



TITLE:

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Continuous Production of Polyethylene on Semi-Industrial Scale

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Although there are many patents¹⁾ as to the methods of commercial production of polyethylene, there is but one report on I. G. process²⁾ that describes the details of apparatus and operating conditions for its continuous production. In our laboratory a small plant, having a daily capacity of 10 kg., in which ethylene was continuously polymerized in gaseous phase with oxygen as a catalyst, was installed and we were able to obtain various experimental results which are herewith reported.

Experimental apparatus and operation

The ethylene was prepared from ethyl alcohol by dehydration and purified by fractional distillation using two fractionation columns successively. Then, the purified ethylene was polymerized at the pressure of 800–1450 atm. and temperature of 150–240°C. The apparatus are illustrated schematically in Fig. 1.

Ethyl alcohol in a reservoir (1) was sent up to a head tank (2), then forwarded to evaporators (4) through a rotameter (3). The alcohol vapor was sent to dehydrators (5) packed with alumina granules and was dehydrated into ethylene at the temperature of about 350°C.

The ethylene thus prepared was cooled with water in a cooler (6) and, after separating water in a separator (7), it was washed with water in a washing tower (9) and stored in a crude ethylene holder (10). Then, the crude ethylene, after being washed in an alkaliwashing tower (11), was compressed to 35 atm. with an ethylene compressor (16) and cooled up to -30°C in a cooler (14) for liquefaction. A part of the liquefied ethylene was sent to fractionation columns, while the remaining liquid ethylene was used as a coolant for the upper parts of the fractionation columns. The fractional distillation of the ethylene was conducted in two fractionation columns (19) and (20) at -40°C and 15 atm. From the bottom of the first

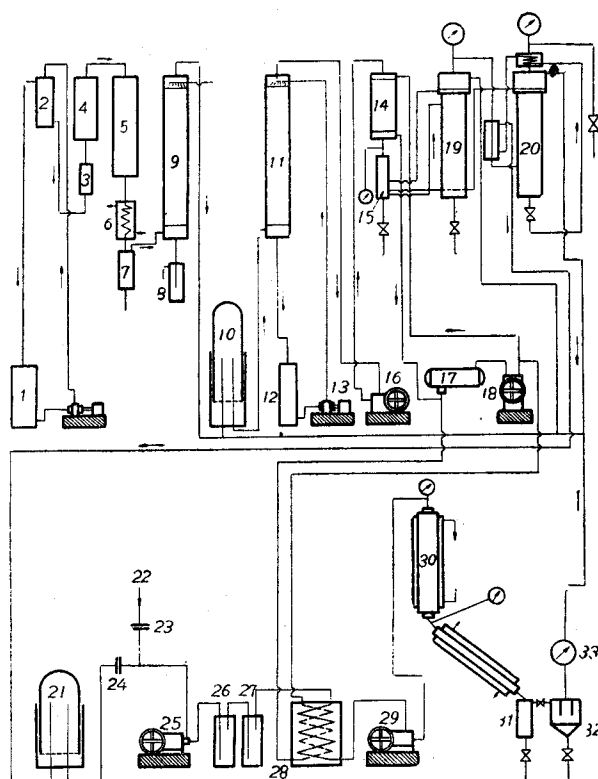


Fig. 1.

- | | |
|-----------------------------------|---|
| 1) Alcohol Reservoir | 18) Ammonia Compressor |
| 2) Head Tank | 19)20) Fractionation Columns |
| 3) Rotameter | 21) Pure Ethylene Holder |
| 4) Evaporator | 22) Equipment adding Oxygen |
| 5) Dehydrator | 23) Oxygen Flow-meter |
| 6) Cooler | 24) Ethylene Flow-meter |
| 7) Separator | 25) Pure Ethylene Compressor |
| 8) Seal Tank | 26)27) Water and Oil Separators |
| 9) Water-washing Tower | 28) Ethylene Liquefier |
| 10) Crude Ethylene Holder | 29) Ethylene Plunger Pump
(2000 atm.) |
| 11) Alkali Solution-washing Tower | 30) Reaction Tube |
| 12) Alkali Solution Reservoir | 31) Polyethylene Separator at
High Pressure |
| 13) Alkali Solution Pump | 32) Polyethylene Separator at
Atmospheric Pressure |
| 14) Ethylene Liquefier | 33) Gas Meter |
| 15) Liquid Ethylene Reservoir | |
| 16) Crude Ethylene Compressor | |
| 17) Ammonia Reservoir | |

