaOH content in titration (mL)
	B	is	Composition of NaOH (mol/l)
	C	is	weight of samples (g)
	Acid content	is	the H^+ exchange capacity (mmole/g sample)

Example from the direct titration method with DI 10 mL+THF 10 mL;

CR-HNO_3 (6M)	NaOH content in titration	1.83	mL
	Composition of NaOH	0.05	mol/L
	weight of samples	0.1076	g
	the H^+ exchange capacity	0.85	mmol/g sample

7. Calculation of the catalyst recovery from the esterification

After the esterification, catalyst was removed from the product to recover. Catalyst was cleaned by using 150 mL of hexane. Then, the catalyst recovery was calculated by following the equation below;

$$catalyst\ recovery\ (\%) = \frac{(A-B)}{A} \times 100 \qquad \text{(A7)}$$

where;	*A*	is	weight of catalyst before esterification (g)
	B	is	weight of catalyst after esterification (g)
	Catalyst recovery	is	catalyst recovered after esterification (%)

Example from the esterification of octanoic acid with octanol on the effect of catalyst loading ;

CR-HNO_3 (6M) 1%	weight of catalyst before esterification	0.0715	g
	weight of catalyst after esterification	0.0245	g
	catalyst recovered after esterification	34.27	%

APPENDIX B

The Calibration Curve in the Esterification

The calibration curve was applied to analyze the acid conversion in the esterification. This curve was plotted by the data obtained from the chromatogram of octanoic acid. Y-axis was the mass ratio of octanoic acid and standard solution while X-axis was the peak area ratio of octanoic acid and internal standard solution. This method used methyl undecanoate (C_{11}) as the internal standard. Table B1 shows the mass ratio and peak area ratio for plot the calibration curve of octanoic acid.

Table B1 The mass ratio and peak area ratio of octanoic acid to internal standard for plot the calibration curve of octanoic acid

Mass ratio of octanoic acid to internal standard	Peak area ratio of octanoic acid to internal standard
0.4222	0.4376
0.7601	0.7603
1.2857	1.2571
1.7190	1.7994
2.2730	2.3411
2.4298	2.4460

Figure B1 shows the calibration curve of the octanoic acid which has R^2 more than 0.99. This calibration curve has the accuracy and able to use in the quantitative analyzing.

