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APPENDICES

Appendix A Experimental Data of Liquid Feed Calibration of GC 5890

1. Benzene

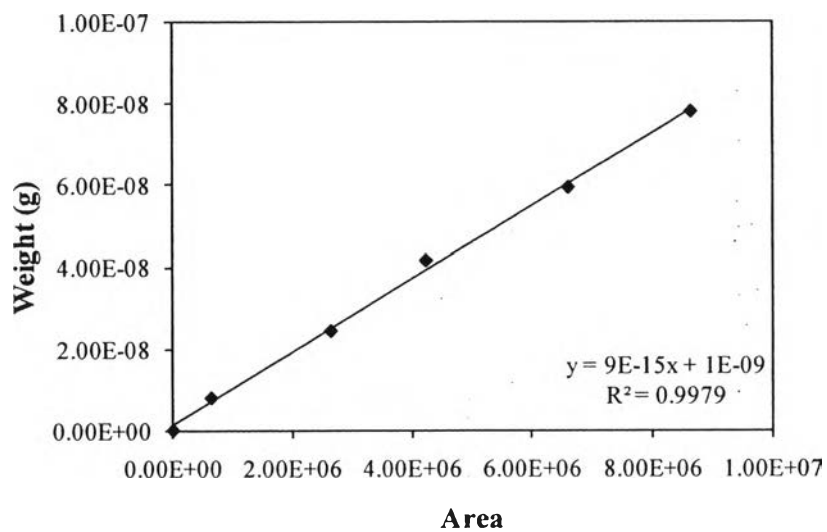


Figure A1 Calibration curve of benzene.

2. Ethanol

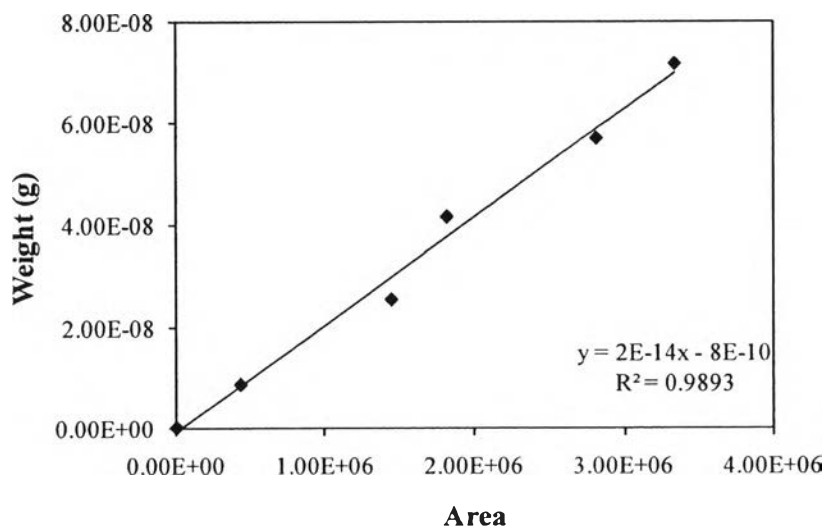


Figure A2 Calibration curve of ethanol.

Appendix B Experimental Data of Gas Flow Calibration of Sierra C100L Mass Flow Controller

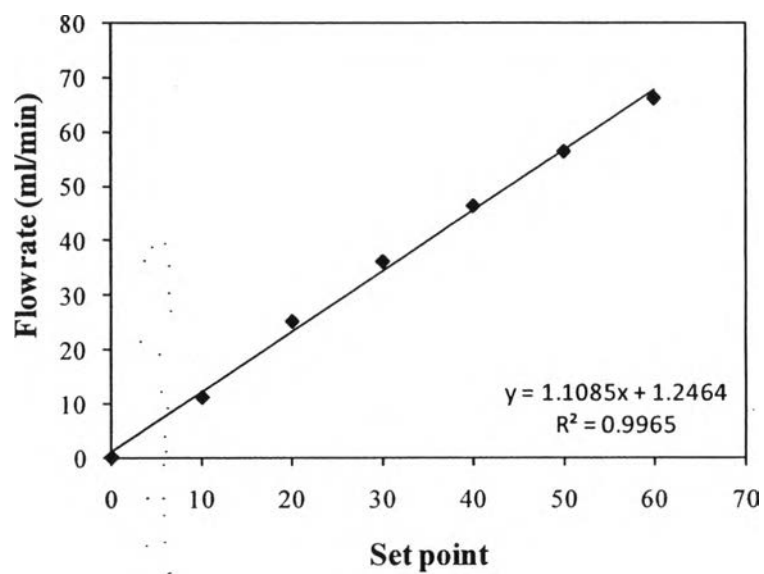


Figure B1 Calibration curve of nitrogen.

