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APPENDIX

Table A.1 Mass flow meter calibration at temperature of 20 °C and pressure of 2 atm.

mass flow meter (ml/min)	actual flow (ml/min)			average actual flow (ml/min)
0	0.00	0.00	0.00	0.00
2	1.91	1.91	1.91	1.91
4	2.50	2.50	2.50	2.50
6	3.48	3.48	3.48	3.48
8	5.58	5.57	5.57	5.57
10	6.79	6.78	6.78	6.78
14	9.61	9.61	9.61	9.61
18	12.50	12.50	12.50	12.50
25	17.70	17.70	17.70	17.70
30	21.10	21.10	21.10	21.10
35	24.90	24.90	25.00	24.93
45	32.10	32.10	32.20	32.13
55	38.50	38.50	38.50	38.50
65	45.20	45.10	45.20	45.17
80	55.70	55.70	55.70	55.70
95	66.10	66.00	66.10	66.07
115	79.60	79.70	79.60	79.63
135	92.50	92.600	92.50	92.53
155	107.00	106.00	107.00	106.67
180	123.00	123.00	123.00	123.00
205	141.00	141.00	141.00	141.00
250	172.00	172.00	171.00	171.67
275	188.00	188.00	188.00	188.00
300	206.00	206.00	206.00	206.00
350	240.00	240.00	240.00	240.00
397	273.00	273.00	273.00	273.00

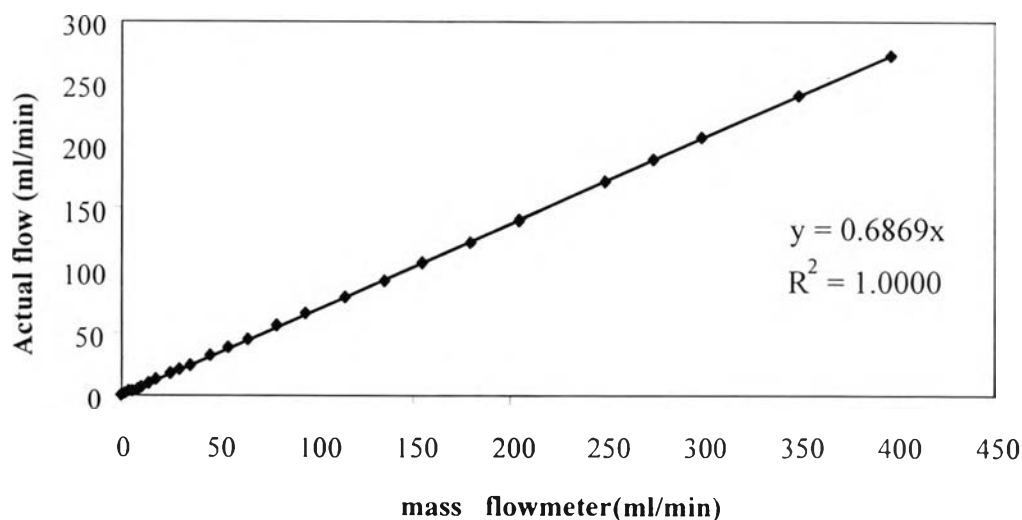


Figure A.1 Calibration curve of mass flow meter.

Actual Flow (ml/min)

$$= [0.6869][\text{Ethylene consumption rate from mass flow meter (ml / min)}]$$

where 0.6869 is correction factor from calibration curve of mass flow meter.

Activity (kgPE/mol-Zr.hr.atm)

$$= \frac{[\text{Ethylene consumption rate (kg / hr)}]}{[\text{Amount of catalyst (mol - Zr)}][\text{Ethylene pressure (atm)}]}$$

Ethylene Consumption Rate (kg/hr)

$$= \frac{[\text{Actual flow (ml / min)}][d (g / l)][60]}{[1000 \times 1000]}$$

where d = the ethylene pressure-density dependence from the ideal behavior (Kissin and Beach, 1984).

$$d = [(5.374 \times 10^{-3}) \times P] \times [\exp(3.469 \times 10^{-4} \times P)]$$

where P = ethylene pressure (atm).

Productivity (kgPE/mol-Zr.hr.atm)

$$= \frac{[\text{Polyethylene product (kg)}]}{[\text{Amount of catalyst (mol - Zr)}][\text{Ethylene pressure (atm)}][\text{Polymerization time (hr)}]}$$

Table A.2 Ethylene consumption of different cocatalyst systems.

