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APPENDIX A

SAMPLE OF CALCULATIONS

A-1 Calculation of the Mole Composition of Reagents on SAPO-34

Preparation

Compositions : 2 Al : 0.6 Si : 2 P : 1.3 TEAOH : 52 H₂O

M.W. of Al (OC₃H₇)₃ = 204.25

The Al (OC₃H₇)₃ was used = 2*204.25 = 408.5 g

M.W. of SiO₂ = 60.10 (SiO₂ in Cataloid 30 %)

The SiO₂ was used = (0.6*60.10*100)/30 = 120.2 g

M.W. of H₃PO₄ = 98.0 (concentration of H₃PO₄ 85 %)

The H₃PO₄ was used = (2*98*100)/85 = 230.59 g

M.W. of TEAOH = 147.26 (concentration of TEAOH 35 %)

The TEAOH was used = (1.3*147.26*100)/35 = 546.97 g

M.W. of H₂O = 18

The H₂O was used = 52*18 = 936 g

Since, there was some water in SiO₂, H₃PO₄, and TEAOH = 475.259 g

The H₂O was added = 460.741 g

For the preparation of SAPO-34 was reduced in 40 times. (/40)

So that

Reagents	Al(OC ₃ H ₇) ₃	SiO ₂	H ₃ PO ₄	TEAOH	H ₂ O
the moles of composition	2	0.6	2	1.3	52
weight of reagent	10.21	3.01	5.76	13.67	11.5

the moles of TEAOH	0.5	1	1.3	1.5
weight of TEAOH	5.26	10.52	13.67	15.78
the moles of SiO ₂	0.6	1	1.5	2
weight of SiO ₂	3.01	5	7.51	10.02
the moles of H ₃ PO ₄	1.5	2	2.5	3
weight of H ₃ PO ₄	4.32	5.76	7.2	8.65

Mole composition of HF = 0.5

M.W. of HF = 20.01 (concentration of HF = 46 %)

The HF was used = $(0.5 \times 20.01 \times 100) / 46 = 21.75$

the moles of HF	0.2	0.3	0.5	1
weight of HF	0.22	0.33	0.54	1.09

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A-2 BET Surface Area Calculation

From BET equation :

$$\frac{x}{v(1-x)} = \frac{1}{v_m C} + \frac{C-1}{V_m C} x \quad (\text{A-2.1})$$

where :

- x = ratio of partial pressure P/P_0
- P_0 = saturated vapour pressure of N_2
(or adsorbed gas)
- P = equilibrium vapour pressure of N_2
- v = amount of adsorption at the equilibrium, c.c.
at the NTP/gm of sample
- v_m = amount of adsorption to cover the surface, c.c.
at the NTP/gm of sample

$$C = \exp(E_1 - E_2 / RT) \quad (\text{A-2.2})$$

where :

- E_1 = heat of adsorption of the first layer
- E_2 = heat of condensation of adsorbed gas

assume $C \rightarrow \infty$, then

$$\frac{x}{v(1-x)} = \frac{1}{v_m} x \quad (\text{A-2.3})$$

let :

- v_m = v_m
- v_m = mean the amount of adsorption to form the N_2
complete monolayer

v = amount of adsorption measuring by G.C.

x = P/P_0

$$\frac{P_b V}{273} = \frac{P_t V}{T} \quad (\text{A-2.4})$$

where : V = constant volume

P_b = pressure at 0°C

P_t = pressure at $t^\circ\text{C}$

T = $273.15 + t$, K

$P_b = (273.15/T) * P_t = 1 \text{ atm}$

partial pressure

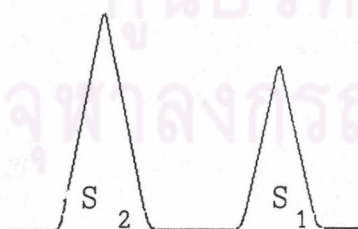
$$P = \frac{[\text{Flow of (He+N}_2) - \text{Flow of He}] * P_b}{\text{Flow of (He+N}_2)} \quad (\text{A-2.5})$$

$$= 0.3 \text{ atm}$$

N_2 saturated vapour pressure, $P_0 = 1.1 \text{ atm} = 836 \text{ mm.Hg}$

$x = P/P_0 = P/1.1$

How to measuring v



1 ml/1 atm at room temperature

desorption N_2 calibration
of N_2 area area

$$v = \frac{S_2}{S_1} \cdot \frac{1}{w} \cdot \frac{273.15}{T} \text{ c.c./g of catalyst} \quad (\text{A-2.6})$$

where : w = weight of sample

$$v_m = \frac{v[1 - (\text{flow of He+N}_2 - \text{flow of He})/1.1]}{\text{flow of He+N}_2} \text{ c.c.NTP/g of catalyst} \quad (\text{A-2.7})$$

