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APPENDICES

Appendix A Biodiesel Analysis

The methyl ester contents were analyzed by using a Hewlett Packard GC model 5890.

Gas Chromatograph (GC)

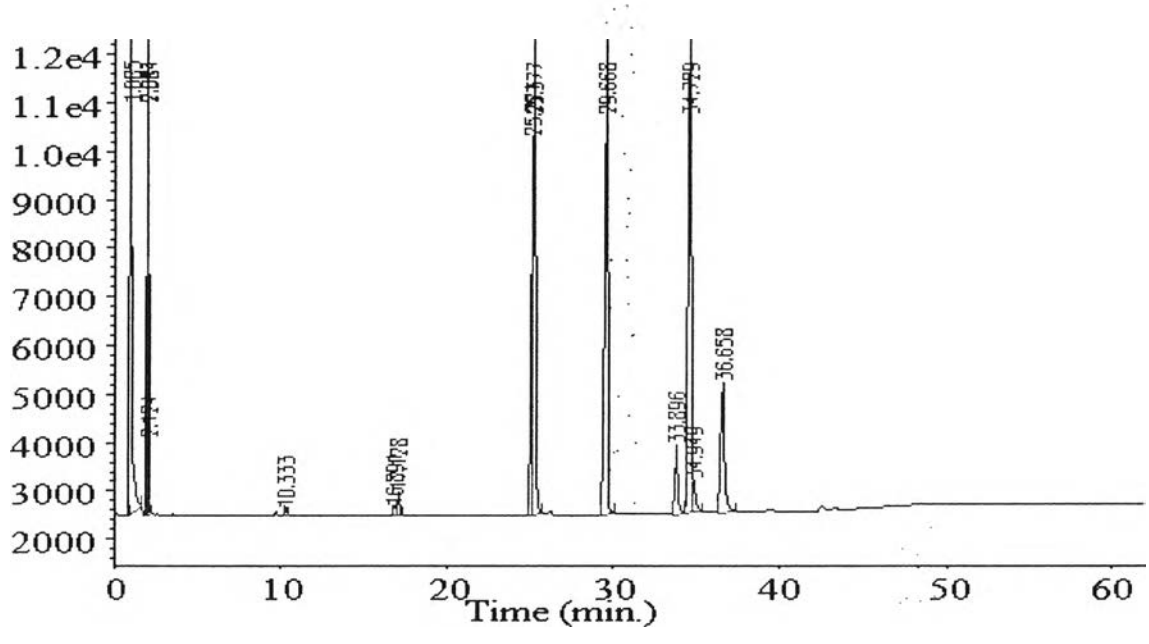


Figure A1 The peaks of methyl ester from Gas Chromatograph (GC).

Table A1 Raw data of 25%K/bentonite from GC

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	1.085	BB S	0.037	8179331	1.02	1.7
2	2.041	BH S	0.014	6243834	1.983	2.072
3	2.084	HB S	0.02	16963	2.072	2.24
4	2.124	BB T	0.019	1479	2.107	2.153
5	10.333	BB	0.073	781	10.25	10.48
6	16.891	BV	0.125	1842	16.78	17.02
7	17.128	VB	0.098	3400	17.02	17.367
8	25.221	BV	0.098	50518	24.993	25.267
9	25.377	VB	0.104	128204	25.267	25.85
*10	29.668	BB	0.127	99308	29.35	30.14
11	33.896	BB	0.172	16179	33.693	34.373
12	34.729	BV	0.12	164829	34.442	34.91
13	34.949	VB	0.171	6853	34.91	35.468
14	36.658	BB	0.205	41904	36.388	37.455

*The peak 10 is methyl hepta decanoate (standard)

The methyl ester content or yield, were determined using Equations (1)-(2)

$$C = \frac{\left(\sum A\right) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \qquad (1)$$

C Methyl ester content or Fatty acid methyl ester (FAME)

$\sum A$ The overall area of methyl ester from C_{14} to C_{24}

A_{EI} The peak area of that which is aligned with methyl hepta decanoate solution

C_{EI} Concentration in mg/ml of methyl hepta decanoate solution

V_{EI} Volume of methyl hepta decanoate solution

m Weight in mg of sample

$$\text{Yield \%} = \frac{\text{Mass of washed and dried methyl ester layer}}{\text{Theoretical mass of methyl ester from mass balance}} \times 100 \qquad (2)$$

Methyl ester yield (%) = (((414510÷99308)×2×10)÷100)×100

= 83.48%

The composition of the reaction mixture samples was determined by the somewhat modified HPLC method of Holćapek *et al.*, (1999) using a Perkin Elmer High Performance Liquid Chromatography.