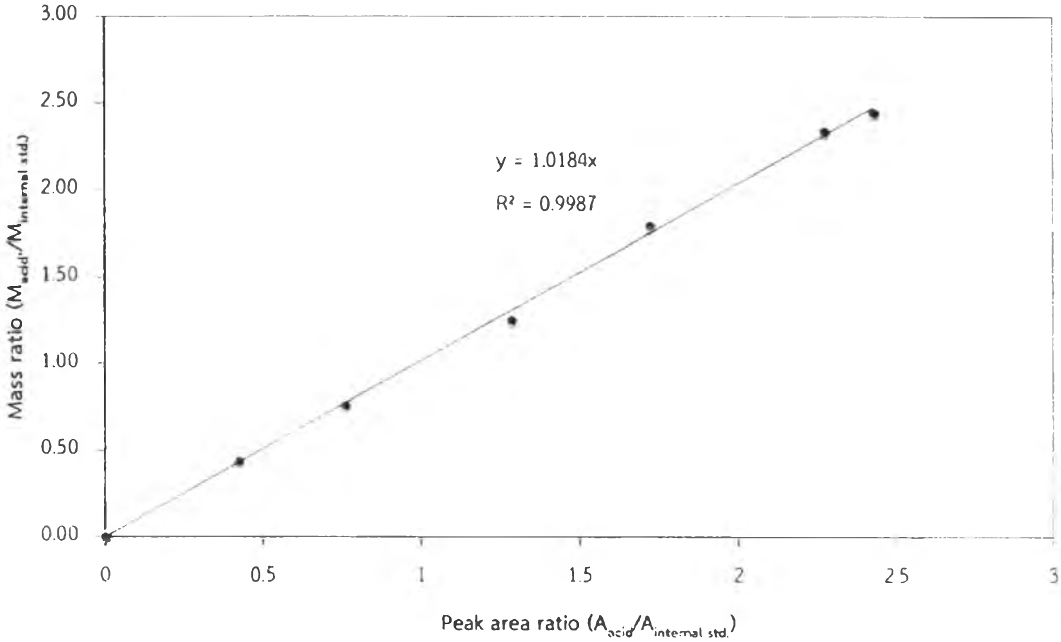

Figure B1 The calibration curve of the octanoic acid

APPENDIX C

Calculation in the Octanoic Acid Conversion in the Esterification

1. The octanoic acid conversion
   a. The calibration curve of the octanoic acid was used to calculate the remained octanoic acid after the esterification.
   b. The peak area ratio of octanoic acid to internal standard was obtained from chromatogram of GC which was calculated in the equation from calibration curve below;

$$y = 1.0184x \qquad \text{(C1)}$$

where; x is the peak area ratio of octanoic acid and internal standard solution

y is the mass ratio of octanoic acid and standard solution

Example from the esterification of octanol with octanoic acid on the effect of catalyst loading ;

CR-HNO_3(6M) 1%	the peak area ratio of octanoic acid and internal standard solution	0.4910
	the mass ratio of octanoic acid and standard solution	0.3821
	the remained octanoic acid from the esterification	0.0012 g

   c. The remained octanoic acid from the esterification was ontained from the calculation.

d. The octanoic acid conversion was calculated by the equation below;

$$octanoic\ acid\ conversion(\%) = \frac{(A - B)}{A} \times 100 \qquad (2)$$

where;	*A*	is	initial mass of octanoic acid (g)
	B	is	mass of octanoic acid after the esterification (g)
	octanoic acid conversion	is	the conversion of octanoic acid to the ester product (%)

Example from the esterification of octanol with octanoic acid on the effect of catalyst loading ;

CR-HNO_3 (6M) 1%	initial mass of octanoic acid	0.0024	g
	mass of octanoic acid after the esterification	0.0012	g
	octanoic acid conversion	50.8	%

2. The retention time (R_t) of alcohol, carboxylic acid and ester product was shown in table C1.

Table C1 The retention time (R_t) of alcohol, carboxylic acid and ester product

Substance	Retention time (min)
Internal standard C_{11} (Methyl undecanoate : $C_{12}H_{24}O_2$)	5.76
Octanol ($C_8H_{18}O$)	3.89
Octanoic acid ($C_8H_{16}O_2$)	4.55
Octyl octanoate (Ester product : $C_{16}H_{32}O$)	7.87
2-ethyl-1-hexanol ($C_8H_{18}O$)	3.56
2-ethyl-1-hexyl octanoate (Ester product : $C_{16}H_{32}O$)	7.89

