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APPENDIX A

A-1   CALCULATION OF Si/Al ATOMIC RATIO FOR ZSM-5 PREPARATION

The calculation is based on weight of Sodium Silicate $(Na_2O.SiO_2.H_2O)$ in B1 and B2 solutions.

M.W. of Si   =   28.0855

M.W. of SiO_2 =   60.0843

Weight percent of SiO_2 in Sodium Silicate   =   28.5

M.W. of Al   =   26.9815

M.W. of $AlCl_3$ =   133.3405

Weight percent purity of $AlCl_3$ =   97

For example, to prepare ZSM-5 at Si/Al atomic ratio of 50. Using Sodium Silicate 69 g with 45 g of water as a B1 solution.

$$\text{mole of Si used} = wt. * \frac{(\%)}{100} * \frac{(M.W. \text{ of } Si)}{(M.W. \text{ of } SiO_2)} * \frac{(1 \text{ mole})}{(M.W. \text{ of } Si)} \quad (A-1.1)$$

$$= 69 * (28.5/100) * (1/60.0843)$$

$$= 0.327 \text{ mole}$$

Si/Al atomic ratio = 50

mole of $AlCl_3$ required = $0.3273/50$ = $6.5458*10^{-3}$ mole

amount of $AlCl_3$ = $6.5458*10^{-3}*133.34*(100/97)$

                             = 0.8998 g

This is the amount of $AlCl_3$ used in A1 and A2 solutions (see Table 4.1).

A-2 CALCULATION OF METAL ION-EXCHANGED H-ZSM-5

Determine the amount of Pt into catalyst = 0.50 wt.%

The catalyst use = x g

So that : from the equation

$$Pt/(x+Pt) \quad = \quad 0.5/100 \qquad \text{(A-2.1)}$$

$$100*Pt \quad = \quad 0.5*(x+Pt)$$

$$(100-0.5)*Pt \quad = \quad 0.5*x$$

thus $\qquad Pt \quad = \quad 0.5*x/(100-0.5) \quad$ g

use $Pt(NH_3)_4Cl_2.H_2O$ (M.W. 352.13, 55% Pt)

weight of $Pt(NH_3)_4Cl_2.H_2O$ = [0.5*x/(100-0.5)]*[100/55] g

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A-3   CALCULATION OF REACTION FLOW RATE

The catalyst used = 0.2100 g

packed catalyst into quartz reactor (Φ = 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}

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

$$\text{Volumetric flow rate} = 2,000*\text{Volume of catalyst}$$
$$= 2,000*\pi*(0.3)^2*x \text{ cc/h}$$
$$= 2,000*\pi*(0.3)^2*x/60 \text{ cc/min}$$

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

where : t = room temperature, $^\circ$C

A-4 CALCULATION OF PRODUCT DISTRIBUTION OF MTG REACTION

Sample : 0.10%Re-0.50%Pt/H-ZSM-5

Reaction condition : Reaction temperature 400°C, GHSV = 2,000 h^{-1},

time on stream 1 h

From Figure A-4.1 :

Porapak Q (TCD)

(ratio of CH_4:CO_2 = 1 : 1.35; this value for each G.C.)

area of CH_4 = 1130 = 1130/1 = 1130

area of CO_2 = 940 = 940/1.35 = 696

CO_2 = CH_4 * a

a = CO_2/CH_4 = 696/1130 = 0.6159

From Figure A-4.2 :

MS-5A (TCD)

(ratio of CH_4 : CO = 1 : 1.13)

area of CH_4 = 1067 = 1067/1 = 1067

area of CO = 0 = 0/1.13 = 0

CO = CH_4 * b

b = CO/CH_4 = 0/1067 = 0

From Figure A-4.3 :