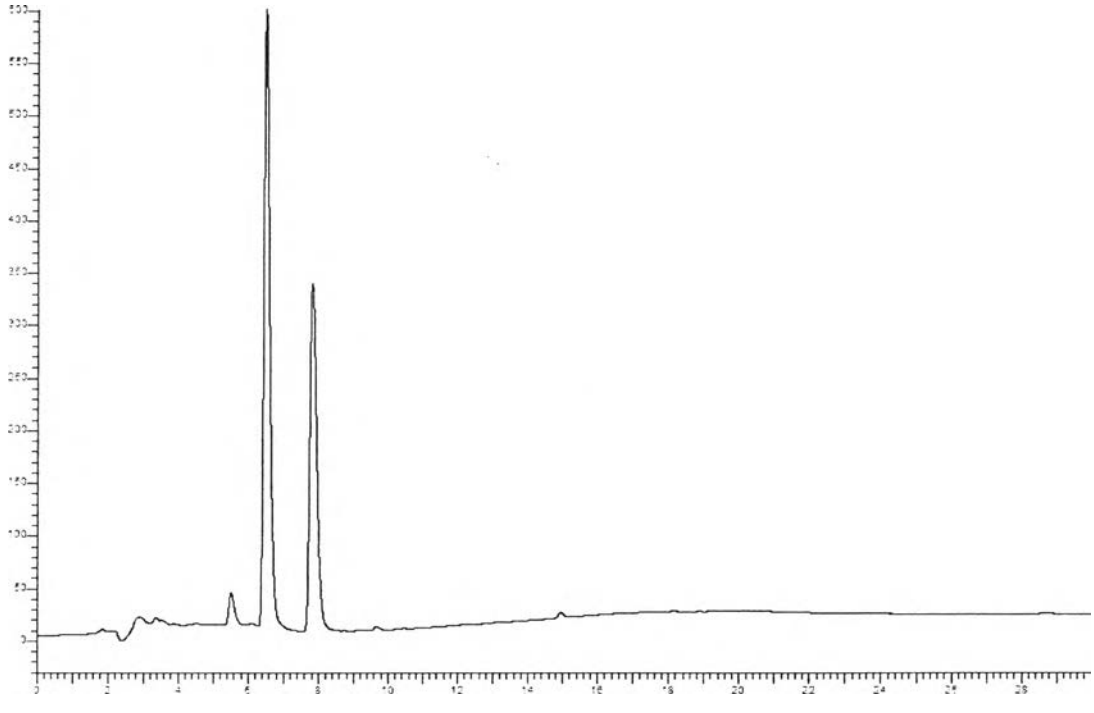


Figure A2 The chromatogram of 25%K bentonite from High Performance Liquid Chromatography (HPLC).

Table A2 Raw data of 25%K/bentonite from HPLC

Time	Area	Height	Area	Norm. Area	BL	Area/ Height	
1.9	78378	7235.87	0.38	0.38	BB	10.8319	
2.265	5189.2	1201.41	0.02	0.02	BB	4.3193	
2.905	382546.16	21831.27	1.83	1.83	BV	17.5229	monoglyceride
2.991	279215.2	21870.51	1.34	1.34	VV	12.7667	
3.388	459918.44	16823.23	2.2	2.2	VB	27.3383	
4.415	21913.46	1641.72	0.1	0.1	BV	13.3479	
4.687	7643.34	724.55	0.04	0.04	VB	10.5491	
5.426	556080.07	47250.95	2.66	2.66	BV	11.7687	
5.984	52170.36	4334.77	0.25	0.25	VV	12.0353	
6.354	10919378.38	887482.53	52.32	52.32	VB	12.3038	ester
7.593	7481875.05	469684.84	35.85	35.85	BE	15.9296	
8.484	23865.6	1051.29	0.11	0.11	EV	22.7013	
9.029	9944.46	344.07	0.05	0.05	VV	28.9024	
9.374	64851.5	5839.19	0.31	0.31	VB	11.1062	
10.255	14618	1460.72	0.07	0.07	BB	10.0074	
11.057	11147.66	454.8	0.05	0.05	BV	24.5111	
11.456	4479.32	276	0.02	0.02	VV	16.2294	diglyceride
11.843	7701.17	873.81	0.04	0.04	VV	8.8133	
11.956	5916.45	670.61	0.03	0.03	VV	8.8225	
14.653	167582.22	9056.77	0.8	0.8	VV	18.5035	
16.393	124581.08	1641.68	0.6	0.6	VV	75.8863	
16.815	33245.82	1636.82	0.16	0.16	VV	20.3112	
17.01	23919.13	1645.75	0.11	0.11	VV	14.5339	
17.315	25676.84	1542.82	0.12	0.12	VV	16.6428	triglyceride
17.842	14426.62	1234.94	0.07	0.07	VB	11.6820	
18.582	5140.8	452.45	0.02	0.02	BB	11.3621	

