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APPENDIX

Calculations of Activity and Productivity :

Activity (kgPE/mol-Zr*atm*h)

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

Ethylene Consumption Rate (kg/hr)

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

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).

Actual Flow (ml/min)

= Ethylene consumption rate from mass flow meter (ml/min)

Productivity (KgPE/mol-Zr*atm*h)

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

Table A.1 Ethylene consumption of different Al/Zr ratio at [Zr] = 3 μmol using TEA catalyst system.

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
0	0	0	0
1	204	187	94
2	200	181	91
3	146	135	55
4	145	133	54
5	136	128	53
6	135	121	45
7	127	120	41
8	120	115	31
9	111	111	28
10	108	103	19
11	108	100	19
12	107	96	18
13	100	94	18
14	98	92	18
15	98	92	17
16	97	86	17
17	95	82	17
18	86	78	16
19	84	78	17
20	82	75	17

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
21	79	64	17
22	78	62	16
23	75	61	15
24	76	55	14
25	74	53	15
26	72	52	13
27	71	51	11
28	70	50	10
29	68	49	9
30	65	49	9
31	63	49	9
32	60	47	9
33	59	45	9
34	56	45	9
35	54	44	9
36	52	42	9
37	48	41	0
38	45	40	0
39	41	38	0
40	38	38	0

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
41	37	31	0
42	36	25	0
43	35	23	0
44	34	21	0
45	31	21	0
46	30	21	0
47	28	18	0
48	28	18	0
49	28	18	0
50	26	16	0
51	22	16	0
52	22	16	0
53	22	8	0
54	20	8	0
55	19	8	0
56	19	8	0
57	18	8	0
58	16	8	0
59	9	8	0
60	9	8	0

Table A.2 Ethylene consumption of different Al/Zr ratio at [Zr] = 5 μmol using TEA catalyst system.

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
0	0	0	0
1	1379	1131	1065
2	1259	1097	1040
3	1018	953	606
4	939	740	584
5	842	531	469
6	820	447	409
7	601	423	392
8	583	423	386
9	575	399	307
10	355	353	281
11	300	307	246
12	257	237	235
13	215	227	212
14	208	223	192
15	159	222	190
16	129	217	178
17	123	211	158
18	119	200	147
19	118	195	145
20	111	193	143

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
21	110	186	138
22	105	180	136
23	100	170	135
24	96	148	132
25	87	126	124
26	85	119	113
27	84	115	108
28	83	105	103
29	79	100	96
30	77	97	92
31	70	95	88
32	64	85	78
33	58	84	78
34	58	80	77
35	54	74	75
36	52	74	73
37	51	68	73
38	51	64	72
39	50	58	69
40	49	58	67

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
41	46	56	66
42	44	48	65
43	44	48	64
44	44	47	61
45	42	44	56
46	41	44	46
47	38	40	41
48	38	40	34
49	36	37	33
50	35	36	30
51	33	31	30
52	32	29	30
53	32	26	30
54	31	25	30
55	29	24	30
56	28	24	30
57	21	24	30
58	21	24	29
59	21	24	29
60	21	24	29

Table A.3 Ethylene consumption of different Al/Zr ratio at [Zr] = 8 μmol using TEA catalyst system.

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
0	0	0	0
1	1376	958	761
2	1265	925	653
3	940	640	636
4	856	604	485
5	665	600	453
6	655	483	447
7	647	477	378
8	568	446	330
9	586	411	311
10	518	324	300
11	445	300	294
12	422	239	257
13	412	237	251
14	336	237	248
15	250	222	246
16	186	215	246
17	165	199	243
18	140	199	227
19	122	196	224
20	108	187	224

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
21	90	178	216
22	84	177	216
23	74	176	210
24	72	172	209
25	72	167	190
26	67	164	182
27	66	162	171
28	64	156	161
29	61	146	156
30	60	145	149
31	59	143	147
32	58	139	146
33	58	138	136
34	56	136	134
35	56	123	133
36	54	114	122
37	54	104	122
38	51	100	122
39	49	100	114
40	45	99	112