$$S_b = S \cdot v_m \quad (\text{A-2.8})$$

where : S = surface area from literature of N_2
 $= 4.373 \text{ m}^2/\text{c.c. of } N_2$

so that : $S_b = 4.373 v_m \text{ m}^2/\text{g of catalyst}$

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A-3 TPD Calculation

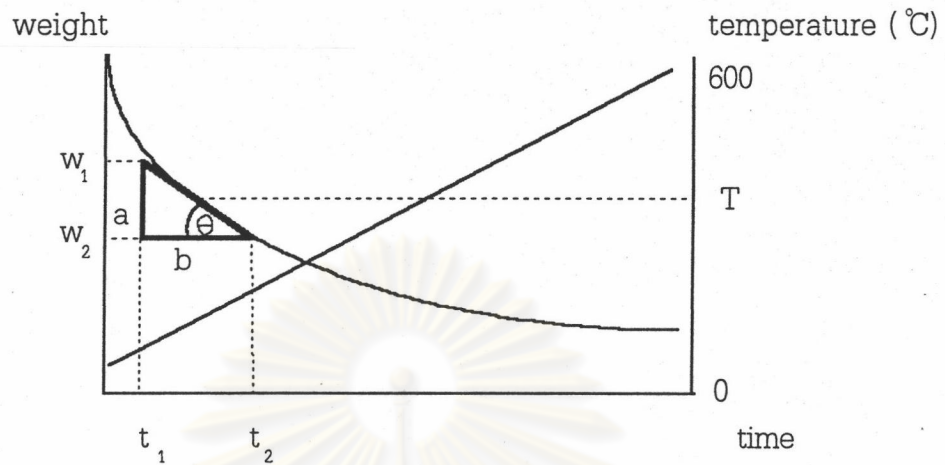


Figure A-3 Plot of weight loss and temperature vs. time

chart speed = 0.25 cm/min

Range = 10 mg

w = weight of catalyst

w_w = weight of water

w_o = weight of dry catalyst = $w - w_w$

dw = $\frac{10 \text{ mg} \times a \text{ cm}}{25}$ (A-3.1)

dt = $\frac{60 \text{ sec} \times b \text{ cm}}{0.25}$ (A-3.2)

$\frac{dw}{dt}$ = $\frac{[10 \text{ mg} \times 0.25 \text{ cm} \times a]}{25 \text{ cm} \times 60 \text{ sec} \times b} / w_o$ (A-3.3)

Plot $\frac{dw}{dt}$ vs. temperature.

w_o

A-4 Calculation of Reaction Flow Rate

The catalyst used = 0.2100 g

packed catalyst into quartz reactor ($\Phi = 0.6$ cm)

determine the average high of catalyst bed = x cm

So that, volume of catalyst bed = $\pi*(0.3)^2 *x$ cc-cat.

used GHSV (Gas Hourly Space Velocity) = 2,000 h⁻¹

$$\text{GHSV} = \frac{\text{Volumetric flow rate}}{\text{Volume of catalyst}} = 2,000 \text{ h}^{-1}$$

$$\text{Volumetric flow rate} = 2,000 * \text{Volume of catalyst}$$

$$= 2,000 * \pi * (0.3)^2 * x \text{ cc/h}$$

$$= 2,000 * \pi * (0.3)^2 * x / 60 \text{ cc/min}$$

$$\text{at STP : Volumetric flow rate} = \frac{\text{Volumetric flow rate} * (273.15 + t)}{273.15}$$

where : t = room temperature, °C

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A-5 Calculation for Percentage of MeOH Conversion

Assume that the temperature of sampling syringe was 95 °C.

Volume of syringe = 2 ml

hence,

$$\text{Volume of MeOH in 2 ml of sample} = 2 \cdot 10^{-3} \cdot Y \quad \text{l} \quad (\text{A-5.1})$$

where : Y = % concentration of MeOH in feed stream line

for example, Y = 20% MeOH

$$\begin{aligned} \text{then, volume of MeOH in syringe} &= 2 \cdot 10^{-3} \cdot 0.2 \quad \text{l} \\ &= 0.0004 \quad \text{l} \end{aligned}$$

The amount of carbon from a 2 ml syringe of feed MeOH calculated as follows:

assume MeOH vapour obey ideal gas law, i.e.,

$$\begin{aligned} \text{MeOH (at STP) 22.4 l compose with C} &= 12 \quad \text{g} \\ \text{MeOH (at STP) } V_1 \quad \text{l compose with C} &= (12/22.4) \cdot V_1 \quad \text{g} \quad (\text{A-5.2}) \end{aligned}$$