3. The chromatogram from the esterification of alcohol with carboxylic acid without catalyst

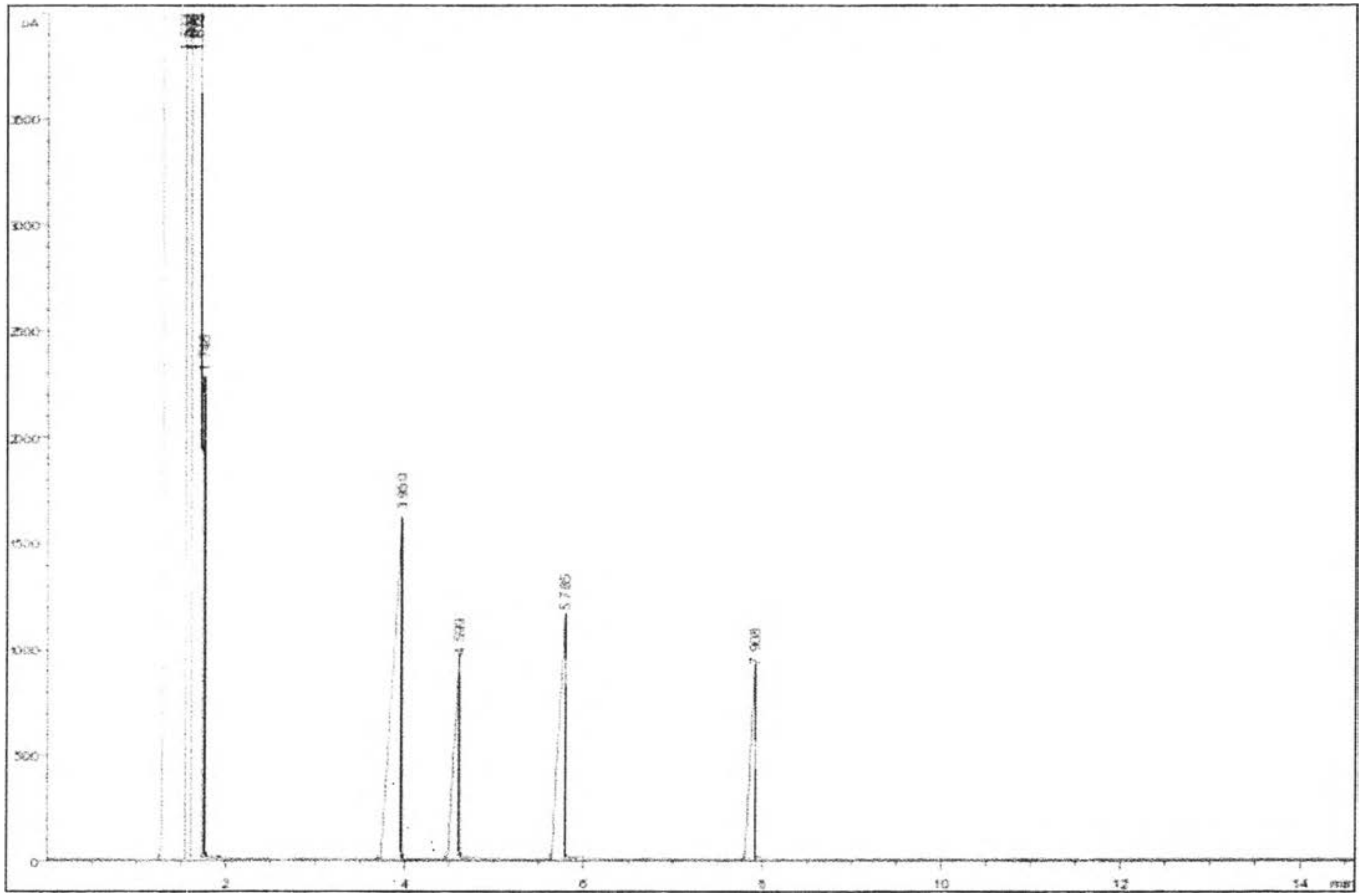

Figure C1 Chromatogram from the esterification of octanol with octanoic acid

