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INFLUENCE OF TECHNOLOGICAL PARAMETERS OF HIGHPRESSURE POLYETHYLENE SYNTHESIS ON THE CONDITIONS FOR SAFE REMOVAL OF RESIDUAL MONOMER

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The article presents the research results concerning the influence of highpressure polyethylene synthesis plant parameters on the content of residual ethylene in the polymer. The developed method for determining dissolved ethylene in obtained fresh polyethylene is shown.

Incomplete conversion of ethylene during polymerization (no more than 20%) requires separating the polymer from the monomer and returning unreacted ethylene to the cycle. Separation is usually carried out in two stages: in the highpressure separator at a pressure of 18-25 MPa and in the lowpressure separator at a pressure of 50-400 kPa.At the same time, up to 0,2% ethylene remains in granulate, depending on the previous separation conditions in the separators [1,2]. To determine the relationship, the influence of such technological parameters as pressure and temperature in separators, the melt flow index, and the productivity of synthesis plants on the monomer content in the fresh polymer is considered.

To determine the content of the residual monomer in polyethylene, the method of chromatography of the gas environment in which the polymer was degassed was used. The selected sample of polyethylene weighing 1±0,2 kg was distributed evenly for its degassing. At the same time, the necessary technological parameters were registered for the research. At intervals, a sample of polyethylene weighing 3±0,05 grams was transferred to a 500 cm^3 gas pipette. Polyethylene was degassed in a gas pipette for about a day to establish equilibrium state (figure 1).

Figure 1. – Degassing of the samples of polyethylene

The first sample was introduced into the pipette immediately after the selection of granules to determine the initial content of ethylene in polyethylene. After holding the air sample was sent for chromatographic analysis [3-7].

The obtained values of the hydrocarbon concentration in the air sample were recalculated to obtain the value of the ethylene content in the polymer (1):

$$C = \frac{T_0 \cdot V \cdot C \cdot M}{22{,}4 \cdot T_1 \cdot m} \tag{1}$$

Where *m* – weight of a polyethylene sample in a gas pipette, g.; *V* –volume of the gas pipette, L.; *C*– concentration of hydrocarbon in the air sample, % vol.; *M* –molar mass of the hydrocarbon, g/mol; T_0– air temperature under normal conditions, K; T_1 – air temperature during the research, K.

The content of residual ethylene in the polymer is determined by the formula (2):

$$x = \frac{Y \cdot P}{H} \tag{2}$$

Where *x*- ethylene content in the liquid phase, mass fraction; *H*- Henry's constant; *P*- pressure, atm.; *Y*- molar fraction of ethylene in gaseous phase.

The dependence of the Henry's constant on the temperature for ethylene is described by the equation (3):

$$ln\,H = 8{,}173 - \frac{148300}{T^2} \tag{3}$$

Where T – temperature, К [8].

Results, their discussion and perspectives. The results of the research are shown in table 1.

Table 1. – Results of the research on the content of residual ethylene in polyethylene

Low pressure separator		High pressure separator		Melt flow index, g/10min	Productivity, kg/h	Content of ethylene in LDPE, mg/kg		Deviation from the calculated,%
Pressure, atm.	Temperature, °C	Pressure, MPa	Temperature, °C			calculated	factual	
Autoclave reactor								
Grade 12203-250								
1,49	193	20,1	225	26,5	990	832,3	537,24	35,5
1,7	191	20,7	209	25,3	1940	955,2	736,39	22,9
Grade10903-020								
1,53	194	20,6	222	2,06	1480	852,2	647,36	24,0
1,66	196	21,7	223	2,04	2170	919,2	749,37	18,5
Tubular reactor								
Grade 15803-020								
3,03	193	23,9	208	2,11	10000	1692,6	1210,6	28,5
3,55	195	24,5	209	2,18	11500	1971,5	1448,8	26,5

As seen in the table, there is a good convergence of the results of the calculated and actual content of residual ethylene in polyethylene. The existing discrepancies (from 18,5 to 35,5%) are explained by removing some of the ethylene from the LDPE directly at the granulation stage and cooling granulate with water from 190-200°C to 40-60°C. Ethylene released at this stage is quantified in the exhaust air.

Dependence of the ethylene content in granulate on the pressure and temperature in high and low pressure separators. The results of the study of the parameters of the lowpressure separators show that the increase in pressure in the lowpressure separator leads to a significant (almost proportional) increase in the calculated and actual content of residual ethylene in polyethylene.The content of the residual monomer in the polymer increases by 20% when the pressure increases from 3,03 to 3,55 atmospheres (absolute) for the 15803-020 polyethylene grade. Double increase of the residual monomer content was observed at the pressure increase in the separators from 1,66 to 3,55 atmospheres (absolute) when comparing polymers of grades 10903-020 and 15803-020 with melt flow indexes of about 2g/10min.

The effect of pressure in highpressure separators on the content of dissolved ethylene in the polymer is also observed. When comparing the analyses results for each grade of polyethylene it can be seen that the increase in pressure in the high pressure separators leads to insufficient degassing of the polyethylene melt, which transported to the lowpressure separator with higher ethylene content. At the same time, with pressure increase in the highpressure separator, the increase in pressure is observed in the lowpressure separator, as a result of which the concentration of residual ethylene in the melt increases.

The research of the dependence of the monomer content in the polymer on the temperature in the separators showed that this parameter affects the quality of LDPE degassing to a lesser extent than the pressure. At the same time, temperature decrease in the highpressure separator leads to deterioration of degassing of the melt. This can be observed on polyethylene of the grade 12203-250. The decrease of the melt temperature from 225°C to 209°C negatively affected its degassing in the highpressure separator and the subsequent increase of the load on the lowpressure separator, which led to the increase of residual ethylene concentration in polyethylene [9].

Dependence of the ethylene content in granulate on the polymer melt flow indexes. The research showed that polyethylene grade 12203-250 with a melt flow index of 25g/10min is degassed more completely in comparison with LDPE grade 10903-020, which has a melt flow index of 2g/10min. When comparing the ethylene content in polyethylene with a melt flow index of 26,5g/10min and polyethylene with a melt flow index of 2,06 g/10min it was observed that at almost the same pressure in the lowpressure separator, the ethylene content in polyethylene of 12203-250 was 20% lower than in LDPE of 10903-020. As a polymer with a high melt flow index has lower viscosity, this allows to degas it better in high and low pressure separators, especially after removing ethylene from the melt, which is in the form of bubbles.

The relationship between the productivity and ethylene content in fresh polyethylene. The effect of synthesis productivity on polymer degassing can be seen in all three grades of polyethylene. When comparing the process parameters and the content of dissolved monomer in the LDPE, it can be seen that an increase in productivity leads to pressure increase in the separators. This is due to the fact that increase in productivity leads to decrease of time the melt presence in the separators. There is also increase in the pressure drop between apparatuses, resistances of which increase with increasing productivity.

Thus, the influence of such parameters as temperature and pressure in separators, melt flow index, and plant productivity on the concentration of residual ethylene in granulated polyethylene was confirmed.

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