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APPENDIX A

SAMPLE OF CALCULATIONS

A-1 Calculation of Si/Metal Atomic Ratio for Metallosilicates Preparation

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

Molecular Weight of Si = 28.0855

Molecular Weight of SiO_2 = 60.0843

Weight percent of SiO_2 in Sodium Silicate = 28.5

Using Sodium Silicate 69 g with 45 g of water as a B1 and B2 solution.

$$\text{Mole of Si used} = \text{wt.} \times \frac{(\%)}{100} \times \frac{(\text{M.W. of Si})}{(\text{M.W. of SiO}_2)} \times \frac{(1 \text{ mole})}{(\text{M.W. of Si})} \qquad \text{(A-1.1)}$$

$$= 69 \times (28.5/100) \times (1/60.0843)$$

$$= 0.3273 \text{ mole}$$

MFI Catalyst

For example, to prepare MFI catalyst at Si/Al atomic ratio of 40 by using $AlCl_3$ for aluminum source.

Molecular Weight of Al = 26.9815

Molecular Weight of $AlCl_3$ = 133.3405

Si/Al atomic ratio of 40

mole of $AlCl_3$ required = 0.3273/40 = 8.1825×10^{-3} mole

amount of $AlCl_3$ = $8.1825 \times 10^{-3} \times 133.3405$

= 1.0911 g

Zn-silicate and Zn,Al-silicate Catalyst

For example, to prepare Zn-silicate with Si/Zn atomic ratio of 40 by using $ZnSO_4.7H_2O$ for aluminum source.

Molecular Weight of Zn = 65.39

Molecular Weight of $ZnSO_4.7H_2O$ = 287.54

Si/Zn atomic ratio of 40

mole of $ZnSO_4.7H_2O$ required = 0.3273/40 = 8.1825×10^{-3} mole

amount of $ZnSO_4.7H_2O$ = $8.1825 \times 10^{-3} \times 287.54$

= 2.353 g

This is the amount of $AlCl_3$, $Ga_2(SO_4)_3.nH_2O$ and/or $ZnSO_4.7H_2O$ used in A1 and B1 solutions.

A-2 Calculation of Metal Ion-exchanged ZSM-5 and Metallosilicates

Platinum ion-exchange

Determine the amount of Pt into catalyst = 0.1 wt.%

The catalyst use = X g

So that : from the equation

Pt/(X + Pt) = 0.1/100

100 x Pt = 0.1 x (X + Pt)

(100 - 0.1) x Pt = 0.1 x X

thus Pt = (0.1 x X)/(100 - 0.1) g

use $Pt(NH_3)_4Cl_2.H_2O$ (Molecular Weight = 252.13, 55 % Pt)

Weight of $Pt(NH_3)_4Cl_2.H_2O$ = [0.1 x X/(100 - 0.1)] x [100/55] g

Zinc ion-exchange

Determine the amount of Zn loaded into catalyst = 0.5 wt.%

The catalyst use = X g

So that : from the equation

Zn/(X + Zn) = 0.5/100

100 x Zn = 0.5 x (X + Zn)

(100 - 0.5) x Zn = 0.5 x X

thus weight of zinc, Zn = 0.5 x X/(100 - 0.5) g

use $ZnSO_4.7H_2O$ (Molecular Weight = 287.54, 21.98 %Zn)