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
41	42	97	96
42	42	91	94
43	42	62	85
44	34	59	83
45	32	55	82
46	31	54	74
47	30	54	74
48	30	53	72
49	29	53	70
50	27	51	69
51	21	51	69
52	19	50	69
53	16	47	69
54	16	47	69
55	16	46	69
56	16	46	69
57	16	45	69
58	16	45	69
59	16	45	69
60	16	45	69

Table A.4 Ethylene consumption of different Al/Zr ratio at [Zr] = 10 μmol using TEA catalyst system.

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
0	0	0	0
1	1339	1348	1372
2	1339	1314	1114
3	1337	932	919
4	1093	785	646
5	991	638	632
6	781	586	488
7	672	576	486
8	639	538	463
9	535	437	445
10	400	378	429
11	389	399	369
12	361	373	347
13	343	338	306
14	332	334	296
15	322	319	260
16	315	311	251
17	311	294	227
18	294	273	223
19	261	241	216
20	231	239	210

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
21	222	195	205
22	218	141	200
23	214	132	199
24	154	119	194
25	129	106	189
26	128	95	185
27	123	87	183
28	117	85	182
29	113	83	174
30	108	79	141
31	103	77	139
32	92	77	138
33	90	76	127
34	84	73	107
35	80	72	104
36	79	70	100
37	79	65	91
38	78	64	84
39	78	53	78
40	77	47	71

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 50	Al/Zr = 80	Al/Zr = 100
41	76	35	68
42	76	35	66
43	75	35	58
44	75	35	58
45	73	35	52
46	71	34	51
47	69	34	49
48	68	34	44
49	67	34	42
50	67	32	42
51	67	32	41
52	67	32	40
53	67	32	38
54	67	31	38
55	67	31	38
56	67	31	38
57	67	31	38
58	67	31	38
59	67	31	38
60	67	31	38

Table A.5 Ethylene consumption of different Al/Zr ratio using TBA catalyst system at [Zr] = 10 μmol, T = 20 °C and Pressure = 1 bar.

Time (min)	Ethylene consumption (ml/min)from mass flow meter			
	Al/Zr = 600	Al/Zr = 1000	Al/Zr = 1400	Al/Zr = 1800
0	0	0	0	0
1	18	89	3	0
2	428	347	236	0
3	399	417	325	30
4	383	539	418	100
5	375	534	506	225
6	365	533	513	251
7	361	527	500	247
8	320	481	473	244
9	300	399	467	235
10	255	392	454	229
11	247	382	408	227
12	238	380	403	225
13	237	380	396	224
14	222	377	377	219
15	199	354	375	217
16	193	345	374	211
17	191	331	367	209
18	188	330	365	205
19	184	319	356	201
20	174	317	352	200

Time (min)	Ethylene consumption (ml/min)from mass flow meter			
	Al/Zr = 600	Al/Zr = 1000	Al/Zr = 1400	Al/Zr = 1800
21	158	316	328	200
22	149	315	328	187
23	148	290	325	185
24	142	278	317	182
25	141	269	306	181
26	139	262	279	179
27	138	244	269	173
28	138	227	262	169
29	136	222	260	164
30	136	215	260	160
31	135	213	258	148
32	133	211	256	146
33	130	209	254	142
34	128	208	253	137
35	123	205	252	134
36	121	200	251	132
37	119	197	250	129
38	116	196	248	128
39	116	191	247	126
40	115	190	240	125

Time (min)	Ethylene consumption (ml/min)from mass flow meter			
	Al/Zr = 600	Al/Zr = 1000	Al/Zr = 1400	Al/Zr = 1800
41	115	189	238	120
42	113	189	235	114
43	112	187	232	105
44	112	186	232	102
45	111	186	232	100
46	111	184	231	100
47	110	184	231	96
48	110	181	230	90
49	108	180	229	88
50	108	180	229	85
51	106	179	228	84
52	99	179	228	83
53	95	177	228	78
54	94	177	227	77
55	94	176	226	77
56	94	175	226	68
57	94	171	226	67
58	94	170	224	61
59	94	169	224	57
60	94	169	222	48

Table A.6 Ethylene consumption of different Al/Zr ratio using TBA catalyst system at [Zr] = 10 μmol, T = 30 °C and Pressure = 1 bar.