Appendix C Experimental Data of Liquid Feed Flow Calibration of Gilson 307 Pump

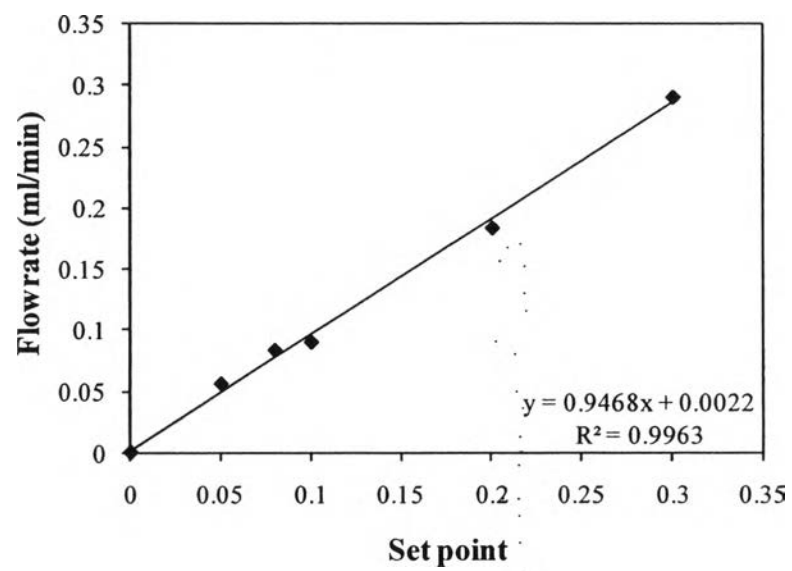


Figure C1 Calibration curve of liquid feed.

Appendix D Calculation of Si/Al Ratio and Theoretical Acidity

From the chemical composition determined by XRF method, the Si/Al ratio is calculated as follows:

The general formula of HZSM-5 is $Al_nSi_{96-n}O_{192}$

In the case of HZSM-5 (45),

$$\begin{array}{llll} SiO_2 & = & 98.937 \text{ wt\%} & Al_2O_3 = 0.93 \text{ wt\%} \\ SiO_2 & = & 1.65 \text{ mol} & Al_2O_3 = 0.009 \text{ mol} \\ SiO_2/Al_2O_3 & = & 180 & \end{array}$$

SiO_2 has O atom 3.29 mol in total O atom 3.32 mol

From the general formula, SiO_2 has O atom 190.3 mol in total O atom 192 mol. So, SiO_2 has Si atom 95.15 mol.

$$\begin{array}{ll} \text{From } Al_nSi_{96-n}O_{192}, & n = 96 - 95.15 \\ & n = 0.85 \end{array}$$

$$\begin{array}{ll} \text{So, Si} & = 95.15 \\ \text{Al} & = 0.85 \\ \text{Si/Al} & = 112 \end{array}$$

From the chemical composition determined by XRF method, the theoretical acidity of zeolite is calculated as follows:

The general formula of HZSM-5 is $Al_nSi_{96-n}O_{192}$

In the case of HZSM-5 (45) with,

$$\begin{array}{ll} Si & = 95.15 \\ Al & = 0.85 \end{array}$$

From the above, the general formula of HZSM-5 is $Al_{0.85}Si_{95.15}O_{192}$. The weight of unit cell of HZSM-5 (U) is

$$\begin{array}{ll} U & = 0.85(1) + 0.85(26.98) + 93.91(28.09) + 192(15.99) \\ U & = 5766.627 \text{ g} \end{array}$$

The theoretical acidity ($[H^+]$) of HZSM-5 (45) is

$$\begin{array}{ll} [H^+] & = 0.85/5766.627 \\ [H^+] & = 0.147 \text{ mmol/g} \end{array}$$

Appendix E Experimental Data of Catalytic Activity Test for Alkylation of Benzene with Ethanol over HZSM-5 Catalyst.