weight of $ZnSO_4.7H_2O$ = [0.5 x X/(100 - 0.5)] x [100/21.98] g

A-3 NH_3 Temperature programmed Desorption Calculation

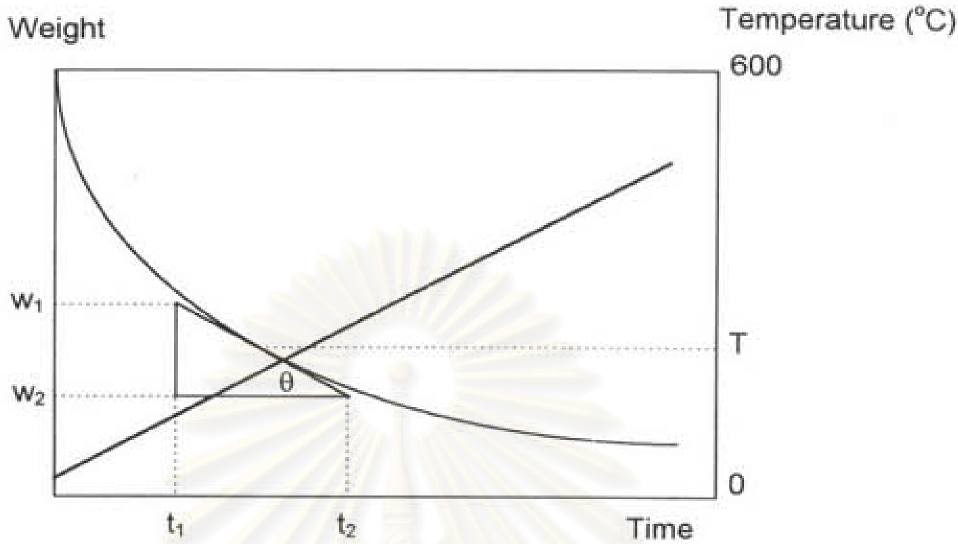


Figure A-3 Plot of weight loss and temperature versus time.

Chart speed	=	0.25 cm/min.			
Range	=	10 mg			
w	=	weight of catalyst			
w_w	=	weight of water			
w_d	=	weight of dry catalyst	=	$w - w_w$	
dw	=	10 mg x (a / 25 cm)			(A-2.1)
dt	=	60 sec x (b / 0.25 cm)			(A-2.2)
$\frac{(dw/dt)}{w_d}$	=	$\frac{(10 \text{ mg} \times 0.25 \text{ cm} \times a)/(60 \text{ sec} \times 25 \text{ cm} \times b)}{w_d}$			(A-2.3)

Plot $\frac{(dw/dt)}{w_d}$ versus temperature.

A-4 Calculation of Reaction Flow Rate.

The catalyst used = 0.5000 g

packed catalyst into quartz reactor (inside diameter = 0.6 cm)

determine the average high of catalyst bed = H cm. So that,

$$\text{Volume of bed} = \pi \times (0.3)^2 \times h \ \text{cc-cat.}$$

Used Gas Hourly Space Velocity (GHSV) = 2000 h^{-1}

$$\text{GHSV} = \frac{\text{Volumetric flow rate}^1}{\text{Volume of bed}}$$

$$\text{Volumetric flow rate}^1 = 2000 \times \text{Volume of bed}$$

$$= 2000 \times \pi \times (0.3)^2 \times H \quad \text{cc/h}$$

$$= (2000 \times \pi \times (0.3)^2 \times H)/60 \quad \text{cc/min.}$$

at STP condition :

$$\text{Volumetric flow rate} = \text{Volumetric flow rate}^1 \times (273.15 + T)/273.15$$

where T = room temperature, °C.

A-5 Calculation of Conversion and Hydrocarbon Distribution of Propane Dehydrogenation

The propane dehydrogenation activity and product distribution was evaluated as follow :

$$\text{Propane Conversion (\%)} = \frac{(\text{Propane}_{in} - \text{Propane}_{out}) \times 100}{\text{Propane}_{in}}$$

For example : NH_4-Zn,Al-silicate (Si/Zn = 100, Si/Al = 40)

Reaction condition : Reaction temperature 600 °C, GHSV = 10000 h^{-1},

feed 20 % propane N_2 balance, 1 h time on stream.