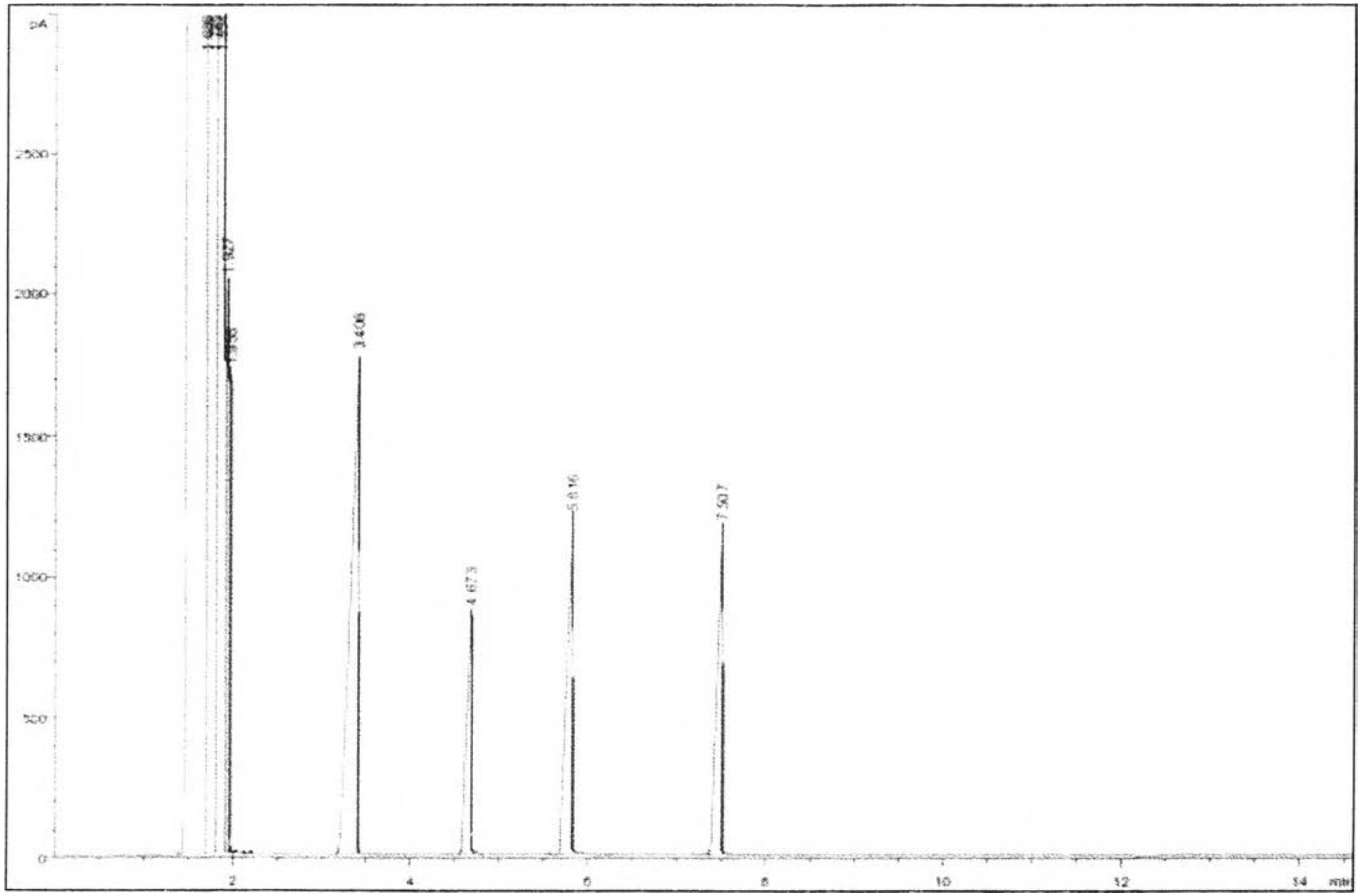

Figure C3 Chromatogram from the esterification of 2-ethyl-1-hexanol with octanoic acid

4. The chromatogram from the esterification of alcohol with carboxylic acid by using the oxidized crumb rubber as catalyst