Table E1 Catalytic activity testing over HZSM-5 with different Si/Al ratio at temperature 300°C, B/E = 1, WHSV = 8 h⁻¹

Component	Si/Al	Conversion (%)					
		1 h	2 h	3 h	4 h	5 h	6 h
Benzene	77	59.39	61.67	64.05	64.73	64.73	62.40
	112	51.80	55.46	55.34	54.98	56.34	54.22
	109	36.18	32.39	36.59	34.08	33.01	38.21
Ethanol	77	96.93	98.75	99.34	98.75	98.75	95.95
	112	93.23	92.24	92.62	91.25	92.95	93.15
	109	91.72	91.69	91.88	92.69	92.41	92.26

Table E2 Catalytic activity testing on different temperature for HZSM-5 (A), B/E = 1, WHSV = 8 h⁻¹

Component	Temperature (°C)	Conversion (%)					
		1 h	2 h	3 h	4 h	5 h	6 h
Benzene	300	59.39	61.67	64.05	64.73	64.73	62.40
	350	49.09	45.28	46.81	47.03	46.21	48.32
	400	42.03	42.97	44.31	43.97	44.87	45.79
	500	26.60	30.95	28.12	24.13	25.80	26.81
Ethanol	300	96.93	98.75	99.34	98.75	98.75	95.95
	350	92.44	91.83	94.67	93.59	96.02	96.62
	400	88.51	88.31	91.21	92.20	89.45	90.39
	500	87.65	87.91	87.07	86.54	84.91	85.77

Table E4 Product distribution at different temperature over HZSM-5 (A), B/E = 1, WHSV = 8 h⁻¹, and Time on stream = 6 h.

Component	Product distribution (wt%)			
	liquid phase		gas phase	
	300°C	350°C	300°C	350°C
ethylene	0.00	0.00	2.66	0.44
methanol	0.06	0.09	0.28	0.54
toluene	1.10	10.20	3.27	31.25
EB	47.75	46.47	69.33	52.04
xylenes	1.47	4.84	3.68	5.98
cumene	3.02	2.18	2.31	0.98
propyl-benzene	3.28	3.93	1.88	1.10
p-ethyl toluene	2.21	3.01	1.37	1.15
o-ethyl toluene	0.12	0.09	0.13	0.18
1,2,3-trimethylbenzene	0.30	0.84	0.18	0.22
(2-methylpropyl)-benzene	0.28	0.20	0.11	0.05
(1-methylpropyl)-benzene	0.49	0.22	0.26	0.11
indane	0.72	2.78	0.20	0.74
1-propenyl benzene	0.19	0.77	0.06	0.20
1,4-diethylbenzene	21.02	8.07	6.86	1.31
1,3-diethylbenzene	12.50	4.37	4.30	0.78
1,2-diethylbenzene	1.05	1.07	0.95	0.38
2-butenylbenzene	0.14	0.97	0.07	0.21
1-butenylbenzene	0.40	0.83	0.30	0.33
m-ethylcumene	0.51	0.50	0.23	0.13
p-ethylcumene	0.32	0.22	0.13	0.05
1-Methyl-4-sec-butylbenzene	0.81	0.55	0.40	0.13
1-butenyl-benzene	0.48	0.36	0.20	0.05
1-methyl-1H-Indene	0.22	0.69	0.10	0.18
1,2-dihydro-Naphthalene	0.27	0.61	0.13	0.16
1,2,3,4-tetrahydronaphthalene	0.27	1.47	0.10	0.24
naphthalene	0.18	1.72	0.13	0.42
(1-ethyl-1-propenyl)-Benzene	0.44	0.62	0.16	0.08
2-methyl-Naphthalene	0.40	2.31	0.20	0.57
Total	100.00	100.00	100.00	100.00

Table E5 Product distribution at different temperature over HZSM-5 (A), B/E = 1, WHSV = 8 h⁻¹, and Time on stream = 6 h (Continued)

Component	Product distribution (wt%)			
	liquid phase		gas phase	
	400°C	500°C	400°C	500°C
ethylene	0.00	0.00	2.41	2.54
methanol	0.10	0.03	1.99	0.86
toluene	14.54	29.32	23.02	55.12
EB	45.52	19.42	46.24	23.73
xylenes	6.06	14.49	10.20	12.38
cumene	1.56	0.50	1.26	0.28
propyl-benzene	2.57	1.11	1.22	0.51
p-ethyl toluene	2.49	2.09	1.57	0.94
o-ethyl toluene	0.36	0.38	0.39	0.17
1,2,3-trimethylbenzene	0.62	0.65	0.46	0.19
indane	3.86	4.96	1.60	0.84
1-propynyl benzene	1.23	13.23	0.53	0.57
1,4-diethylbenzene	3.87	0.69	0.99	0.25
1,3-diethylbenzene	1.92	0.40	0.65	0.15
1,2-diethylbenzene	0.64	0.10	0.52	0.02
2-butenylbenzene	0.93	0.47	0.41	0.05
1-butenylbenzene	1.41	0.54	0.74	0.09
1-methyl-indane	0.53	0.32	0.27	0.04
1-methyl-1H-indene	0.90	1.01	0.30	0.12
1,2-dihydro-naphthalene	0.74	0.73	0.30	0.10
1,2,3,4-tetrahydronaphthalene	1.11	0.30	0.42	0.06
naphthalene	2.41	0.12	1.28	0.65
2-methylnaphthalene	3.87	7.42	1.45	0.13
1-methylnaphthalene	1.11	0.03	1.04	0.05
1-ethyl-naphthalene	0.66	0.46	0.21	0.05
2,6-dimethyl-naphthalene	0.48	0.75	0.30	0.06
1,6-dimethyl-naphthalene	0.49	0.49	0.23	0.03
Total	100	100	100	101.00