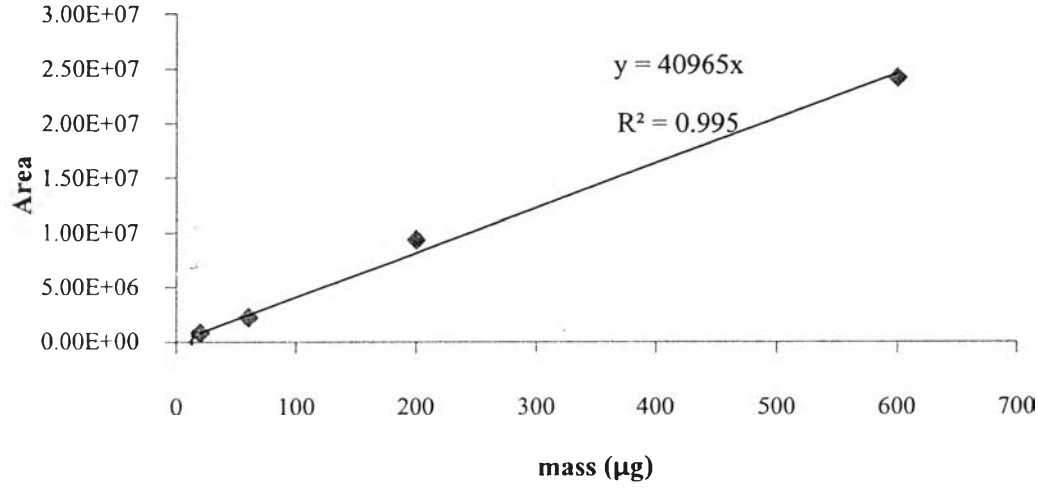
19.173	3089.2	387.04	0.01	0.01	BB	7.9816
19.563	3860.11	336.14	0.02	0.02	BV	11.4836
19.777	14036.78	779.85	0.07	0.07	VV	17.9993
20.094	8282	923.31	0.04	0.04	VV	8.9699
20.392	35281.2	1601.16	0.17	0.17	VB	22.0348
23.738	14234.8	340.69	0.07	0.07	BB	41.7823
29.41	10776.2	295.23	0.05	0.05	BB	36.5010