From the equation of state,

$$(P_1 V_1)/T_1 = (P_2 V_2)/T_2 \quad (\text{A-5.3})$$

where : P_1, P_2 = total pressure of a system at condition 1 and 2, respectively

V_1, V_2 = total volume of a system at condition 1 and 2, respectively

T_1, T_2 = temperature of a system at condition 1 and 2, respectively

which 1 represents STP condition, 2 represents the consider condition. For this system, we assumed that $P_1 = P_2$ (atmospheric pressure), then :

$$V_1 = (V_2/T_2) * T_1 \quad (\text{A-5.4})$$

Substituted (A-5.4) into (A-5.2) and absolute temperature (T_1) = 273.15 K, gives

$$C_{\text{MeOH},i} = 12/22.4 * (V_2 * 273.15) / (273.15 + t) \quad (\text{A-5.5})$$

where : $C_{\text{MeOH},i}$ = quantity of C for input MeOH
 t = temperature of syringe

The quantity of output MeOH can be calculated from G.C. analysis which calibration factor for MeOH * = $8.085 * 10^{-4}$ (unit area/l).
 * : obtained from calibration data of Mr. Hagiwara, Catalyst Engineering Laboratory, Kyoto University.

hence, the amount of C for output MeOH is

$$C_{\text{MeOH},o} = 8.085 * 10^{-4} * \text{ITG}_{\text{MeOH}} * 10^{-6} * 273.15 / (273.15 + 95) * 12 / 22.4 \text{ g} \quad (\text{A-5.6})$$

where : $C_{\text{MeOH},o}$ = quantity of C for output MeOH

then,

$$\begin{aligned} \% \text{ MeOH conversion} &= (2 * 10^{-3} * Y) - 8.085 * 10^{-10} * \text{ITG}_{\text{MeOH}} * 100 / (2 * 10^{-3} * Y) \\ &= 100 - 8.085 * 10^{-5} * \text{ITG}_{\text{MeOH}} / 2 * Y \end{aligned} \quad (\text{A-5.7})$$

A-6 Calculation of Product Distribution of MTO Reaction

Sample : SAPO-34/HF (HF=0.5)

Reaction condition : Reaction temperature 450 °C, GHSV = 2,000 h⁻¹,
time on stream 1 h.

From Figure A-6-1 :

Porapak Q (TCD)

area of MeOH = 459074 (20 % balanced with N₂ 80 %)

From Figure A-6.2 :

Porapak Q (TCD)

(ratio of CH₄:CO₂ = 1 : 1.35; this value for each G.C.)

area of CH₄ = 5465 = 5465/1 = 5465

area of CO₂ = 321 = 321/1.35 = 238

CO₂ = CH₄ * a

a = CO₂/CH₄ = 238/5465 = 0.0435

area of MeOH = 0 area of DME = 0

From Figure A-6.3 :

MS-5A (TCD)

(ratio of CH₄ : CO = 1 : 1.13)