From Figure A-5.1

VZ-10 (feed)

area of feed propane = 2511332

VZ-10 (product at 1 h time on stream)

area of CH_4, C_1 = 115536

area of C_2 = 58680

area of C_2= = 201464

area of propane rested = 1197482

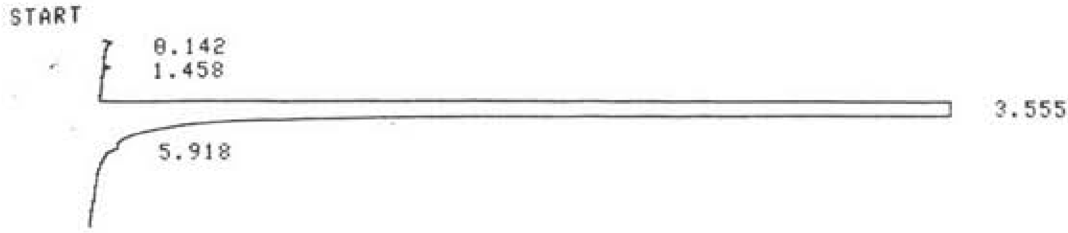
area of C_3= = 493740

area of C_4 = 823 + 1474 = 2297

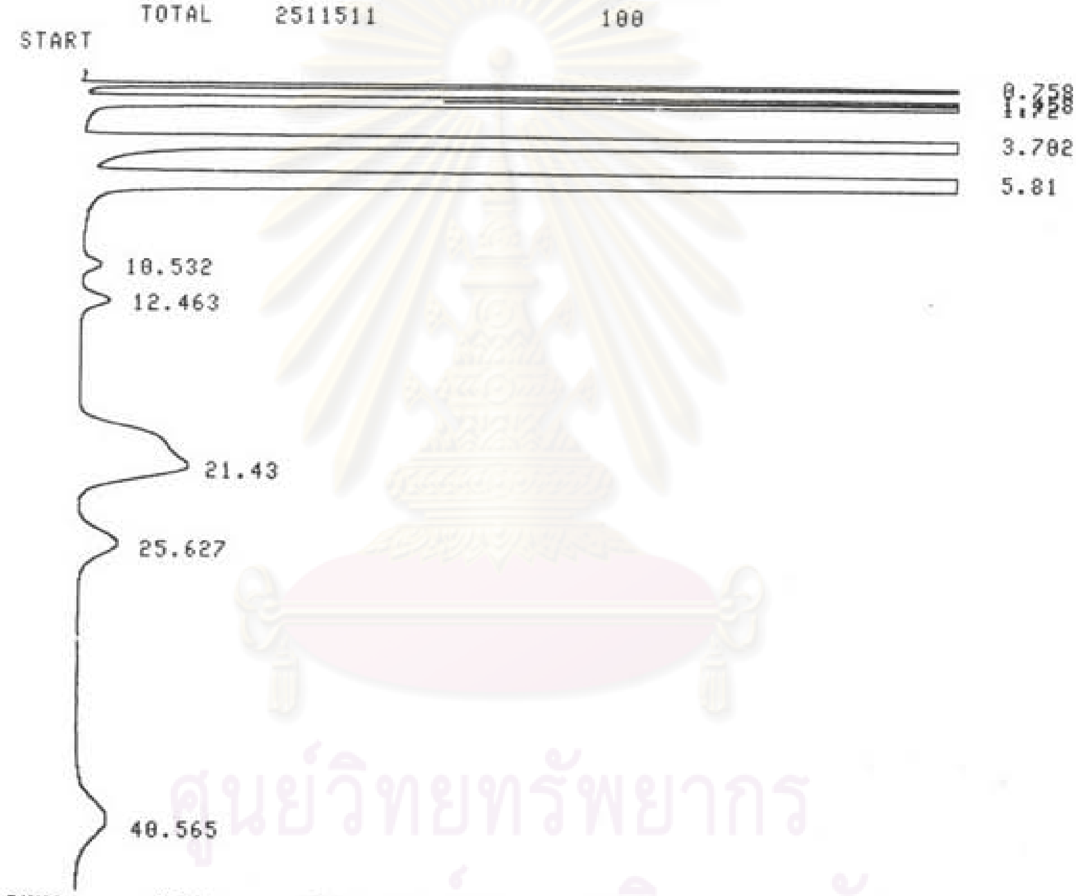
area of C_4= = 19761 + 4188 = 23949

area of C_1-C_4 = 115536+58680+201464+1197482+493740+2297+23949

= 2093148



PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.142	58			0.002	
2	1.458	55			0.0022	
3	3.555	2511332	S		99.9929	Propane
4	5.918	75	T		0.003	
	TOTAL	2511511			100	



PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.758	115536			5.5068	Methane
2	1.458	58680	V		2.7969	Ethane
3	1.72	201464	V		9.6025	Ethylene
4	3.702	1197482			57.076	Propane
5	5.81	493740	V		23.5333	Propylene
6	10.532	823			0.0392	Butane
7	12.463	1474			0.0703	Butane
8	21.43	19761			0.9419	Butene
9	25.627	4188			0.1996	Butene
10	40.565	4899			0.2335	
	TOTAL	2098046			100	

From Figure A-5.2

Silicon OV-1 (1 h)

determine all of hydrocarbon area into 3 parts

first part are the area of C_1-C_4 = 1299380

second part are the area of C_5+ = 2217

third part are the area of aromatics = 365475

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

$$\text{area of } C_1 \text{ (OV-1)} = \frac{\text{area of } C_1\text{(VZ-10) x area of } C_1\text{-}C_4\text{(OV-1)}}{\text{area of } C_1\text{-}C_4 \text{ (VZ-10)}}$$

$$= \frac{115536 \times 1299380}{2093148}$$

$$= 71722$$

The other were caculated as same as C_1

area of C_2 (OV-1) = 36427

area of C_2= (OV-1) = 125064

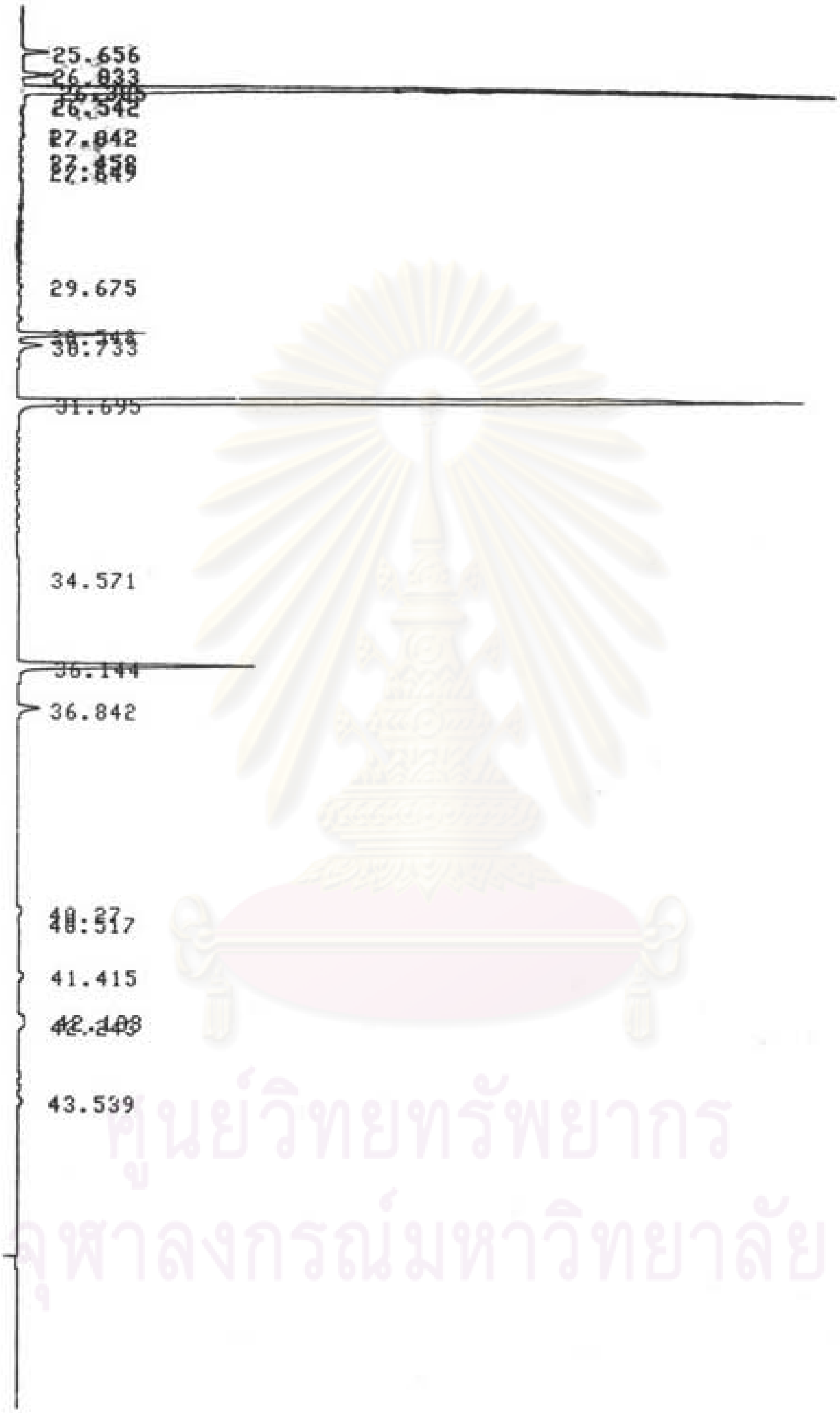
area of C_3 (OV-1) = 743370

area of C_3= (OV-1) = 306503

area of C_4 (OV-1) = 1426

area of C_4= (OV-1) = 14867


1.955
4.725
5.856
6.185
11.200
17.946
20.981
21.942
22.475
22.854
23.689
24.267


25.656
26.542
27.842
29.675
30.733
31.695
34.571
36.144
36.842
40.517
41.415
43.539

CHROMATOGRAM 1 MEMORIZED

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.042	238			0.0143	
2	1.955	24			0.0015	