} triglyceride

Calibration curve

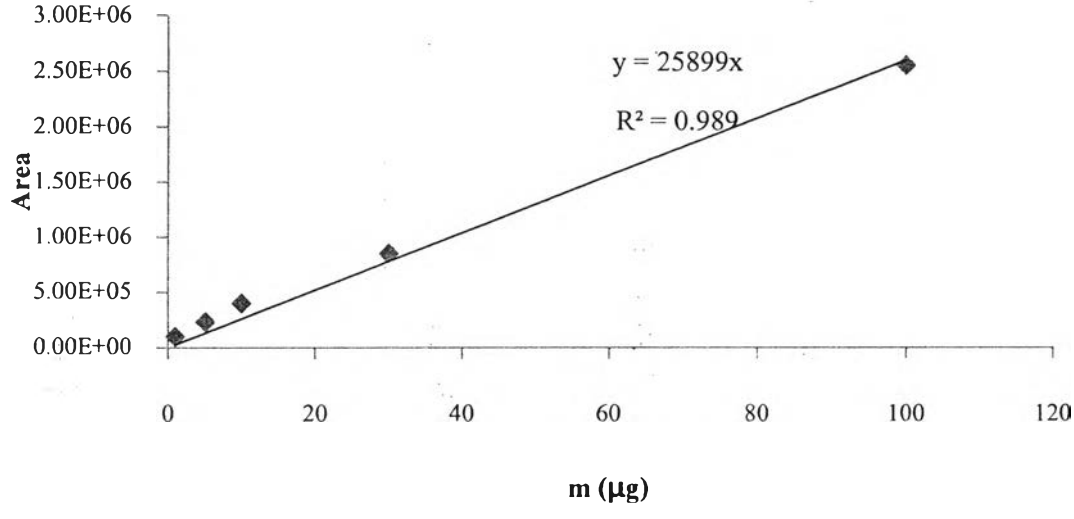
Ethyl oleate

Amount of std	Area	Rs
20	824370.4	41218.52
60	2221263.77	37021.06283
200	9424591.97	47122.95985
600	24191677.4	40319.46233
	Average	41420.50125



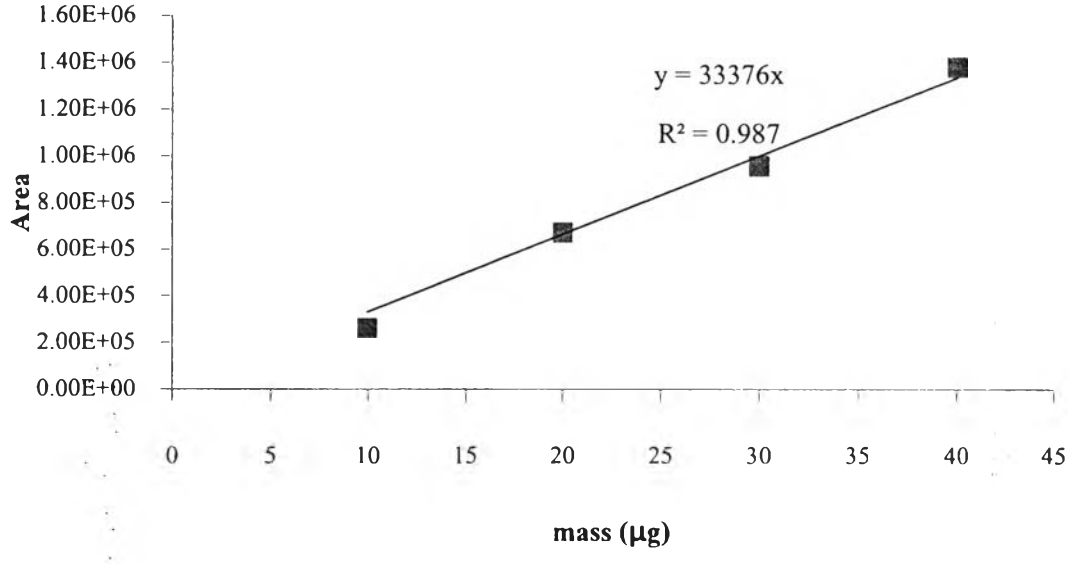
Triglyceride

Amount of std	Area	Rf
1	98460	98460
5	234123.6	46824.72
10	400853.94	40085.394
30	852209.6	28406.98667
	Average	47849.84533



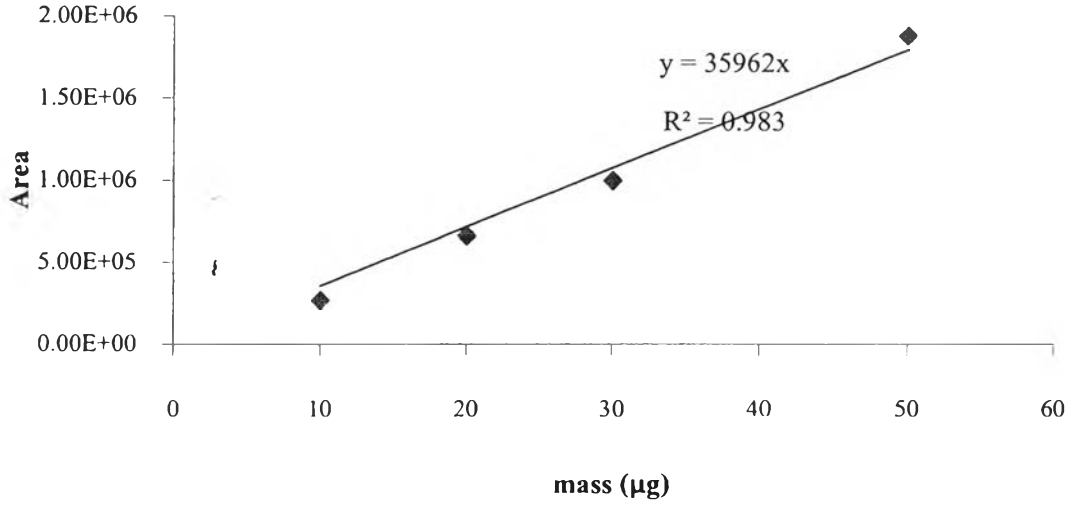
Diglyceride

Amount of std	Area	Rf
10	265421.7	26542.17
20	675897.775	33794.88875
30	959131.55	31971.05167
40	1379564.69	34489.11725
	Average	31699.30692