Time (min)	Ethylene consumption (ml/min)from mass flow meter			
	Al/Zr = 600	Al/Zr = 800	Al/Zr = 1000	Al/Zr = 1200
0	0	0	0	0
1	0	0	1231	135
2	435	369	1400	480
3	522	425	1299	643
4	625	479	1217	614
5	558	499	1115	518
6	527	481	1048	503
7	511	449	1043	496
8	465	399	922	495
9	430	375	731	492
10	298	331	709	449
11	273	262	616	446
12	267	256	549	432
13	265	163	506	427
14	249	147	431	372
15	208	140	404	371
16	191	136	390	367
17	186	128	385	366
18	175	125	377	351
19	159	88	376	348
20	154	82	344	345

Time (min)	Ethylene consumption (ml/min)from mass flow meter			
	Al/Zr = 600	Al/Zr = 1000	Al/Zr = 1400	Al/Zr = 1800
21	151	66	315	331
22	146	62	263	330
23	141	60	238	330
24	134	59	209	329
25	112	58	194	328
26	97	58	176	327
27	97	48	163	326
28	92	46	162	324
29	90	44	146	318
30	86	41	136	316
31	85	39	124	313
32	84	36	116	310
33	83	34	105	307
34	79	33	100	305
35	77	28	96	301
36	75	26	89	298
37	72	25	85	296
38	70	22	83	287
39	70	22	81	272
40	70	22	80	255

Time (min)	Ethylene consumption (ml/min)from mass flow meter			
	Al/Zr = 600	Al/Zr = 1000	Al/Zr = 1400	Al/Zr = 1800
41	68	21	80	232
42	64	21	80	222
43	63	20	78	219
44	60	19	73	211
45	58	19	73	211
46	58	15	72	209
47	53	15	72	204
48	51	14	68	198
49	48	13	65	197
50	46	9	63	188
51	45	9	60	163
52	44	6	59	153
53	41	5	57	151
54	40	5	57	149
55	38	4	57	137
56	38	4	55	128
57	36	4	54	126
58	36	4	53	124
59	35	3	52	122
60	35	3	52	112

Table A.7 Ethylene consumption of different Al/Zr ratio using TBA catalyst system at [Zr] = 10 μmol, T = 50 °C and Pressure = 1 bar.

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 600	Al/Zr = 800	Al/Zr = 1000
0	0	0	0
1	845	1016	1178
2	872	973	1105
3	656	884	978
4	527	742	798
5	489	600	654
6	472	540	573
7	445	483	475
8	442	430	410
9	388	383	364
10	383	358	330
11	376	333	300
12	356	300	294
13	314	283	260
14	276	282	252
15	258	268	241
16	219	264	228
17	215	257	221
18	210	253	217
19	205	244	198
20	200	229	197

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 600	Al/Zr = 800	Al/Zr = 1000
21	185	228	194
22	183	213	191
23	181	200	190
24	179	194	190
25	179	188	189
26	178	186	189
27	177	185	189
28	167	183	186
29	166	183	174
30	164	183	171
31	164	179	160
32	152	177	160
33	150	177	151
34	149	177	149
35	136	176	148
36	135	176	145
37	135	175	136
38	134	174	130
39	132	173	121
40	132	173	120

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 600	Al/Zr = 800	Al/Zr = 1000
41	131	172	118
42	130	172	110
43	128	168	110
44	126	166	109
45	124	166	107
46	120	158	104
47	120	152	104
48	118	146	104
49	118	146	100
50	117	145	94
51	117	142	94
52	116	136	93
53	114	130	93
54	113	128	91
55	111	124	91
56	100	124	89
57	94	104	89
58	89	104	88
59	88	104	88
60	77	92	71

Table A.8 Ethylene consumption of different temperature using TBA catalyst system at Al/Zr ratio = 1000, [Zr] = 10 μmol, T = 50 °C and Pressure = 1 bar.