3	3.09	1276947			76.5863	
4	3.26	19642	SV		1.178	
5	3.481	62	T		0.0037	C_1-C_4
6	3.587	75	T		0.0045	
7	3.698	296	TV		0.0178	
8	3.789	1108	TV		0.0664	
9	3.916	1250	TV		0.075	
10	4.041	1738	V		0.1042	
11	4.258	108	V		0.0065	
12	4.397	111	V		0.0067	
13	4.725	15			0.0009	
14	5.056	21			0.0013	C_5+
15	5.35	25			0.0015	
16	5.493	15			0.0009	
17	5.7	137	V		0.0082	
18	5.775	47	V		0.0028	
19	6.185	197444			11.8419	
20	6.481	79	V		0.0048	
21	6.625	23	V		0.0014	
22	11.288	120942			7.2536	
23	17.108	26			0.0015	
24	17.386	2160	V		0.1295	
25	17.946	23916	V		1.4344	
26	18.924	3614			0.2168	
27	19.171	5236	V		0.3141	
28	20.981	60			0.0036	
29	21.942	23			0.0014	
30	22.475	128			0.0077	
31	22.854	309			0.0185	
32	23.689	109			0.0065	
33	24.267	427			0.0256	
34	24.364	603	V		0.0362	
35	25.656	127			0.0076	
36	26.033	150	V		0.009	Aromatics
37	26.305	4537			0.2721	
38	26.542	20	V		0.0012	
39	27.042	20			0.0012	
40	27.458	18			0.0011	
41	27.649	15	V		0.0009	
42	29.675	25			0.0015	
43	30.548	508			0.0305	
44	30.733	152	V		0.0091	
45	31.695	3156			0.1893	
46	34.571	16			0.0009	
47	36.144	1223			0.0734	
48	36.042	131			0.0079	
49	40.27	41			0.0025	
50	40.517	14	V		0.0008	
51	41.415	51			0.0031	
52	42.108	54			0.0032	
53	42.243	69	V		0.0041	
54	43.539	49			0.0029	
	TOTAL	1667333			100	

For Flame Ionization Detector

$$\text{Normalized Weight percent} = \frac{\text{Peak area}}{\text{Relative sensitivity}}$$