Time(min)	Ethylene consumption (ml/min) from mass flow meter			
	TMA/Zr	Zr/B(C ₆ F ₅) ₃	TMA/Zr/B(C ₆ F ₅) ₃	TMA/B(C ₆ F ₅) ₃ /Zr
0	0	0	0	0
1	0	0	2	0
2	2	1	8	1
3	2	1	8	1
4	2	1	8	1
5	2	1	7	1
6	2	1	7	1
7	1	1	6	1
8	1	1	6	2
9	1	1	5	2
10	1	1	5	2
11	1	1	5	2
12	1	1	5	2
13	1	0	4	2
14	1	0	4	2
15	1	0	4	2
16	1	0	4	2
17	1	0	4	2
18	1	0	4	2
19	1	0	3	2
20	1	0	3	2
21	1	0	3	2
22	1	0	3	2
23	1	0	3	2
24	1	0	3	2
25	1	0	3	2
26	1	0	3	2
27	1	0	3	2
28	1	1	3	2
29	1	1	3	2
30	1	1	3	3

Table A.2 (continued) Ethylene consumption of different cocatalyst systems.

Time(min)	Ethylene consumption (ml/min) from mass flow meter			
	TMA/Zr	Zr/B(C ₆ F ₅) ₃	TMA/Zr/B(C ₆ F ₅) ₃	TMA/B(C ₆ F ₅) ₃ /Zr
31	1	1	3	3
32	1	1	3	3
33	1	0	3	3
34	1	0	3	3
35	1	0	3	3
36	1	0	3	3
37	1	0	3	3
38	1	0	3	3
39	1	0	2	3
40	1	0	2	3
41	1	0	2	3
42	1	0	2	3
43	0	0	2	3
44	0	0	2	3
45	0	0	2	3
46	0	0	2	3
47	0	0	2	3
48	0	0	2	3
49	0	0	2	3
50	0	0	2	3
51	0	0	2	3
52	0	0	2	3
53	0	0	2	3
54	0	0	2	3
55	0	0	2	3
56	0	0	2	3
57	0	0	2	3
58	0	0	2	3
59	0	0	2	3
60	0	0	2	3

Table A.3 Ethylene consumption at varying [Zr].

Time(min)	Ethylene consumption (ml/min) from mass flow meter			
	Zr = 50 μmol	Zr = 30 μmol	Zr = 20 μmol	Zr = 10 μmol
0	0	0	0	0
1	312	186	89	8
2	293	155	78	12
3	278	140	68	16
4	263	129	60	17
5	248	120	53	17
6	233	114	48	16
7	218	108	44	14
8	207	104	41	13
9	196	100	38	12
10	186	97	35	12
11	176	94	33	11
12	168	92	31	10
13	160	89	30	10
14	154	88	28	9
15	148	86	27	9
16	143	84	26	8
17	139	83	25	8
18	135	81	24	7
19	132	80	23	7
20	129	79	22	7
21	126	78	22	7
22	123	77	21	6
23	120	75	20	6
24	118	74	20	6
25	116	73	19	6
26	114	72	19	6
27	112	72	18	5
28	110	71	18	5
29	108	70	17	5
30	106	69	17	5
31	105	68	17	5
32	104	68	16	5
33	103	67	16	5
34	101	66	16	5

Table A.3 (*continued*) Ethylene consumption at varying [Zr].

Time(min)	Ethylene consumption (ml/min) from mass flow meter			
	Zr = 50 μmol	Zr = 30 μmol	Zr = 20 μmol	Zr = 10 μmol
35	100	66	15	4
36	99	65	15	4
37	98	64	15	4
38	97	64	14	4
39	96	63	14	4
40	95	63	14	4
41	94	62	14	4
42	94	62	13	4
43	93	61	13	4
44	92	60	13	4
45	91	60	13	4
46	91	59	13	4
47	90	59	12	4
48	89	59	12	4
49	89	58	12	3
50	88	58	12	3
51	88	57	12	3
52	87	57	11	3
53	86	57	11	3
54	86	56	11	3
55	85	56	11	3
56	85	56	11	3
57	84	55	11	3
58	84	55	11	3
59	83	55	10	3
60	82	54	10	3

Table A.4 Ethylene consumption at varying [Al]/[Zr] ratio.

Time(min)	Ethylene consumption (ml/min) from mass flow meter			
	[Al]/[Zr] = 100	[Al]/[Zr] = 80	[Al]/[Zr] = 60	[Al]/[Zr] = 50
0	0	0	0	0
1	36	32	20	8
2	36	30	21	12
3	34	28	20	16
4	32	25	19	17
5	31	22	18	17
6	29	20	17	16
7	28	18	16	14
8	27	17	14	13
9	26	16	13	12
10	26	15	12	12
11	25	14	12	11
12	24	13	11	10
13	24	13	10	10
14	24	12	10	9
15	23	12	9	9
16	23	12	9	8
17	22	11	9	8
18	22	11	8	7
19	22	11	8	7
20	21	10	8	7
21	21	10	8	7
22	21	10	7	6
23	20	10	7	6
24	20	9	7	6
25	20	9	7	6
26	20	9	7	6
27	20	9	6	5
28	19	9	6	5
29	19	9	6	5
30	19	9	6	5
31	19	8	6	5
32	18	8	6	5
33	18	8	6	5
34	18	8	6	5

Table A.4 (*continued*) Ethylene consumption at varying [Al]/[Zr] ratio.