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 600	Al/Zr = 800	Al/Zr = 1000
0	0	0	0
1	89	1231	1178
2	347	1400	1105
3	417	1299	978
4	539	1217	798
5	534	1115	654
6	533	1048	573
7	527	1043	475
8	481	922	410
9	399	731	364
10	392	709	330
11	382	616	300
12	380	549	294
13	380	506	260
14	377	431	252
15	354	404	241
16	345	390	228
17	331	385	221
18	330	377	217
19	319	376	198
20	317	344	197

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 600	Al/Zr = 800	Al/Zr = 1000
21	316	315	194
22	315	263	191
23	290	238	190
24	278	209	190
25	269	194	189
26	262	176	189
27	244	163	189
28	227	162	186
29	222	146	174
30	215	136	171
31	213	124	160
32	211	116	160
33	209	105	151
34	208	100	149
35	205	96	148
36	200	89	145
37	197	85	136
38	196	83	130
39	191	81	121
40	190	80	120

Time (min)	Ethylene consumption (ml/min)from mass flow meter		
	Al/Zr = 600	Al/Zr = 800	Al/Zr = 1000
41	189	80	118
42	189	80	110
43	187	78	110
44	186	73	109
45	186	73	107
46	184	72	104
47	184	72	104
48	181	68	104
49	180	65	100
50	180	63	94
51	179	60	94
52	179	59	93
53	177	57	93
54	177	57	91
55	176	57	91
56	175	55	89
57	171	54	89
58	170	53	88
59	169	52	88
60	169	52	71

Table A.9 Ethylene consumption of different catalyst system at Al/Zr ratio = 1000, [Zr] = 10 μmol, T = 50 °C and Pressure = 1 bar.

Time (min)	Ethylene consumption (ml/min)from mass flow meter	
	TEA	TBA
0	0	0
1	1372	89
2	1114	347
3	919	417
4	646	539
5	632	534
6	488	533
7	486	527
8	463	481
9	445	399
10	429	392
11	369	382
12	347	380
13	306	380
14	296	377
15	260	354
16	251	345
17	227	331
18	223	330
19	216	319
20	210	317

Time (min)	Ethylene consumption (ml/min)from mass flow meter	
	TEA	TBA
21	205	316
22	200	315
23	199	290
24	194	278
25	189	269
26	185	262
27	183	244
28	182	227
29	174	222
30	141	215
31	139	213
32	138	211
33	127	209
34	107	208
35	104	205
36	100	200
37	91	197
38	84	196
39	78	191
40	71	190

Time (min)	Ethylene consumption (ml/min)from mass flow meter	
	TEA	TBA
41	68	189
42	66	189
43	58	187
44	58	186
45	52	186
46	51	184
47	49	184
48	44	181
49	42	180
50	42	180
51	41	179
52	40	179
53	38	177
54	38	177
55	38	176
56	38	175
57	38	171
58	38	170
59	38	169
60	38	169

Table A.10 Productivity of TBA catalyst system using different temperature.

Al/Zr ratio	Productivity (kgPE/mol-Zr*atm*h)		
	T = 20 °C	T = 30 °C	T = 50 °C
200	0	0	0
400	630	672	955
600	627	1344	**1085**
800	629	**1375**	1014
1000	1109	1316	914
1200	1173	655	
1400	**1220**		
1600	936		

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