Table E6 Catalytic activity testing on different WHSV for HZSM-5 (A), B/E = 1, T = 300 °C.

Component	WHSV (h ⁻¹)	Conversion (%)					
		1 h	2 h	3 h	4 h	5 h	6 h
Benzene	5	64.46	65.61	68.72	67.97	70.53	68.25
	8	59.39	61.67	64.05	64.73	64.73	62.40
	10	58.15	58.52	55.86	52.84	53.23	50.82
	12	45.82	52.41	49.18	49.04	47.07	40.45
	14	46.19	45.01	47.64	40.68	38.96	36.59
	20	16.01	13.47	11.48	10.58	12.65	14.08
Ethanol	5	97.74	98.51	99.49	98.62	98.07	99.23
	8	96.93	98.75	99.34	98.75	98.75	95.95
	10	99.62	98.62	99.63	99.41	99.52	97.76
	12	99.00	98.91	99.38	99.64	98.82	99.32
	14	99.45	99.76	98.35	97.73	99.52	99.40
	20	95.38	94.75	95.87	94.74	96.27	95.85

Table E9 Catalytic activity testing on different feed ratio for HZSM-5 (A), WHSV = 8 h^{-1} , $T = 300 \text{ }^\circ\text{C}$.

Component	B/E (mol/mol)	Conversion (%)					
		1 h	2 h	3 h	4 h	5 h	6 h
Benzene	1	59.39	61.67	64.05	64.73	64.73	62.40
	2	51.05	50.76	52.03	54.09	52.71	53.51
	3	47.67	47.03	49.52	51.22	50.12	49.87
	4	45.29	45.99	45.13	45.03	45.30	46.07
Ethanol	1	96.93	98.75	99.34	98.75	98.75	95.95
	2	98.40	96.81	98.31	99.04	97.84	99.51
	3	93.37	94.88	94.73	93.18	93.93	93.25
	4	91.22	89.44	92.38	91.56	89.26	90.46

Table E10 Product distribution of liquid sample at different feed ratio for HZSM-5 (A), WHSV = 8 h⁻¹, T = 300 °C, and Time on stream = 6 h

Component	product distribution (wt%)			
	1	2	3	4
ethylene	0.00	0.00	0.00	0.00
methanol	0.06	0.01	0.01	0.01
toluene	1.10	2.31	1.67	1.51
EB	47.75	60.46	65.93	72.69
xylene	1.47	1.13	0.85	0.97
cumene	3.02	1.62	1.75	1.16
propyl-benzene	3.28	2.28	2.67	2.04
p-ethyl toluene	2.21	1.66	1.17	0.86
o-ethyl toluene	0.12	0.11	0.06	0.07
1,2,3-trimethylbenzene	0.30	0.14	0.09	0.07
(2-methylpropyl)-benzene	0.28	0.18	0.21	0.13
(1-methylpropyl)-benzene	0.49	0.22	0.23	0.13
indane	0.72	0.77	0.53	0.84
1-propenyl benzene	0.19	0.17	0.13	0.16
1,4-diethylbenzene	21.02	15.80	14.75	11.41
1,3-diethylbenzene	12.50	9.16	7.21	5.28
1,2-diethylbenzene	1.05	0.62	0.50	0.76
2-butenylbenzene	0.14	0.14	0.08	0.09
1-butenylbenzene	0.40	0.39	0.25	0.21
m-ethylcumene	0.51	0.28	0.22	0.18
p-ethylcumene	0.32	0.13	0.12	0.07
1-Methyl-4-sec-butylbenzene	0.81	0.42	0.35	0.22
1-butyryl-benzene	0.48	0.24	0.19	0.12
1-methyl-1H-Indene	0.22	0.18	0.13	0.13
1,2-dihydro-Naphthalene	0.27	0.18	0.15	0.13
1,2,3,4-tetrahydronaphthalene	0.27	0.21	0.13	0.14
naphthalene	0.18	0.34	0.16	0.17
(1-ethyl-1-propenyl)-Benzene	0.44	0.33	0.23	0.20
2-methyl-Naphthalene	0.40	0.51	0.25	0.24
Total	100.00	100.00	100.00	100.00