column (19) impurities of higher boiling points were removed, while from the top of the second column those of lower boiling points, i. e. CO, N₂, H₂, etc. were eliminated and the pure ethylene accumulated in the bottom of the second column was sent to and stored in a pure ethylene holder (21). The purity of the refined

ethylene was of approximately 0.002% oxygen content. After adding the required quantity of oxygen, the ethylene was compressed to 40 atm. by a compressor (25) and liquefied at -25°C . Then it was further compressed up to the required reaction pressure using a high pressure plunger pump (7l/hr.) (29) equipped with a jacket in which liquid alcohol at -25°C was circulated and was sent into a reaction tube. The reactor used was of 15 mm. inside diameter with 5 m in length, through the outer jacket of which the heating oil was circulated in order to keep the reactor at the necessary temperature. A part of the polyethylene produced in the reaction tube was separated in a high pressure separator (31) in liquid form under the reaction pressure and was drained from the lower part of it, while, at the same time, another part thereof was separated from the unreacted ethylene after reducing the pressure to the atmospheric. The unreacted ethylene was led to the crude ethylene holder.

For the analysis of oxygen contents in the ethylene, a part of ethylene was led onto a platinum catalyst and the temperature rise caused by the combustion of ethylene with existing oxygen was measured with a differential thermocouple. Molecular weights of the polyethylenes obtained were determined from viscosities of the tetralin solution at 75°C by using the following Staudinger's formula.

$$\lim_{c \rightarrow 0} (\eta_{sp.}/C_{gm}) = KM$$

where $K = 0.93 \times 10^{-4}$.

However, the products not only considerably lacked the uniformity, but also the distribution range of their molecular weights seemed to be rather wide (this can be also inferred from the wide range of the melting points as shown in Table 1 and 2) and when they were allowed to stand as it was, there existed some insoluble part in every case under the condition of measuring molecular weight, for example about 10% of insolubles was contained even in the products of 20,000—25,000 molecular weight and as to the product of the higher molecular weight, it reached 70%. Under the circumstances, the molecular weights in the table indicate those obtained from the soluble part. However, when the sample was subjected to a roll working, the product of the lower molecular weight became completely soluble, while in the case of the higher molecular weight, there remained still some insoluble parts.

Result of Experiments

The results of experiments obtained by changing amount of oxygen at different temperatures and pressures are shown in Table 1 and 2. The reaction temperatures in these tables are the temperatures of the circulating oil for heating at the inlet of reactor. In Fig. 2 and 3, the yields given in Table 1 and 2 are respectively plotted against oxygen for each temperature and pressure.

Table 1. Effect of Temperature (at 1150 atm.).