VZ-10 (FID)

area of CH_4 = 9391

area of CO_2 = a * area of CH_4 = 0.6157 * 9391 = 5782

area of CO = b * area of CH_4 = 0 * 9391 = 0

STOP
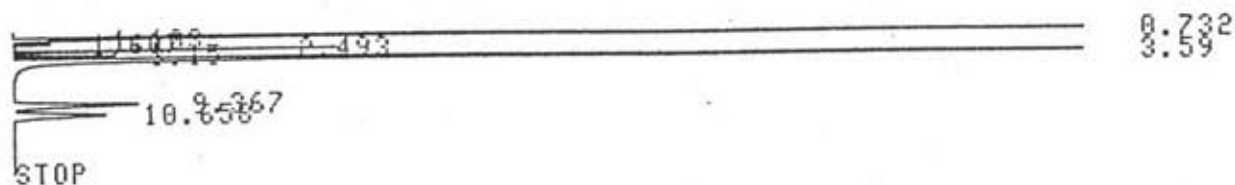
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.732	1725741	S		90.192	
2	1.103	1130	T		0.0591	CH_4
3	1.607	940			0.0491	CO_2
4	2.493	10610			0.5545	
5	3.15	4055			0.2119	
6	3.59	143992			7.5254	
7	9.367	14502			0.7579	
8	10.658	12439			0.6501	
	TOTAL	1913408			100	

Figure A-4.1   Peaks of product from Porapak Q (TCD)

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.857	19533			1.2605	
2	1.248	175050	SV		11.296	O_2
3	1.562	3126	T		0.2017	
4	1.758	1345833	V		86.8469	
5	3.298	1067			0.0688	CH_4
6	4.258	3107			0.2005	
7	5.24	1947	V		0.1256	
	TOTAL	1549662			100	

Figure A-4.2   Peaks of product from MS-5A (TCD)

area of C_2-C_4 paraffin = 344486

area of $C_2^=$ = 72174

area of $C_3^=$ = 114732

area of $C_4^=$ = 169835

area of C_1-C_4(paraffin, olefin)+Co_2+CO = 710617+9391+5782+0

= 725790

From Figure A-4.4

Silicon OV-1 (FID)

determine all of hydrocarbon area into 3 parts

first part are the area of C_1-C_4(p,o)+CO_2+CO = 69566

second part are the area of C_5^+ = 20601

third part are the area of aromatics = 28150

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

area of CO_2(OV-1) = $\dfrac{\text{area of } CO_2(\text{VZ-10}) * \text{area of } C_1\text{-}C_4(p,o) + CO_2 + CO(\text{OV-1})}{\text{area of } C_1\text{-}C_4(p,o) + CO_2 + CO(\text{VZ-10})}$

= (5782 * 69566)/725790 = 554

where p = paraffin; o = olefin

The same calculation of CO_2

CO = 0

C_1 = 900

C_2-C_4(p) = 33018

$C_2^=$ = 6918

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.83	9391			1.3091	C_1
2	1.685	26102			3.6388	C_2
3	2.033	72174	V		10.0615	$C_2^=$
4	4.545	93601			13.0486	C_3
5	7.115	114732			15.9943	$C_3^=$
6	12.42	194425			27.1039	$i-C_4$
7	14.783	30358	V		4.2321	$n-C_4$
8	25.567	62223			8.6743	
9	30.765	12493	V		1.7416	$C_4^=$
10	42.527	95119			13.2601	
11	51.065	6712	V		0.9357	
TOTAL		717329			100	