Time(min)	Ethylene consumption (ml/min) from mass flow meter			
	[Al]/[Zr] = 100	[Al]/[Zr] = 80	[Al]/[Zr] = 60	[Al]/[Zr] = 50
35	18	8	5	4
36	18	8	5	4
37	18	8	5	4
38	17	8	5	4
39	17	8	5	4
40	17	8	5	4
41	17	7	5	4
42	17	7	5	4
43	17	7	5	4
44	17	7	5	4
45	17	7	5	4
46	16	7	5	4
47	16	7	5	4
48	16	7	4	4
49	16	7	4	3
50	16	7	4	3
51	16	7	4	3
52	16	6	4	3
53	16	6	4	3
54	16	6	4	3
55	16	6	4	3
56	16	6	4	3
57	16	6	4	3
58	15	6	4	3
59	15	6	4	3
60	15	6	4	3

Table A.5 Ethylene consumption of prealkylated zirconocene.

Time(min)	Ethylene consumption (ml/min) from mass flow meter			
	TMA/Zr/ B(C ₆ F ₅) ₃	TMA/B(C ₆ F ₅) ₃ / (Zr+100TMA)	TMA/ B(C ₆ F ₅) ₃ / (Zr+200TMA)	TMA/ B(C ₆ F ₅) ₃ / (Zr+300TMA)
0	0	0	0	0
1	8	1	0	0
2	12	2	0	1
3	16	4	0	1
4	17	4	1	1
5	17	5	1	1
6	16	5	1	1
7	14	5	1	1
8	13	5	1	1
9	12	5	1	1
10	12	5	1	1
11	11	5	1	1
12	10	5	1	1
13	10	5	1	1
14	9	5	1	1
15	9	5	1	1
16	8	5	2	1
17	8	5	2	1
18	7	5	2	1
19	7	5	2	1
20	7	5	2	1
21	7	4	2	1
22	6	4	2	1
23	6	4	2	1
24	6	4	2	1
25	6	4	2	1
26	6	4	2	1
27	5	4	2	1
28	5	4	2	1
29	5	4	2	1
30	5	4	2	1
31	5	4	2	1
32	5	4	2	1
33	5	4	2	1
34	5	4	2	1
35	4	4	2	1
36	4	4	2	1
37	4	4	2	1

Table A.5 (continued) Ethylene consumption of prealkylated zirconocene.

Time(min)	Ethylene consumption (ml/min) from mass flow meter			
	TMA/Zr/ B(C ₆ F ₅) ₃	TMA/B(C ₆ F ₅) ₃ / (Zr+100TMA)	TMA/ B(C ₆ F ₅) ₃ / (Zr+200TMA)	TMA/ B(C ₆ F ₅) ₃ / (Zr+300TMA)
38	4	4	2	1
39	4	4	2	1
40	4	4	2	2
41	4	4	2	2
42	4	4	2	2
43	4	3	2	2
44	4	3	2	2
45	4	3	2	2
46	4	3	2	2
47	4	3	2	2
48	4	3	2	2
49	3	3	2	2
50	3	3	2	2
51	3	3	2	2
52	3	3	2	2
53	3	3	2	2
54	3	3	2	2
55	3	3	2	2
56	3	3	2	2
57	3	3	2	2
58	3	3	2	2
59	3	3	2	2
60	3	3	2	2

Table A.6 Ethylene consumption of prealkylated and preactivated zirconocene.

Time(min)	Ethylene consumption (ml/min) from mass flow meter	
	500TMA+B(C6F5)3+(100TMA+Zr)	500TMA+(B(C6F5)3+100TMA+Zr)
0	0	0
1	0	1
2	1	5
3	1	8
4	1	7
5	1	6
6	1	5
7	1	5
8	1	4
9	1	4
10	1	3
11	1	3
12	1	3
13	1	3
14	1	2
15	1	2
16	1	2
17	1	2
18	1	2
19	1	2
20	1	2
21	1	1
22	1	1
23	1	1
24	1	1
25	1	1
26	1	1
27	1	1
28	1	1
29	1	1
30	1	1
31	1	1
32	1	1
33	1	1
34	1	1

Table A.6 (*continued*) Ethylene consumption of prealkylated and preactivated zirconocene.

Time(min)	Ethylene consumption (ml/min) from mass flow meter	
	500TMA+B(C6F5)3+(100TMA+Zr)	500TMA+(B(C6F5)3+100TMA+Zr)
35	1	1
36	1	1
37	1	1
38	1	1
39	1	1
40	1	1
41	1	1
42	1	1
43	1	1
44	1	1
45	1	1
46	1	1
47	1	1
48	2	1
49	2	1
50	2	1
51	2	1
52	2	1
53	2	1
54	2	1
55	2	1
56	2	1
57	2	1
58	2	1
59	2	1
60	2	1

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