Expt. No.	Temp. (°C)	Oxygen Content (%)	Flow Rate of C ₂ H ₄ (Kg/hr.)	Yield			Molecular Weight	Melting Point (°C)	Mechanical Properties		Electrical Properties		
				Total (g)	(g/hr.)	(%)			Tensile Strength (kg/mm ²)	Elongation (%)	Frequency (Mc.)	Dielectric Const. (ε)	Dielectric Loss (tan δ × 10 ⁴)
58	150	0.020	3.38	708	217	6.4	44,000	115-220	1.39	260	1.5	2.36	7
60	"	0.021	3.08	598	220	7.2	37,000	107-165	1.50	300	"	2.34	14
59	"	0.023	3.06	449	286	9.4	52,000	107-150	1.60	320	"	2.30	"
61	"	0.031	3.09	935	365	11.8	37,000	109-117	1.20	210	"	2.34	11
55	160	0.018	3.10	899	320	10.3	40,000	108-120	1.42	230	"	2.35	4
54	"	0.019	"	1180	367	11.8	38,000	"	1.25	450	"	2.34	3
57	"	0.023	"	1125	413	13.3	32,000	"	1.50	400	"	2.35	5
56	"	0.032	"	1120	361	11.6	35,000	102-116	1.77	420	"	"	3
65	170	0.016	"	1283	384	12.4	36,000	109-149	1.57	430	1.6	2.33	9
72	"	0.017	3.00	1651	392	13.1	35,000	110-145	—	—	—	—	—
64	"	0.020	3.07	1532	460	15.0	27,800	108-117	1.62	450	1.6	2.32	4
63	"	0.025	3.10	1100	456	14.7	32,000	101-108	"	460	"	2.34	"
62	"	0.028	"	1140	436	14.1	"	108-120	1.08	230	"	2.36	6
67	180	0.008	3.55	592	271	7.6	36,400	117-150	2.30	450	"	2.33	3
66	"	0.010	2.87	1131	303	10.9	38,000	112-134	1.66	460	"	"	5
68	"	0.013	3.00	1141	411	13.7	27,750	104-110	1.50	470	"	2.34	3
105	190	0.002	3.50	516	129	3.7	39,900	108-125	2.13	"	1.5	2.33	"
106	200	"	3.43	428	143	4.2	31,700	106-115	1.83	430	"	2.34	"
107	210	0.003	3.23	657	172	5.3	47,500	107-117	1.42	340	"	2.33	"
108	220	0.002	3.15	401	176	5.6	28,900	109-116	2.16	600	"	"	"
109	230	0.0025	3.28	595	187	5.7	26,800	102-110	1.72	570	"	"	"
137	"	0.0037	3.30	2016	295	8.9	25,300	95-108	—	—	—	—	—
135	"	0.0040	"	994	350	10.6	22,400	—	—	—	—	—	—
140	"	0.0042	"	1761	348	10.5	23,200	97-106	—	—	—	—	—
139	"	0.0043	"	2282	410	12.4	20,600	98-103	—	—	—	—	—
136	"	0.0045	"	1888	252	7.6	20,500	103-107	—	—	—	—	—
110	240	0.0040	3.18	710	229	7.2	25,800	105-108	1.33	520	1.5	2.33	4

Effect of oxygen:

It was found that the yield of polyethylene was greatly influenced by oxygen content as shown in Fig. 2 and 3 and in case oxygen was increased beyond maximum point, not only the yield but also the molecular weight decreased rapidly, the reaction finally transformed into an explosive reaction of $C_2H_4=CH_4+C$, and left nothing but soot. It was also recognized that with the oxygen content slightly lower than the amount which causes explosion, only waxy paraffins with lower molecular weights were produced. Consequently, an extremely delicate control of the amount of oxygen feeded is necessary for commercial production of polyethylene. Another thing that was recognized by this experiment was the fact that the molecular weight of the product generally decreased as the oxygen content increased. This tendency is clearly testified by the experiment at 1350 atm. in Table 2.

Table 2. Influence of Pressure. (at 160°C.).

Expt. No.	Press. (atm.)	Oxygen Content (%)	Flow Rate of C_2H_4 (Kg./hr.)	Yield		Molecular Weight	Melting Point (°C)	Mechanical Properties		Electrical Properties		
				Total (g)	(g./hr.)			(%)	Tensile Strength (kg./mm ²)	Elongation (%)	Frequency (Mc.)	Dielectric Const. (ε)
48	800	0.030	3.20	196	56	35,500	107-121	1.05	220	1.5	2.32	9
49	"	0.040	"	662	170	25,000	88-106	"	130	"	2.36	"
50	"	0.050	"	216	120	21,000	86-102	1.24	120	"	2.34	14
44	1000	0.025	3.05	140	140	32,000	110-185	1.64	500	"	2.32	8
46	"	0.030	3.14	877	240	33,000	105-112	—	—	"	2.33	5
52	"	"	3.20	1752	220	25,000	98-115	1.22	580	"	2.29	6
47	"	0.035	"	579	193	27,000	119-132	1.04	380	"	2.33	16
55	1150	0.018	3.10	899	320	40,000	108-120	1.42	230	"	2.35	4
54	"	0.019	"	1180	367	37,000	105-115	1.43	430	"	2.34	3
57	"	0.023	"	1125	413	32,000	108-130	1.67	400	"	"	5
56	"	0.028	"	1120	360	35,000	102-116	1.77	420	"	2.35	3
33	1350	0.016	3.00	783	309	83,000	145-260	—	—	—	—	—
34	"	0.018	"	1733	450	66,000	115-185	1.86	492	4.5	2.40	4
27	"	0.022	2.96	2166	476	41,000	105-125	1.60	440	4.2	2.35	6
37	"	0.023	3.00	6566	455	37,000	101-108	1.90	410	1.5	"	5
30	"	0.025	3.03	2684	255	—	—	—	—	—	—	—