Compound	Peak area,A	Relative sensitivity,R	A/R
methane	71722	0.97	73940
ethane	36427	0.97	37554
ethylene	125064	1.02	122612
propane	743370	0.98	758541
propylene	306503	1.04	294714
butane	1426	1.09	1308
butene	14867	1.05	14159
C_5+	2217	1.00	2217
benzene	197444	1.12	176289
Toluene	120942	1.07	113030
other aromatics	47089	1.00	47089
		Total area	1641453

Hence : Product distribution (wt.%)

C_1 = [area C_1) x 100]/[total area - area of C_3]

= (73940 x 100) / (1641453 - 758541)

= 7.76 %

C_2 = 3.94 %

C_2= = 13.54 %

C_3= = 33.18 %

C_4 = 0.15 %

$C_4=$ = 1.61 %

C_5+ = 0.24 %

aromatics = 39.57 %

$$\text{Propane conversion} = \frac{(2511332 - 1197482)}{2511332} \times 100$$

$$= 52.32\ \%$$

A-6 Response Factors for Gas Chromatographic analysis

Table I Relative sensitivity data for Flame Ionization Detector

Compound	Relative Sensitivity	Compound	Relative Sensitivity
Normal Paraffins		3,3-Dimethylheptane	1.00
Methane	0.97	2,4-Dimethyl-3-ethylpentane	0.99
Ethane	0.97	2,2,3-Trimethylhexane	1.01
Propane	0.98	2,2,4-Trimethylhexane	0.99
Butane	1.09	2,2,5-Trimethylhexane	0.99
Pentane	1.04	2,3,3-Trimethylhexane	1.00
Hexane	1.03	2,3,5-Trimethylhexane	0.96
Octane	1.00	2,4,4-Trimethylhexane	1.01
Nonane	0.97	2,2,3,3-Tetramethylpentane	1.00
Branched Paraffins	0.98	2,2.3,4-Tetramethylpentane	0.99
Isopentane	1.05	2,3,3,4-Tetramethylpentane	0.99
2,2-Dimethybutane	1.04	3,3,5-Trimethylheptane	0.99
2,3-Dimethybutane	1.03	2,2,3,4-Tetramethylhexane	1.01
2-Methylpentane	1.05	2,2,4,5-Tetramethylhexane	1.00
3-Methylpentane	1.04	Cyclopentanes	
2-Methylhexane	1.02	Cyclopentane	1.04
3-Methylhexane	1.02	Methylcyclopentane	1.01
2,2-Dimethylpentane	1.02	Ethylcyclopentane	1.00
2,3-Dimethylpentane	0.99	1,1-Dimethylcyclopentane	1.03
2,4-Dimethylpentane	1.02	T-1,2-Dimethylcyclopentane	1.01
3,3-Dimethylpentane	1.03	C-1,2-Dimethylcyclopentane	1.00
3-Ethylpentane	1.02	T-1,3-Dimethylcyclopentane	1.00
2,2,3-Trimethylbutane	1.02	C-1,3-Dimethylcyclopentane	1.00
2-Methylheptane	0.97	1MT2-Ethylcyclopentane	1.01
3-Methylheptane	1.01	1MC2-Ethylcyclopentane	1.00
4-Methylheptane	1.02	1MT3-Ethylcyclopentane	0.97
2,2-Dimethylhexane	1.01	1MC3-Ethylcyclopentane	1.00
2,3-Dimethylhexane	0.99	1,1,2-Trimethylcyclopentane	1.03
2,4-Dimethylhexane	0.99	1,1,3-Trimethylcyclopentane	1.04
2,5-Dimethylhexane	1.01	T-1,2C3-Trimethylcyclopentane	1.00
3,4-Dimethylhexane	0.99	T-1,2C4-Trimethylcyclopentane	0.98
3-Ethylhexane	1.00	C-1,2T3-Trimethylcyclopentane	0.98
2-Methyl-3-ethylpentane	0.98	C-1,2T4-Trimethylcyclopentane	0.99
2,2,3-Trimethylpentane	1.02	Isopropycyclopentane	0.98
2,2,4-Trimethylpentane	1.00	n-Propylcyclopentane	0.97
2,3,3-Trimethylpentane	1.01	Cyclohexanes	
2,3,4-Trimethylpentane	0.99	Cyclohexane	1.01
2,2-Dimethylheptane	0.97	Methylcyclohexane	1.01