Figure A-4.3   Peaks of product from VZ-10 (FID)
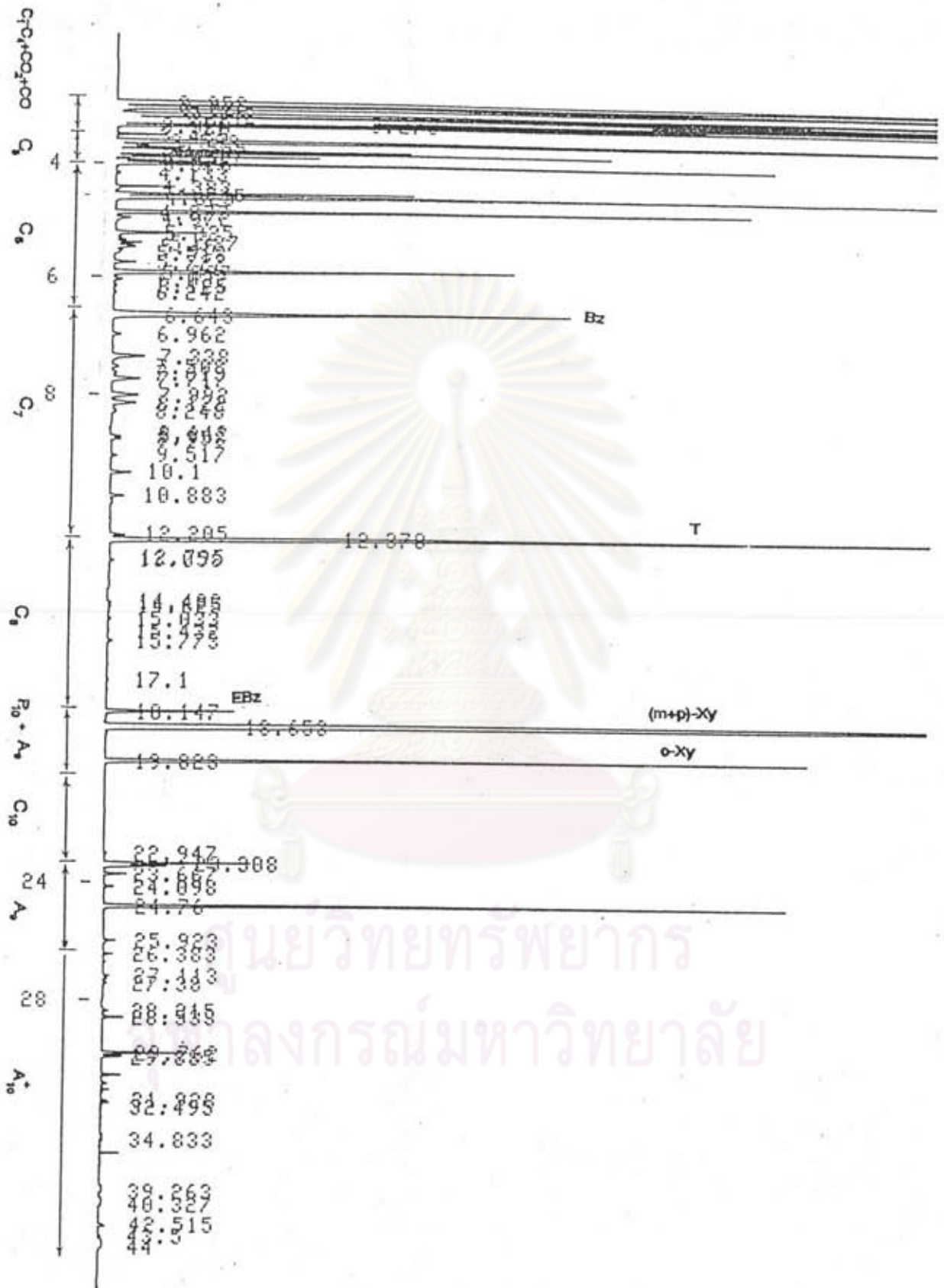
Figure A-4.4   Peaks of product from Silicon OV-1 (FID)

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	2.952	12268			10.3688	
2	3.025	23588	V		19.9364	
3	3.142	22113	V		18.6892	
4	3.207	8589	V		7.2595	$C_1C_4+CO_2+CO$
5	3.273	1586	V		1.3403	
6	3.328	1356	V		1.1464	
7	3.485	66			0.0555	
8	3.593	10086			8.5242	
9	3.787	1343	V		1.135	
10	3.852	306			0.2582	
11	3.975	1203			1.0166	
12	4.383	121			0.1023	
13	4.545	667			0.5641	
14	4.625	3260	V		2.7549	
15	4.877	1330			1.1239	
16	5.225	223			0.1885	C_5^+
17	5.387	75	V		0.0634	
18	5.45	63	V		0.0531	
19	5.722	59			0.0499	
20	5.897	1050			0.8879	
21	6.643	1510			1.2766	Benzene
22	7.338	131			0.1105	
23	7.717	104			0.088	
24	7.992	107			0.0904	
25	8.122	94			0.0797	
26	10.1	116			0.0983	
27	10.883	76			0.0641	
28	12.205	84			0.0708	
29	12.378	6657	V		5.6264	Toluene
30	18.147	598			0.5055	
31	18.653	1.1477			9.7003 }	Xylene
32	19.823	3040			2.5694 ⌡	
33	23.308	880			0.7438	
34	23.667	101			0.0855	
35	24.76	2808			2.3731	
36	25.923	58			0.0493	
37	28.533	91			0.0765	Aromatics
38	29.762	332			0.2803	
39	29.885	71			0.0597	
40	34.833	75			0.0638	
41	39.263	106			0.0896	
42	40.327	119			0.1003	
43	42.515	96			0.0809	
44	44	236			0.1992	
TOTAL		118317			100	