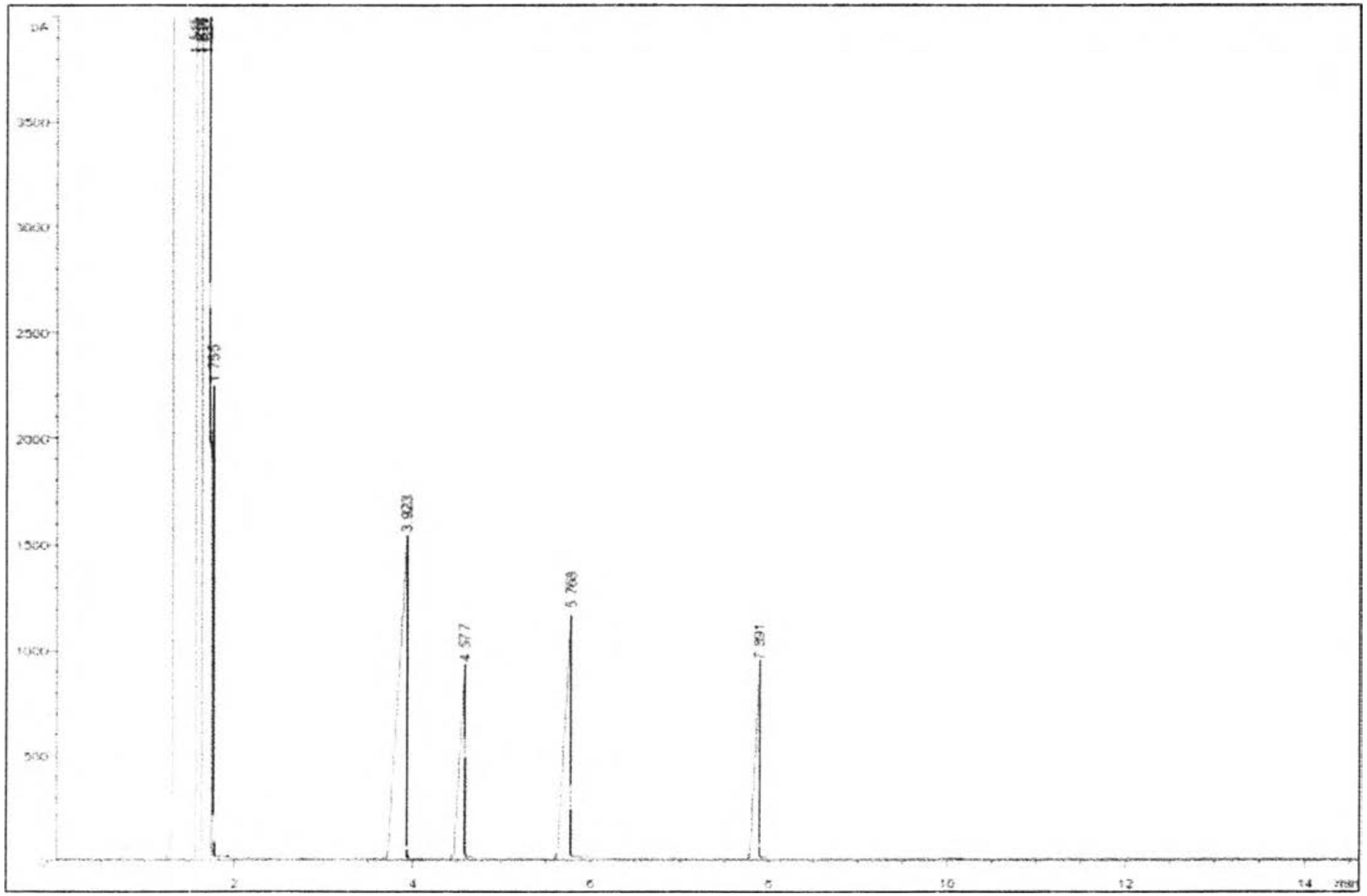

Figure C5 Chromatogram from the esterification of octanol with octanoic acid by using CR-HNO_3 (6M) as the catalyst