area of CH₄ = 5576 = 5576/1 = 5576

area of CO = 667 = 667/1.13 = 590

CO = CH₄ * b

b = CO/CH₄ = 590/5576 = 0.1059

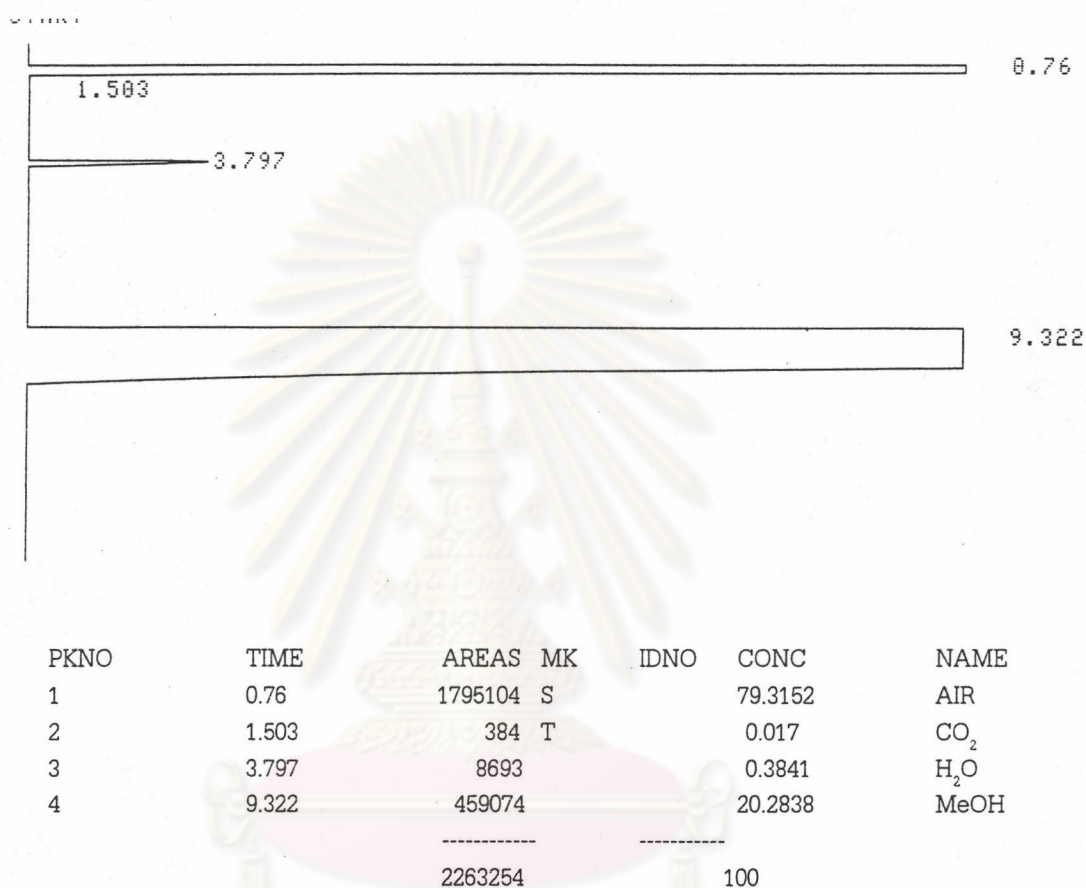


Figure A-6.1 Peaks of feed from Porapak Q (TCD)

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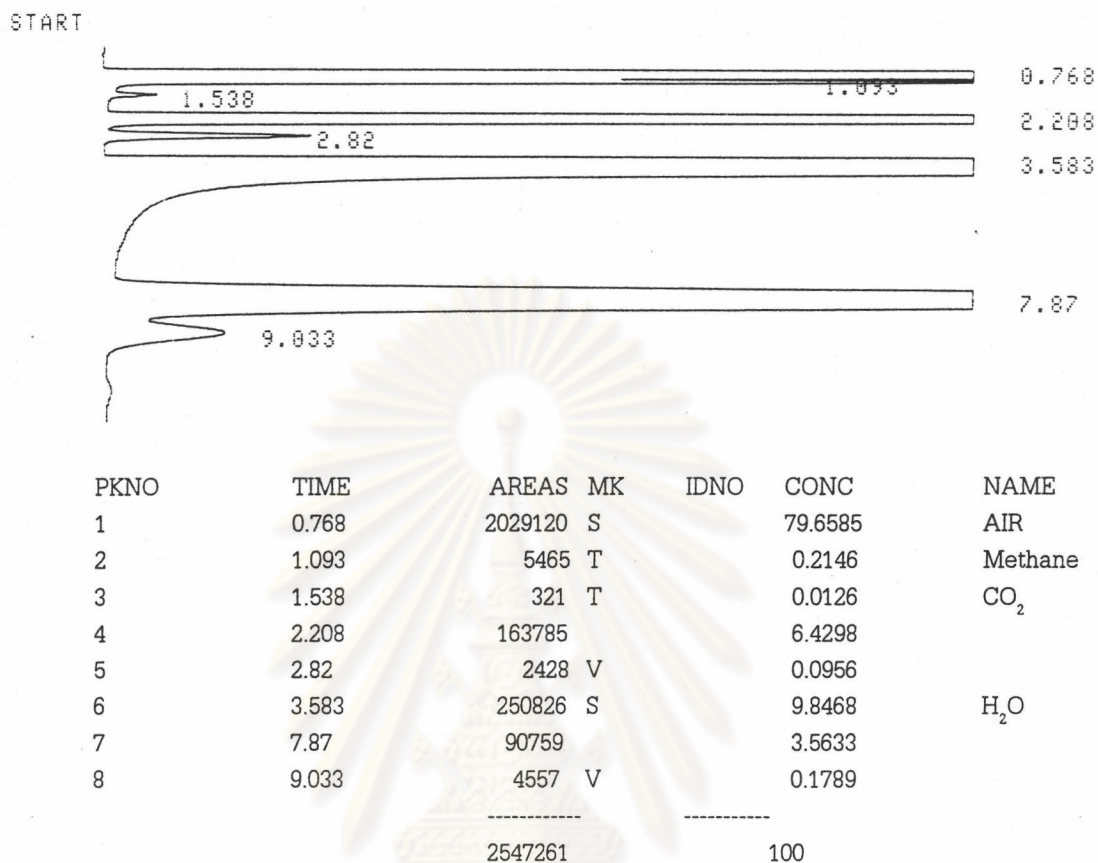