Figure A-4.4 Continue.

$$C_3^= \quad = \quad 10997$$

$$C_4^= \quad = \quad 16278$$

Hence : Product Distribution (C-wt.%)

$$C_1 \quad = \quad (\text{area of } C_1 * 100)/\text{total area of OV-1}$$

$$= \quad 900*100/118317 \quad = \quad 0.76 \%$$

$$C_2\text{-}C_4(p) \quad = \quad 33018*100/118317 \quad = \quad 27.91 \%$$

$$C_2^= \quad = \quad 6918*100/118317 \quad = \quad 5.85 \%$$

$$C_3^= \quad = \quad 10997*100/118317 \quad = \quad 9.29 \%$$

$$C_4^= \quad = \quad 16278*100/118317 \quad = \quad 13.76 \%$$

$$C_5^+ \quad = \quad 20601*100/118317 \quad = \quad 17.41 \%$$

$$\text{aromatics} \quad = \quad 28150*100/118317 \quad = \quad 23.79 \%$$

$$CO_2 \quad = \quad 554*100/118317 \quad = \quad 0.47 \%$$

$$CO \quad = \quad 0*100/118317 \quad = \quad 0.00 \%$$

$$\text{Benzene} \quad = \quad 1510*100/118317 \quad = \quad 1.28 \%$$

$$\text{Toluene} \quad = \quad 6657*100/118317 \quad = \quad 5.63 \%$$

$$\text{Xylene} \quad = \quad 14517*100/118317 \quad = \quad 12.27 \%$$

A-5 BET SURFACE AREA CALCULATION

From BET equation :

$$\frac{x}{v(1-x)} = \frac{1}{v_m C} + \frac{C-1}{V_m C} * x \qquad (A-5.1)$$

where : x = ratio of partial pressure P/P_o

P_o = saturated vapour pressure of N_2

(or adsorped 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 = $\exp(E_1-E_2/RT)$ \qquad (A-5.2)

where : E_1 = heat of adsorption of the first layer

E_2 = heat of condensation of adsorbed gas

assume $C \longrightarrow \infty$, then

$$\frac{x}{v(1-x)} = \frac{1}{v_m C} * x \qquad (A-5.3)$$

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.

$x = P/P_O$

$$\frac{P_b V}{273} = \frac{P_t V}{T} \qquad (A-5.4)$$

where : $V =$ constant volume

$P_b =$ pressure at 0^oC

$P_t =$ pressure at t^oC

$T = 273.15 + t, K$
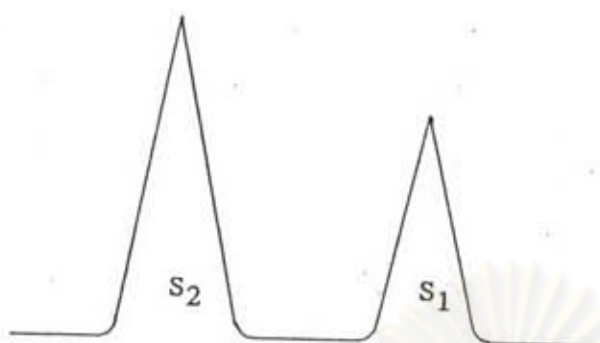
$P_b = (273.15/T)*P_t = 1$ atm

partial pressure

$$P = \frac{[\text{Flow of } (He+N_2) - \text{ Flow of He}] * P_b}{\text{Flow of } (He+N_2)} \qquad (A-5.5)$$

$= 0.3$ atm

N_2 saturated vapour pressure, $P_O = 1.1$ atm $= 836$ mm.Hg

$x = P/P_O = P/1.1$

How to measuring v

1 ml/1 atm at room temperature

desorption N_2 calibration
of N_2 area   area

$$v = \frac{S_2}{S_1} * \frac{1}{w} * \frac{273.15}{T} \quad \text{c.c./g of catalyst} \qquad (A-5.6)$$

where :   w = weight of sample

$$v_m' = \frac{v[1-(\text{flow of He}+N_2 - \text{flow of He})/1.1]}{\text{flow of He}+N_2} \qquad (A-5.7)$$
c.c.NTP/g of catalyst

$$S_b = S * v_m' \qquad (A-5.8)$$

where :   S = surface area from literature of N_2

= 4.373 m^2/c.c. of N_2

so that : S_b = 4.373 v_m' m^2/g of catalyst

A-6   TPD CALCULATION
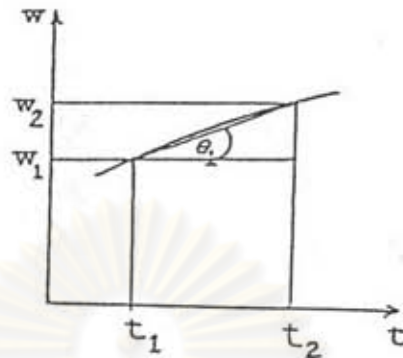
Figure A-6.1 Plot of weight loss vs. time