Table I Relative sensitivity data for Flame Ionization Detector (continued)

Compound	Relative Sensitivity	Compound	Relative Sensitivity
Ethylcyclohexane	1.01	Isopropanol	0.53
1,1-Dimethylcyclohexane	1.03	n-Butanol	0.66
T-1,2-Dimethylcyclohexane	1.01	Isobutnol	0.68
C-1,2-Dimethylcyclohexane	0.99	sec.-Butanol	0.63
T-1,4-Dimethylcyclohexane	0.99	tert.-Butanol	0.74
1MT4-Ethylcyclohexane	0.98	Amyl alcohol	0.71
1MC4-Ethylcyclohexane	0.96	Methylisobutylcarbinol	0.74
1,1,2-Trimethylcyclohexane	1.01	Methylamyl alcohol	0.65
Isopropylcyclohexane	0.98	Hexyl alcohol	0.74
Cycloheptane	1.01	Octyl alcohol	0.85
Aromatics		Decyl alcohol	0.84
Benzene	1.12	Pentoxol	0.60
Toluene	1.07	Aldehydes	
Ethylbenzene	1.03	Butyraldehyde	0.62
para-Xylene	1.00	Heptanoic aldehyde	0.77
meta-Xylene	1.04	Octaldehyde	0.78
ortho-Xylene	1.02	Capric aldehyde	0.80
1M2-Ethylbenzene	1.02	Acids	
1M3-Ethylbenzene	1.01	Formic	0.01
1M4-Ethylbenzene	1.00	Acetic	0.24
1,2,3-Trimethylbenzene	0.98	Propionic	0.40
1,2,4-Trimethylbenzene	0.97	Butyric	0.48
1,3,5-Trimethylbenzene	0.98	Hexanoic	0.63
Isopropylbenzene	0.97	Heptanoic	0.61
n-Propylbenzene	1.01	Octanoic	0.65
1M2-Isopropylbenzene	0.99	Esters	
1M3-Isopropylbenzene	1.01	Methylacetate	0.20
1M4-Isopropylbenzene	0.99	Ethylacetate	0.38
sec.-Butylbenzene	1.00	Isopropylacetate	0.49
tert.-Butylbenzene	1.02	sec.-Butylacetate	0.52
n-Butylbenzene	0.98	Isobutylacetate	0.54
Unsaturates		n-Butylacetate	0.55
Acetylene	1.07	Isoamylacetate	0.62
Ethylene	1.02	Methylamylacetate	0.63
Hexene-1	0.99	Ethyl-(2)-ethylhexanoate	0.72
Octene-1	1.03	Hexylcaproate	0.78
Decene-1	1.01	Cellosolve acetate	0.50
Alcohols		Nitrogen Compounds	
Methanol	0.23	Acetonitrile	0.39
Ethanol	0.46	Trimethylamine	0.46
n-Propanol	0.60	tert.-Butylamine	0.54

Table I Relative sensitivity data for Flame Ionization Detector (continued)

Compound	Relative Sensitivity	Compound	Relative Sensitivity
Diethylamine	0.61	Pentoxone	0.56
Aniline	0.75	Others (Solvents)	
di-n-Butylamine	0.75	Cellosolve	0.45
Ketone		Butyl cellosolve	0.62
Acetone	0.49	Isophorone	0.85
Methylethylketone	0.61	Thiophane	0.57
Methylisobutylketone	0.71		
Ethylbutylketone	0.71		
Diisobutylketone	0.72		
Ethylamylketone	0.80		
Cycolhexane	0.72		

VITA

Mr. Chairat Pongtongcharoen was born in Chachoengsao, Thailand on December 27, 1970. He received his Bachelor Degree of Science from Department of Chemical Technology, Faculty of science, Chulalongkorn University in 1993.