Effect of temperature:

With the given amount of oxygen, the yield of product increased as the temperature rose, hence the maximum yield with the said optimum oxygen content increased as the temperature rose at least up to 170°C as is clearly observed in Fig. 2. But in case of 230°C the maximum yield decreased contrary. As is indicated also by Fig. 2, the optimum oxygen content moved to the lesser range as the temperature rose and the allowable limits of the oxygen content for a favorable production of polyethylene showed a tendency to grow smaller and at 230°C the allowable limit became extremely small.

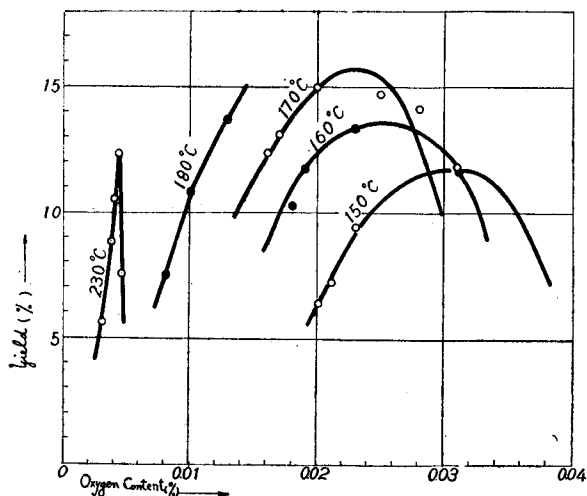


Fig. 2. Effect of Temperature.

and the allowable limits of the oxygen content for a favorable production of polyethylene showed a tendency to grow smaller and at 230°C the allowable limit became extremely small. As is seen from the experimental results of Table 1, the range of the amount of oxygen to be added to produce adequate quantity of polyethylene was 0.0025–0.0045% at this temperature. It was generally observed that the molecular weight of polyethylene was reduced as the temperature rose, and Table 1 is self-explanatory of this tendency.

Influence of reaction pressure: As is clearly indicated in Fig. 3, as the reaction

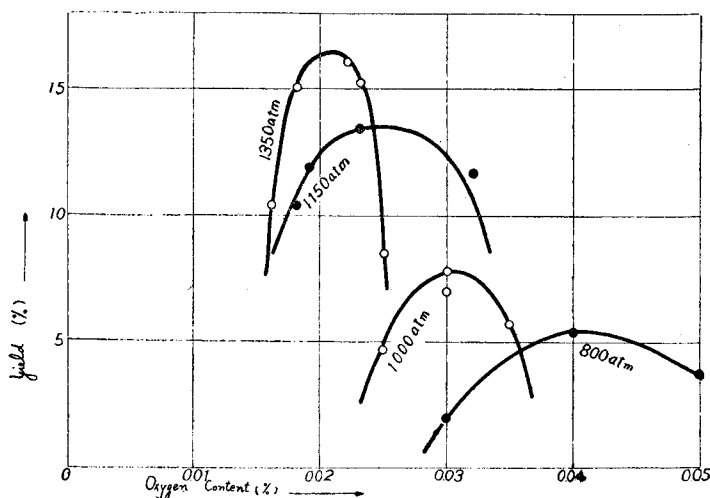


Fig. 3. Influence of Pressure.

pressure rose, the yield of polyethylene and the maximum yield increased with the same amount of oxygen, while the range of allowable limits of the oxygen content became narrower and the optimum oxygen amount approached the range where the amount of added oxygen was smaller. The fact that the molecular weight of the formed polyethylene increases with the elevated reaction pressure will be made clear by comparing the molecular weights for each reaction pressure of Table 2.

Summary

The continuous preparation of polyethylene by the high pressure gaseous phase polymerisation of ethylene with less than 0.05% oxygen as a catalyst at 150—240°C and at 800—1450 atm. was tested and the influences of various conditions for the yield as well as the properties of the obtained polyethylene were made clear.

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