From Figure A-6.1 :

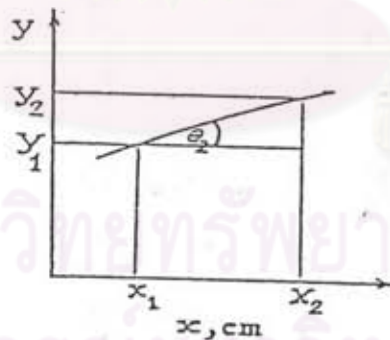$$(\Delta w/\Delta t) = (w_2-w_1)/(t_2-t_1) + \tan \theta_1 \qquad (A-6.1)$$

Figure A-6.2 Plot of full scale chart relating weight loss to speed chart which is related to time.

From Figure A-6.2 :

The recorder condition was adjust follows:

$$25 \quad cm \quad = \quad a \quad mg$$

$$y_1 \quad cm \quad = \quad (a*y_1)/25 \quad mg$$

$$\text{and } y_2 \quad cm \quad = \quad (a*y_2)/25 \quad mg$$

$$\text{chart speed} \quad b \quad cm \quad = \quad 60 \quad sec$$

$$x_1 \quad cm \quad = \quad (60*x_1)/b \quad sec$$

$$x_2 \quad cm \quad = \quad (60*x_2)/b \quad sec$$

$$dw/dt \quad = \quad \frac{(a/25)*(y_2-y_1)}{(60/b)*(x_2-x_1)} \quad = \quad \frac{ab}{(25*60)} \tan \theta \qquad (A-6.2)$$

For TPD curve plot between $(dw/dt)/w_o$ vs. temperature

where : w = dry weight of catalyst and calculated as follows
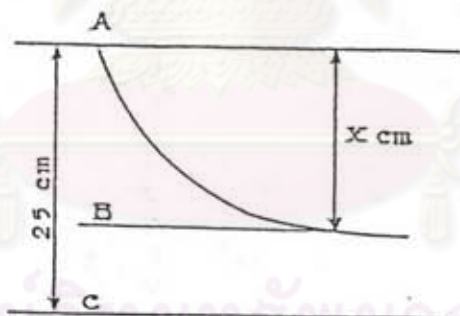
we set full chart scale = a mg

at A position weight of catalyst = a mg

   B position weight of catalyst = ax/25 mg

$$\text{weight loss} \quad = \quad ax/25 \quad mg \qquad (A-6.3)$$

dry wt. of catalyst = wt. of sample before drying - wt. loss (A-6.4)

A-7   CALCULATION FOR PERCENTAGE OF MeOH CONVERSION

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

Volume of syringe = 2 ml

hence,

Volume of MeOH in 2 ml of sample = $2*10^{-3}*Y$ l   (A-7.1)

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

for example, Y = 20% MeOH

then,   volume of MeOH in syringe   = $2*10^{-3}*0.2$ l

                                        = 0.0004   l

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

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

MeOH (at STP) 22.4 l compose with C = 12 g

MeOH (at STP) V_1 l compose with C = $(12/22.4)*V_1$ g (A-7.2)

From the equation of state,

$$(P_1V_1)/T_1 = (P_2V_2)/T_2 \qquad\qquad (A-7.3)$$

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 :

$$V_1 = (V_2/T_2)*T_1 \qquad (A-7.4)$$

Substituted (A-7.4) into (A-7.2) and absolute temperature $(T_1) = 273.15$ K, gives

$$C_{MeOH,i} = 12/22.4)*(V_2*273.15)/(273.15+t) \qquad (A-7.5)$$

where : $C_{MeOH,i}$ = 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

$$C_{MeOH,o} = 8.085*10^{-4}*ITG_{MeOH}*10^{-6}*273.15/(273.15+95)*12/22.4 \quad g$$
$$(A-7.6)$$