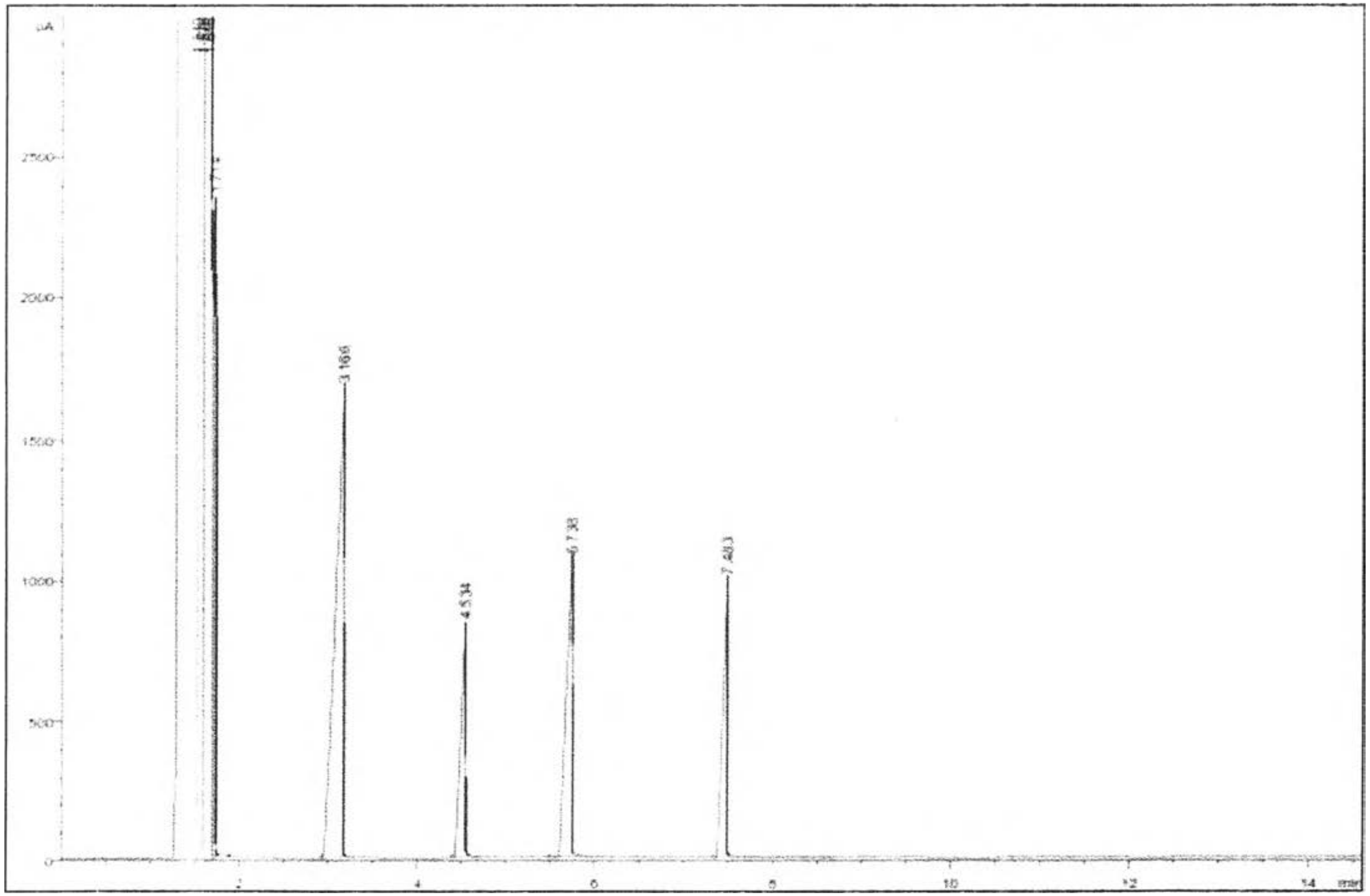

Figure C.6 Chromatogram from the esterification of 2-ethyl-1-hexanol with octanoic acid by using CR-HNO_3 (6M)

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