Figure A-6.2 Peaks of product from Porapak Q (TCD)

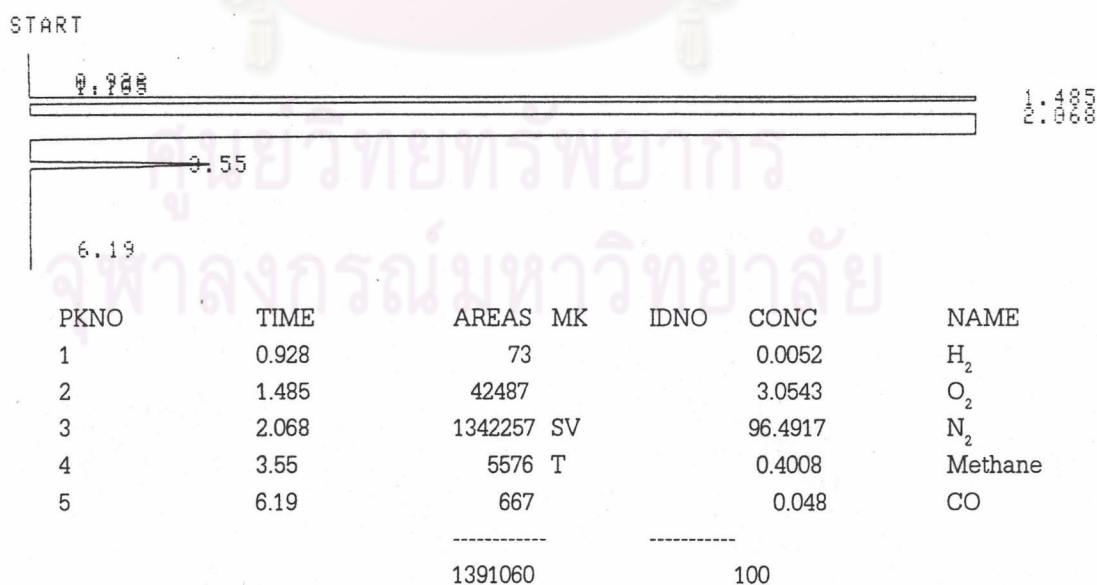


Figure A-6.3 Peaks of product from MS-5A (TCD).

From Figure A-6.4 :

VZ-10 (FID)

$$\begin{aligned}
 \text{area of CH}_4 &= 62560 \\
 \text{area of CO}_2 &= a * \text{area of CH}_4 = 0.0435 * 62560 = 2722 \\
 \text{area of CO} &= b * \text{area of CH}_4 = 0.1059 * 62560 = 6622 \\
 \text{area of C}_2\text{-C}_4 \text{ paraffin} &= 11975 \\
 \text{area of C}_2^- &= 521668 \\
 \text{area of C}_3^- &= 230269 \\
 \text{area of C}_4^- &= 62374 \\
 \text{area of C}_1\text{-C}_4 \text{ (paraffin, olefin)+CO}_2\text{+CO} &= 888846+2722+6622 \\
 &= 898190
 \end{aligned}$$

From Figure A-6.5 :

Silicon OV-1 (FID)

determine all of hydrocarbon area into 3 parts

$$\begin{aligned}
 \text{first part are the area of C}_1\text{-C}_4 \text{ (p,o)+CO}_2\text{+CO+MeOH + DME} &= 292371 \\
 \text{second part are the area of C}_5^+ &= 2337 \\
 \text{third part are the area of aromatics} &= 831
 \end{aligned}$$