Table E11 Product distribution of gas sample at different feed ratio for HZSM-5 (A),
WHSV = 8 h⁻¹, T = 300 °C, and Time on stream = 6 h

Component	product distribution (wt%)			
	1	2	3	4
ethylene	2.66	0.98	0.17	0.08
methanol	0.28	0.22	0.14	0.08
toluene	3.27	8.15	6.93	4.65
EB	69.33	76.77	79.88	85.09
xylenes	3.68	4.60	4.88	5.32
cumene	2.31	1.40	1.51	0.86
propyl-benzene	1.88	1.16	1.29	0.70
p-ethyl toluene	1.37	0.90	0.70	0.39
o-ethyl toluene	0.13	0.12	0.11	0.07
1,2,3-trimethylbenzene	0.18	0.10	0.10	0.05
(2-methylpropyl)-benzene	0.11	0.06	0.06	0.03
(1-methylpropyl)-benzene	0.26	0.11	0.11	0.04
indane	0.20	0.13	0.13	0.12
1-propenyl benzene	0.06	0.03	0.03	0.02
1,4-diethylbenzene	6.86	2.64	2.06	1.32
1,3-diethylbenzene	4.30	1.73	1.19	0.76
1,2-diethylbenzene	0.95	0.46	0.36	0.26
2-butenylbenzene	0.07	0.03	0.03	0.02
1-butenylbenzene	0.30	0.11	0.08	0.04
m-ethylcumene	0.23	0.06	0.05	0.02
p-ethylcumene	0.13	0.03	0.02	0.01
1-Methyl-4-sec-butylbenzene	0.40	0.03	0.04	0.02
1-butynyl-benzene	0.20	0.02	0.01	0.01
1-methyl-1H-Indene	0.10	0.02	0.02	0.01
1,2-dihydro-Naphthalene	0.13	0.02	0.02	0.01
1,2,3,4-tetrahydronaphthalene	0.10	0.03	0.02	0.01
naphthalene	0.13	0.04	0.02	0.01
(1-ethyl-1-propenyl)-Benzene	0.16	0.03	0.02	0.01
2-methyl-Naphthalene	0.20	0.02	0.02	0.01
Total	100.00	100.00	100.00	100.00

Table E12 Stability test over HZSM-5 (A), $T = 300\text{ }^{\circ}\text{C}$, $\text{WHSV} = 8\text{ h}^{-1}$, and $\text{B/E} = 2$.

Time (h)	Benzene conversion (%)	Ethanol conversion (%)	EB selectivity (%)
1	47.89	91.91	57.56
2	48.96	98.21	61.01
3	49.04	98.33	58.76
4	48.02	95.18	60.43
5	46.28	98.82	60.32
6	47.25	96.11	61.51
7	45.84	95.57	59.33
8	44.76	97.93	62.24
9	41.69	95.81	59.48
10	43.91	94.77	62.52
11	45.44	97.60	62.75
12	41.60	98.29	60.36
13	41.42	95.91	62.93
14	43.02	94.07	62.49
15	40.60	95.91	63.07
16	39.62	94.90	62.49
17	39.75	97.24	61.56
18	42.22	94.85	59.52
19	40.75	92.94	63.42
20	40.14	91.82	64.56
21	41.72	94.81	64.50
22	41.56	95.08	63.19
25	41.79	95.42	64.66
28	38.37	89.72	62.57
30	38.92	91.93	58.96
34	22.67	84.55	46.09

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Proceedings:

1. Udomsin, N., Rirksomboon, T., and Jonpatiwut, S. (2010, April 22) Alkylation of Benzene with Ethanol to Ethylbenzene using Commercial HZSM-5 Catalysts. Proceedings of 1st National Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and 16th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.

Presentations:

1. Udomsin, N., Rirksomboon, T., and Jonpatiwut, S. (2010, April 22) Alkylation of Benzene with Ethanol to Ethylbenzene using Commercial HZSM-5 Catalysts. Poster presentation of 1st National Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and 16th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.