Monoglyceride

Amount of std	Area	Rf
10	272161.26	27216.126
20	664779.56	33238.978
30	1001505.8	33383.52667
50	1883756.535	37675.1307
	Average	32878.44034



From Table A2

Time	Area	Area/Slope of ester, mono-di-triglyceride	
1.9	78378	2.267619	monoglyceride
2.265	5189.2	0.150129	
2.905	382546.16	11.06776	
2.991	279215.2	8.077975	
3.388	459918.44	13.30629	
4.415	21913.46	0.534931	ester
4.687	7643.34	0.186582	
5.426	556080.07	13.57452	
5.984	52170.36	1.273535	
6.354	10919378.38	266.5538	
7.593	7481875.05	182.6407	
8.484	23865.6	0.582585	
9.029	9944.46	0.242755	
9.374	64851.5	1.583095	
10.255	14618	0.437979	diglyceride
11.057	11147.66	0.334002	
11.456	4479.32	0.134208	
11.843	7701.17	0.23074	
11.956	5916.45	0.177267	
14.653	167582.22	6.470606	triglyceride
16.393	124581.08	4.810266	
16.815	33245.82	1.283672	
17.01	23919.13	0.923554	
17.315	25676.84	0.991422	
17.842	14426.62	0.557034	
18.582	5140.8	0.198494	
19.173	3089.2	0.119279	

19.563	3860.11	0.549627
19.777	14036.78	0.416086
20.094	8282	2.267619
20.392	35281.2	0.150129
23.738	14234.8	11.06776
29.41	10776.2	8.077975

} triglyceride

*Sample weight = 552 μg

%Monoglyceride = (SUM (Area/Slope)/Sample weight)×100
= (34.86977/552) ×100
= 6.316988

%Ester = (467.1725/552) ×100
= 84.6327

%Diglyceride = (1.314196/552) ×100
= 0.238079

%Triglyceride = (18.69311/552) ×100
= 3.386433

Appendix B Catalyst Characterization

The fresh and spent catalysts were characterized for their characteristic, structure, morphology, and metal composition for describing the results from experiment. The catalysts were characterized by using several techniques.

1. Titration

Standardization of KOH

Potassium acid phatalate 0.1 g in 40 ml

Normality = *(*Wp**1000)÷(204.23*(V-Vb))*

Wp = weight of potassium phatalate (g)

V = amount of KOH titrate (ml)

Vb = amount of KOH blank titrate (ml)

204.23 = molecular weight of potassium phatalate (g/mol)

KOH titration

Time	V_i	V_f	V_f-V_i
1	10	17.75	7.75
2	10	17.85	7.85
		Average	7.8

*V_i = V initial and V_f = V final

Normality = (0.025425×1000)÷(204.23×(7.8-0))

= 0.015960512

Concentration of HCl (HCl = 5ml)

Time	V_i	V_f	V_f-V_i
1	10	16.25	6.25
2	10	16.25	6.25
		Average	6.25

*V_i = V initial and V_f = V final

$C_1V_1 = C_2V_2$

$KOH + HCl \longrightarrow H_2O + KCl$

KOH

$C_1 = 0.01596$

$V_1 = 6.25$

$C_2 = 0.01995$ mol/l

HCl

$C_1 = ?$

$C_2 = 5$

Table B1 Basicity of catalyst

Sample	time	V_i (ml)	V_f (ml)	V_f-V_i (ml)	V_{HCl} (ml)	Amount of catalyst (g)
25%K/bentonite	1	10	12.3	2.3	5	0.0155
	2	10	12.15	2.15	5	0.0162

Back titration	Total basic site (mmol)	Total basic site (mmol/g)	Average
3.95	0.0788	5.08403	5.067
4.1	0.0818	5.04907	

*V_i = V initial and V_f = V final

Back titration = 6.25-(V_f-V_i)

Total basic site (mmol) = Back titration × C_2

Total basic site (mmol/g) = Total basic site (mmol)/Amount of catalyst (g)

2. Temperature-Programmed Desorption of CO_2 (CO_2-TPD)

Temperature-programmed desorption (Micromeristics 2900) was used for observing desorbed molecules from the surface when the surface temperature is increased. The basic properties of the samples were determined using the temperature-programmed desorption of CO_2 (CO_2-TPD), which was used as the probe molecule.