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

then,

% MeOH conversion = $(2*10^{-3}*Y)-8.085*10^{-10}*ITG_{MeOH}*100/(2*10^{-3}*Y)$

$$= 100 - 8.085*10^{-5}*ITG_{MeOH}/2*Y \qquad (A-7.7)$$
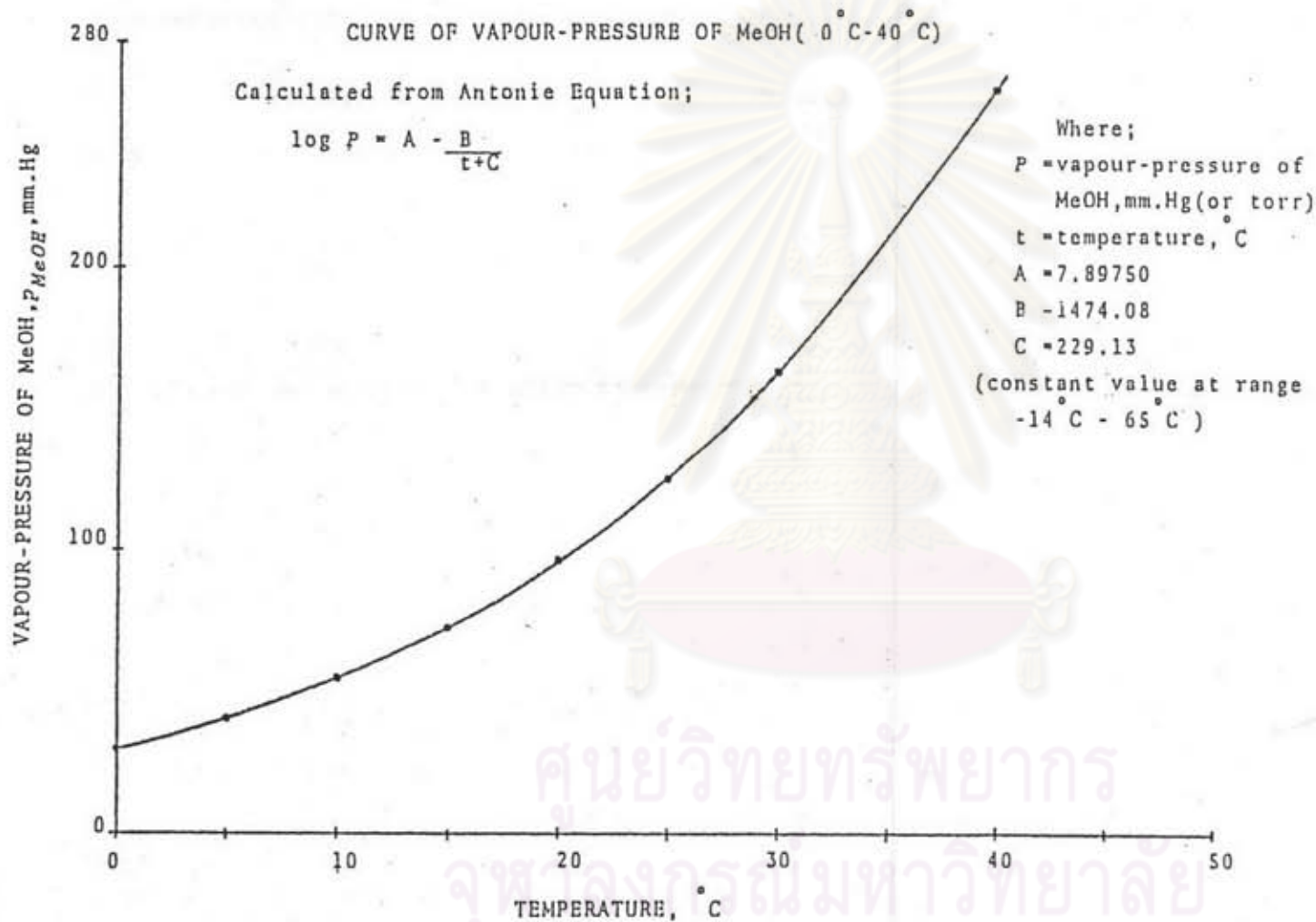
Figure B-1 Curve of vapour pressure of MeOH related to temperature.

VITA

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