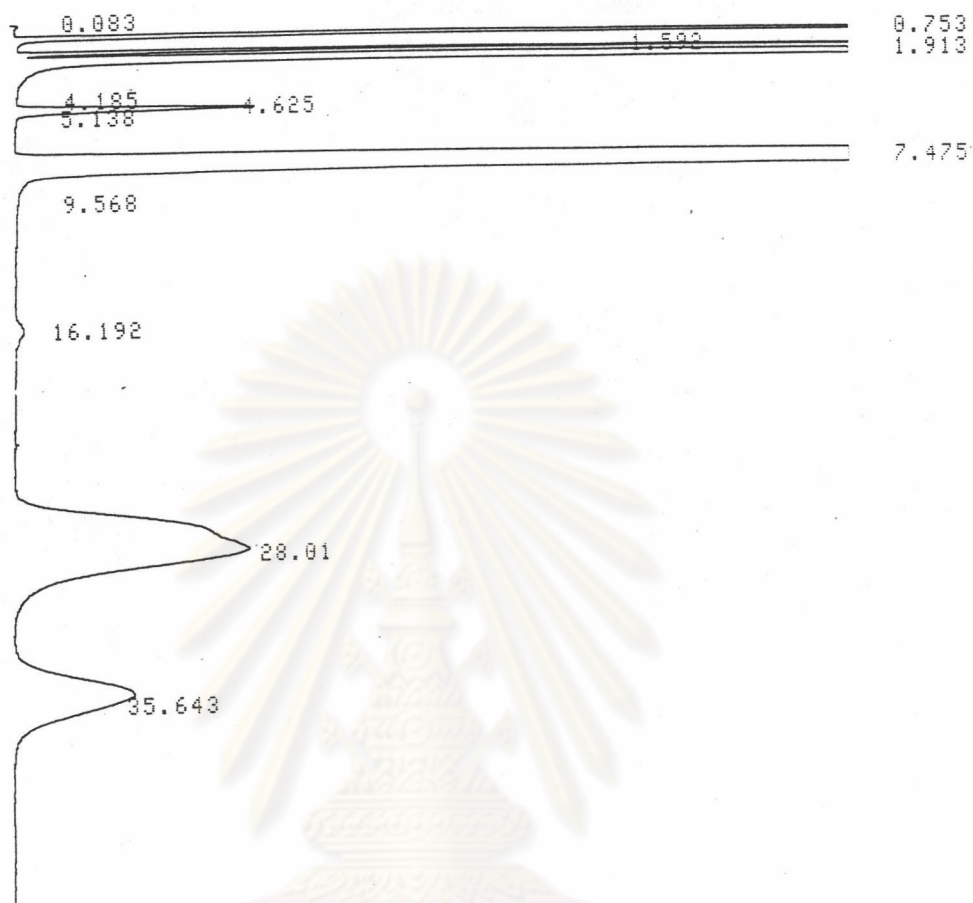
So that : compared the area from VZ-10 to the area of OV-1

$$\text{area of CO}_2 \text{ (OV-1)} = \frac{\text{area of CO}_2 \text{ (VZ-10)*area of C}_1\text{-C}_4 \text{ (p,o)+CO}_2\text{+CO(OV-1)}}{\text{area of C}_1\text{-C}_4 \text{ (p,o)+CO}_2\text{+CO(VZ-10)}}$$

$$= (2722 * 292371)/898190 = 886$$

where p = paraffin; o = olefin

START



PKNO	TIME	AREAS	MK	IDNO	CONC	NAME
1	0.083	42			0.0047	
2	0.753	62560			7.038	CH ₄
3	1.592	6762			0.7607	C ₂ H ₆
4	1.913	521668	SV		58.6877	C ₂ H ₄
5	4.625	4649	SV		0.5231	C ₃ H ₈
6	7.475	230269	S		25.9053	C ₃ H ₆
7	16.192	564			0.0635	C ₄ H ₁₀
8	28.01	44398			4.9948	C ₄ H ₈
9	35.643	17976			2.0223	C ₄ H ₈

888888

100

Figure A-6.4 Peaks of product from VZ-10 (FID).

START



Figure A-6.5 Peaks of product from OV-1 (FID).

PKNO	TIME	AREAS MK	IDNO	CONC	NAME
1	2.95	128156		43.3635	
2	2.993	124166 V		42.0134	
3	3.253	28298 V		9.5752	
4	3.478	429 V		0.1451	C ₁ -C ₄ +CO ₂ +CO
5	3.738	3575 V		1.2096	
6	3.842	1509 V		0.5107	
7	3.963	6238 V		2.1107	

8	4.123	76 V		0.0259	
9	4.415	126		0.0427	
10	4.613	283 V		0.0958	
11	4.947	368		0.1246	C ₅ ⁺
12	5.357	623 V		0.2108	
13	5.415	404 V		0.1366	
14	5.687	319 V		0.1081	
15	5.983	138 V		0.0468	

16	6.092	49 V		0.0167	
17	6.198	26 V		0.0087	
18	6.567	200		0.0676	
19	7.053	22		0.0076	
20	7.558	18		0.006	
21	8.8	52		0.0178	
22	8.883	45 V		0.0151	
23	9.44	48		0.0163	
24	11.05	40		0.0135	
25	12.125	98		0.0332	Aromatics
26	12.3	46 V		0.0156	
27	12.983	27		0.009	
28	14.95	13		0.0045	
29	15.698	31		0.0106	
30	18.625	48		0.0161	
31	19.758	15		0.0051	
32	24.697	18		0.0062	
33	25.85	14		0.0047	
34	31.873	20		0.0066	

				295539	100

Figure A-6.5 Continue.