TPD/R/O 1100
Thermo Electron

Gas Port when Ready: (b) Helium
Gas Port when End: (b) Helium
Sample rate: 1s
Gain: 10
Polarity: +

Pretreatment

Phase	With Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°/min]	Stop at T [°C]	Hold for [min]
Cleaning	Nitrogen	20	Off			5
1:00	Nitrogen	20	Off	10	120	30
2:00	Carbon Dioxide	20	50	0	50	60
3:00	Nitrogen	20	Off			60
4:00	Off					
End Pretreatment with Oven at 50°C						

TPD/R/O

With gas: Helium and flow of 20 ccm/min
Start with oven off, heating rate 10 °/min, stop at 900 °C, hold for 180 min
Temperature at end of experiment 30 °C

Results
Amount gas dsorbed: 240.95247 µmol/g

Baseline
Start at 0.0167 min 97.35107 mV, Stop at 236.0667 min 13.12256 mV

Calibration
Use Calibration Factor: 257.012140 $\cdot 10^{-9}$ mmol/mVs

#	Start[min]	Stop[min]	Maximum[min]	T[°C]	Integral[mVs]	[%]	[µmol/g]
1	9.7833	19.9667	15.4667	178	44904.86	23.02	55.45937
2	41.75	51.8333	42.5167	448	67626.92	34.66	83.52205
3	74.2167	84.5667	75.3833	775	82564.88	42.32	101.97105

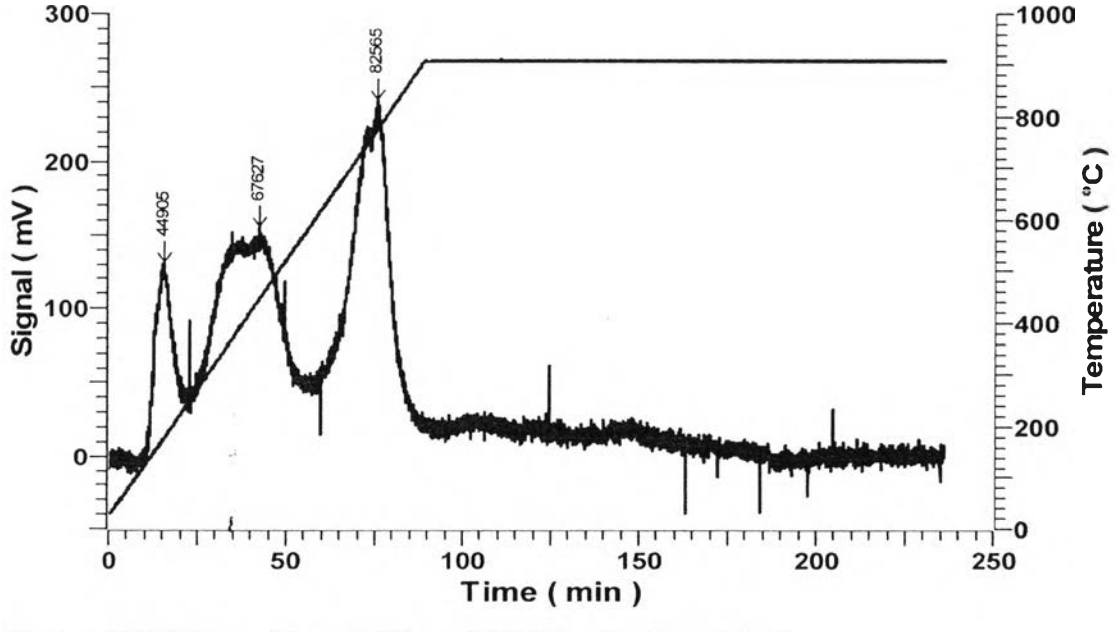


Figure B1 TPD profiles of CO_2 on 25%K/bentonite catalyst.

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Proceedings:

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