The others were calculated as same as CO_2 .

$$\begin{aligned} \text{CO} &= 2156 \\ \text{C}_1 &= 20364 \\ \text{C}_2\text{-C}_4(\text{p}) &= 3898 \\ \text{C}_2^= &= 169809 \\ \text{C}_3^= &= 74955 \\ \text{C}_4^= &= 20303 \end{aligned}$$

For MeOH and DME were calculated as below.

$$\begin{aligned} \text{Factor : area of MeOH in Porapak Q related with in OV-1} &= 1.7 \cdot 10^{-7} \\ \text{area of MeOH} &= \text{area of MeOH (Porapak Q)} \cdot \text{area of C}_1\text{-C}_4(\text{OV-1}) \cdot 1.7 \cdot 10^{-7} \\ &= 0 \end{aligned}$$

$$\begin{aligned} \text{Factor : area of DME in Porapak Q related with in OV-1} &= 4.47 \cdot 10^{-7} \\ \text{area of DME} &= \text{area of DME (Porapak Q)} \cdot \text{area of C}_1\text{-C}_4(\text{OV-1}) \cdot 4.47 \cdot 10^{-7} \\ &= 0 \end{aligned}$$

Hence : Hydrocarbon Distribution (C-wt.%)

$$\begin{aligned} \text{C}_1 &= (\text{area of C}_1 \cdot 100) / [(\text{total area of OV-1}) - (\text{CO}_2 + \text{CO} + \text{MeOH} + \text{DME})] \\ &= 20364 \cdot 100 / 292497 = 6.97 \% \\ \text{C}_2\text{-C}_4(\text{p}) &= 3898 \cdot 100 / 292497 = 1.33 \% \\ \text{C}_2^= &= 169809 \cdot 100 / 292497 = 58.05 \% \\ \text{C}_3^= &= 74955 \cdot 100 / 292497 = 25.63 \% \\ \text{C}_4^= &= 20303 \cdot 100 / 292497 = 6.94 \% \\ \text{C}_5^+ &= 2337 \cdot 100 / 292497 = 0.80 \% \\ \text{aromatics} &= 831 \cdot 100 / 292497 = 0.28 \% \\ \text{MeOH conv.} &= \frac{(\text{area of MeOH feed} - \text{area of MeOH rested}) \cdot 100}{\text{area of MeOH feed}} \\ &= \frac{(459074 - 0) \cdot 100}{459074} = 100 \% \end{aligned}$$

$$\begin{aligned} \text{DME} &= \text{area of DME} / [\text{total area of (OV-1)-(CO}_2\text{+CO+MeOH)}] \\ &= 0/2924297 = 0 \end{aligned}$$



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APPENDIX B

CURVES FOR VAPOUR FEED

B-1 Vapour Pressure Curve of Methanol at Various Temperature

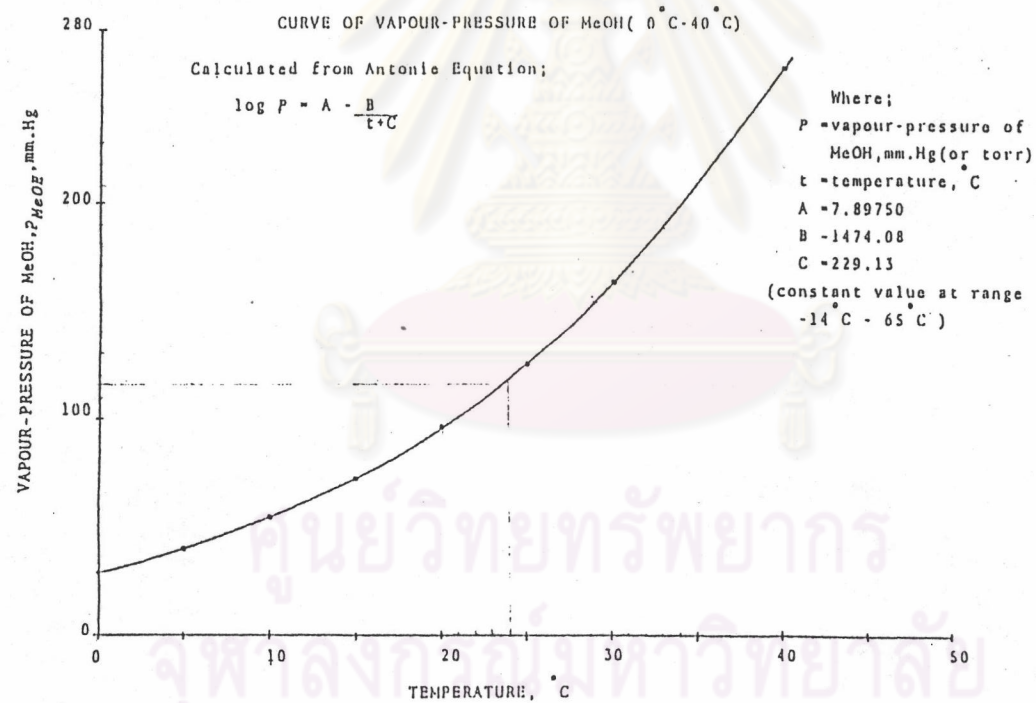


Figure B-1 Curve of vapour pressure of MeOH related to temperature

B-2 Curve of H₂O and MeOH Ratio Composition at Various Temperature of Water-bath.

Checked by used GC(TCD) at conditions : temperature of column 90 °C
temperature of detector 100 °C

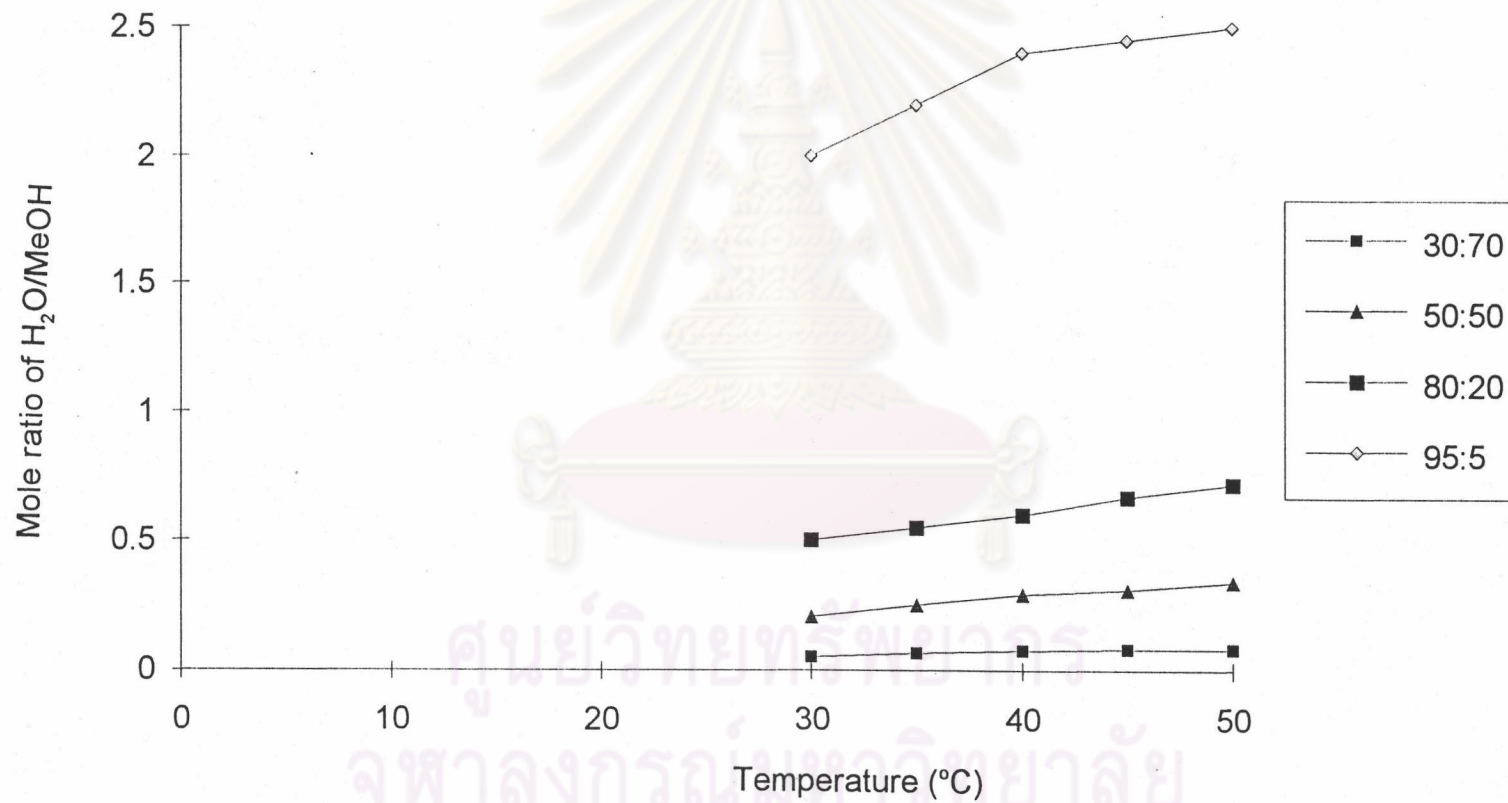


Figure B-2 Calibration curve for mole ratio of water/methanol in vapour phase related to temperature of water-bath at various water/methanol ratio by volume.

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VITA

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